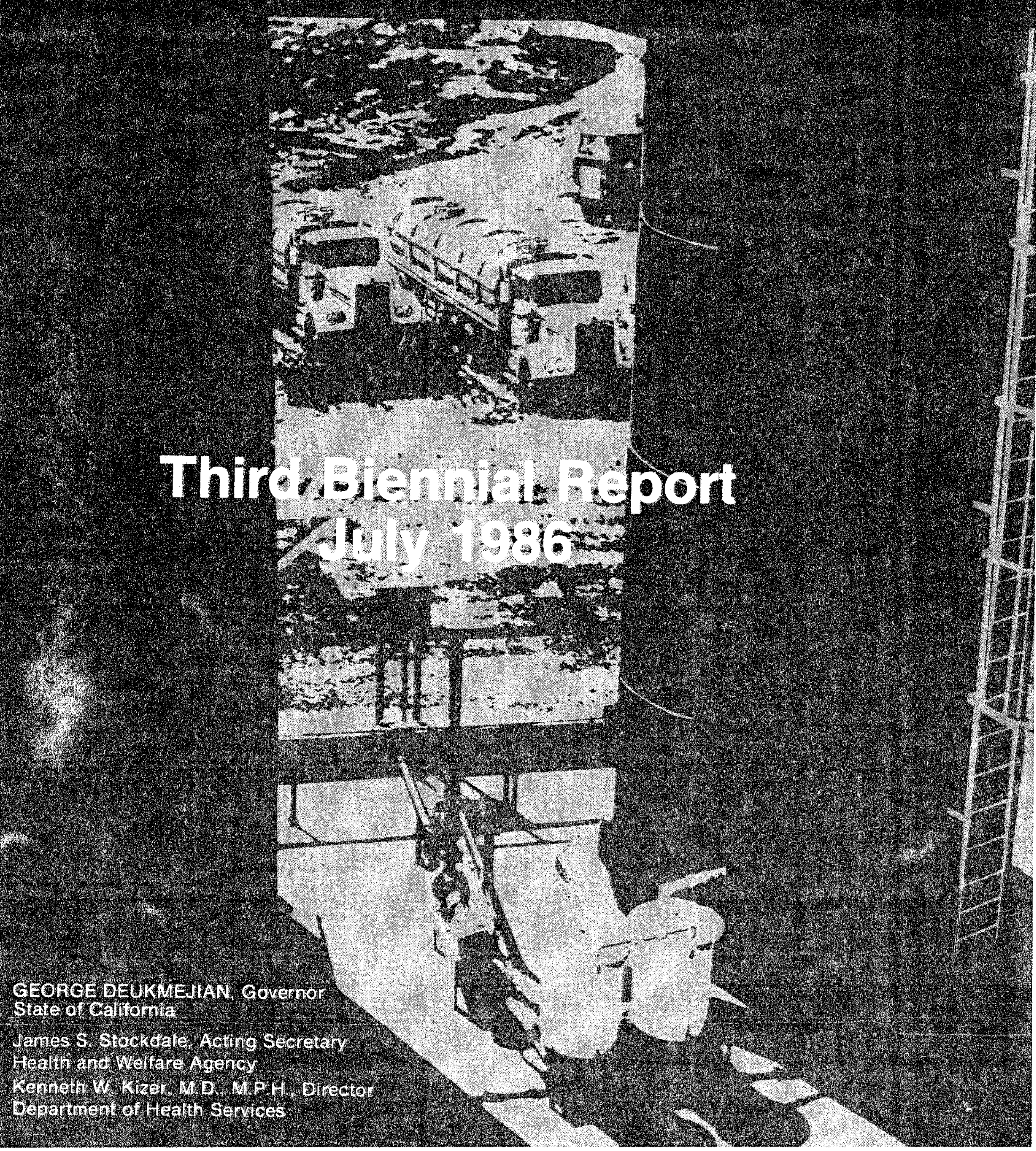
ALTERNATIVE TECHNOLOGY FOR RECYCLING AND TREATMENT OF HAZARDOUS WASTES



Third Biennial Report
July 1986

GEORGE DEUKMEJIAN, Governor
State of California

James S. Stockdale, Acting Secretary
Health and Welfare Agency

Kenneth W. Kizer, M.D., M.P.H., Director
Department of Health Services

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July 1986

The Department of Health Services
Toxic Substances Control Division
Alternative Technology and Policy Development Section

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INTRODUCTION

PREFACE

ACKNOWLEDGEMENTS

PREFACE AND ACKNOWLEDGMENTS

First issued in 1982, the biennial report on Alternative Technologies for Hazardous Waste Recycling and Treatment is required by California statute:

> ... the department shall prepare and issue to the public a report that contains an assessment of the best available technologies for the treatment, storage, recycling, source reduction, and disposal of hazardous waste.... The assessment shall include, but not be limited to, those technologies considered by the department to be the best currently available and an estimate of the unit costs associated with each technology. (California Health and Safety Code, Section 25171.)

The report is a guide for hazardous waste generators seeking alternative waste management techniques. The report also serves as a resource for the public and for policy makers in government and industry. The technologies and economics described in this report are critical considerations for the formulation of California's hazardous waste management policy.

This edition of the report has several new features and a revised format. A new section, Management Strategies, serves as an introduction to waste reduction and the variety of alternatives to land disposal. Source reduction, recycling, and treatment are each described along with examples and the relevant regulatory framework.

The following three sections are similar to previous editions of the report. The Inorganic Wastestream section and Organic Wastestream section consist of chapters which focus on a single waste type. Each chapter presents updated material on the specific technologies of source reduction, recycling, and treatment applicable to the particular waste. The discussion of the biodegradation of hazardous wastes has been considerably expanded. The discussion of air pollution control equipment has been removed; readers interested in that topic should consult the second edition.

The Stabilization Technologies section surveys current stabilization and solidification techniques.

The final section, Site Mitigation, is a new addition to the report. Cleanup of old or abandoned hazardous waste sites is currently the most prominent of the hazardous waste issues. Government and industry must find alternatives to simple redisposal of the contaminated dirt and groundwater. Chapters 13, 14, and 15 summarize the alternatives for treatment of leachate, groundwater, and contaminated soil.

As before, references are listed at the end of each section.

The individuals who made contributions to this report are too numerous to mention. Representatives of industry and consulting firms generously contributed time, information, and materials for this report. Their assistance is gratefully acknowledged. Several individuals reviewed portions of the report. They are Mike Sorenson of the Department of Health Services; Ed Schroeder of the University of California, Davis; John Castelli of Calgon Carbon Corporation; and Mike Lutz of Applied Earth Consultants, Inc. Of course, any inaccuracy or turbidity remains the responsibility of the authors.

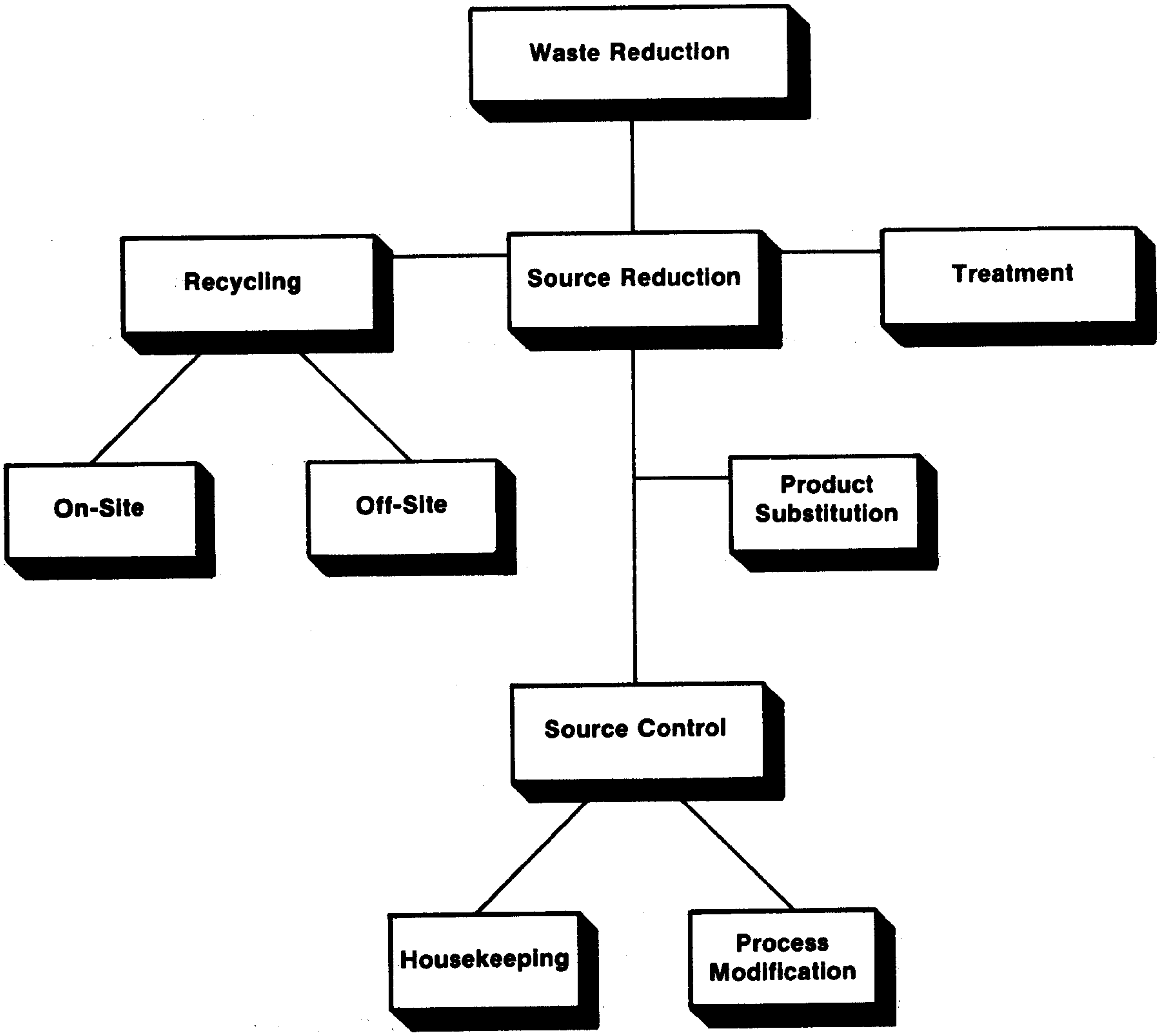
The editor would particularly like to thank Marian Powning, Frances Tsuruda, Margaret Tyler, and Luz Martin of the Department of Health Services Word Processing staff. In addition to providing excellent typing services and editorial suggestions, they cheerfully accepted numerous revisions and rerevisions.

Appendix A was prepared by Bob Hosea and Tim Potter.

Typing of the preliminary drafts by Lisa Martin-Pedlar of the Alternative Technology and Policy Development Section's clerical staff is also gratefully acknowledged.

Teresa Chaney of the Department of Water Resources prepared the figures that grace this report. Her contributions to the final form of the report were invaluable.

WASTE REDUCTION COMPONENTS



INTRODUCTION

There is a wide consensus that society must reduce its dependence on the land disposal of hazardous waste to protect the public health and environment. That consensus was clearly expressed in the 1984 amendments to the Federal Resource Conservation and Recovery Act (RCRA). These amendments in effect require industry to implement alternatives to land disposal. Companies generating and handling hazardous wastes must now certify that they have programs in place to minimize the volume and toxicity of wastes going to land disposal.

The amendments also create a national land disposal restriction program modeled after California's successful program.

This report describes the waste reduction strategies that California industry can use to reduce the volume of waste going to land disposal. Those strategies are:

- o <u>Source Reduction</u> -- Elimination or reduction of generation of hazardous wastes.
- o <u>Recycling and Reuse</u> -- Recycling involves the reprocessing of waste material to a point that it can be used again for the process which generated the waste or for other applications, often requiring lesser purity than the original generating process.
- o <u>Treatment</u> -- Elimination of hazardous characteristics of the wastes so that they are no longer of concern.

Source reduction is the "ideal solution" as it eliminates all the problems associated with hazardous waste generation, storage, transportation, treatment, and residue disposal. However, its implementation may require major technological changes and can become costly. Lesser reduction of hazardous waste volume can usually be accomplished fairly easily by improvements in the manufacturing process, waste segregation, and improved handling.

Recycling feasibility for a given waste is affected by costs of raw material, cost of disposal alternatives, and specific process demands. Often wastes can be recycled, but there is limited market because of the availability of low-cost raw materials.

Treatment has the potential to detoxify most wastes; however, it often shifts the public health and environmental threat from land to other media; such as air or surface water, and usually results in hazardous residues which must be land disposed.

The various components of waste reduction are presented in the adjacent figure.

California has long led the nation in hazardous waste management and waste reduction measures. California's waste hauler manifest program was the model for the RCRA cradle-to-grave hazardous waste tracking system. California's land disposal phase-out program, the first in the nation, has already led to the elimination of land disposal for four separate categories of waste. These wastes are among the wastes to be banned under the federal land disposal restriction program.

California's waste reduction program has four parts:

- o Regulatory.
- o Technical information/technology transfer.
- o Economic incentives.
- o Technical assistance.

The program has been developed with input from industry, environmental groups, and consultants. The Department has also considered the efforts of other states to promote waste reduction. The various program elements are designed to overcome different technical and financial barriers faced by California industry. This program is described more fully in Appendix D.

The hazards and perceived hazards of land disposal have led to a substantial decline in the capacity for land disposal in California. It may be that in a few years commercial land disposal capacity will be available only for the residues of hazardous waste treatment processes. Moreover, hazardous waste generators recognize that they may be held liable for environmental contamination from their wastes many years in the future. Because of the disposal capacity shortage and the threat of "ultimate liability", the need for alternatives to land disposal has never been greater.

MANAGEMENT STRATEGIES

Chapter 1
SOURCE REDUCTION AND ON-SITE RECYCLING

A. INTRODUCTION

This chapter concerns source reduction and on-site recycling. Source reduction measures are in-plant changes which reduce the volume of waste generated, usually by preventing material from entering a waste stream, or which reduce the toxicity of a waste stream. On-site recycling is the reuse of waste materials at the site of generation; all processing and treatment of the waste takes place at the site of generation. As discussed in Chapter 2, off-site recycling often consists of sending the waste to a commercial facility to be purified and returned.

On-site measures are particularly advantageous because they free a generator from the risk and expense of transporting waste. Also, source reduction is preferable to on-site treatment options which often lessen the land disposal of waste by creating air or water pollution, so called cross-media pollution.

Informational, technical, and financial barriers hamper the development and implementation of source reduction measures. The informational barrier has been cited by several studies, including a recent study commissioned by the Department of Health Services (ICF, Inc., 1985), as the principal barrier to the immediate development of many waste reduction measures. Companies are often unaware of opportunities for waste reduction, even when those opportunities are employed by their industry.

The technical barrier inhibits the development of new source reduction and on-site recycling measures which may require extensive research. Unfortunately, source reduction measures are outside the area of expertise of, and consequently, are overlooked by, many research and development departments. Chemical manufacturers are a notable exception.

The financial barrier inhibits source reduction measures that require capital investments. Source reduction investments must compete with revenue generating improvements such as product improvement and new product development. Because of the limitations on corporate funds, source reduction measures are often precluded.

B. GOVERNMENT POLICY AND REGULATIONS

Federal law requires hazardous waste generators to have a program to minimize their generation of hazardous waste. This requirement, which is part of the 1984 amendments to the Resource Conservation and Recovery (RCRA), takes the form of a declaration which must accompany all shipments of hazardous waste:

> "The generator of the hazardous waste has a program in place to reduce the volume and toxicity of such waste to the degree determined by the generator to be economically practicable;...."

The 1984 RCRA amendments also require generators of hazardous waste to submit a biennial report, including a description of their "efforts... to reduce the volume and toxicity of waste generated;...." Facilities which treat, store, or dispose of hazardous wastes are required to make a similar declaration annually.

The California Waste Reduction Program

Source reduction and on-site recycling are particular targets of California's waste reduction program (see Appendix D). The waste audit program is designed to help small generators identify source reduction opportunities. The hazardous waste reduction grant program is one of the few public programs anywhere which supports in-process changes for pollution control. The publications and symposia produced by the Department of Health Services also emphasize source reduction and on-site recycling.

TABLE 1-1

ON-SITE RECYCLING AND SOURCE REDUCTION TECHNIQUES

Process Modification
Material Substitution
Housekeeping Improvements
On-Site Recycling
Waste Segregation

C. CLASSES OF SOURCE REDUCTION AND EXAMPLES

We consider five classes of source reduction and on-site recycling measures (Table 1-1). Although there is significant overlap between these categories they help to clarify the variety of possible waste reduction measures.

Process Modifications

Process modifications include major and minor redesign of manufacturing techniques for the purpose of waste reduction. Examples of process modifications in three industrial processes are discussed below.

Semiconductor Manufacture -- Semiconductor manufacture involves the addition and removal of a layer of paint known as photoresist. The photoresist coating forms a mask on the nascent chip that allows the selective addition of impurities (doping). The impurities give semiconductors their special properties. The traditional process uses negative photoresist which hardens on exposure to light. Negative photoresist must be removed with a blend of organic solvents; the mixture of heavy metals and organic solvents generated by the removal step is a particularly hazardous waste.

The process modification involves the use of positive photoresist which softens on exposure to light. Positive photoresist can be removed with a relatively mild alkaline solution. The waste generated in this removal step is much less hazardous and is more easily managed.

Two emerging doping techniques would eliminate the use of photoresist and paint remover altogether. Laser etching and plasma etching offer improved resolution over current techniques in addition to their waste management advantages. These processes are still at an experimental stage.

Paint Removal -- The waste produced in traditional paint removal processes contains hazardous organic solvents, often both halogenated and aromatic compounds. The Department of Defense is implementing a process that is useful for removal of softer paints from some surfaces and uses significantly less solvent. The surface is bombarded with small plastic spheres which rub off the paint. The waste from this process is a solid and significantly less hazardous than the traditional solvent laden waste. Although this process requires skilled operators and has relatively limited applicability, it offers significant cost savings. At Hill Air Force Base in Ogden, Utah, the necessary equipment was installed for approximately $650,000. It is predicted that the base will save approximately $800,000 annually.

Metal Finishing -- These processes generate large volumes of rinse water. This waste stream is often hazardous and is treated to produce a sludge which, due to the high concentration of metal ions such as cadium and chromium, is certainly hazardous. Countercurrent rinsing, discussed in Chapter 4, is a common process modification that reduces the volume of rinse water generated and can help reduce the volume of sludge generated.

Material Substitution

Most hazardous waste is generated because the desired product is a hazardous material, the starting material contains hazardous components, or a hazardous material is used at an intermediate step. Material substitutions replace the hazardous material with a nonhazardous alternative.

Product Substitutions -- Product substitutions are often motivated by the environmental consequences of the product as well as of the waste. In the early 1970s, chlorinated pesticides such as DDT and 2,4,5 T came under much attack because of their longevity in the environment and the apparent health effects of the residues. To mitigate the effects of these chemical pest controls there was a general transition to the presumed less hazardous phosphate and carbamate-based pesticides.

In the metal coating industry, the highly toxic metal cadmium is being replaced with zinc and other less hazardous metals because of the hazards associated with the cadmium-coated objects.

Input Substitutions -- A common input substitution is the transition to starting materials with fewer impurities. Because less contaminant enters the process, less contaminated product is produced and so less waste is generated.

Aqueous Substitution -- Most material substitutions are not easily classified as input substitutions or product substitutions. For example, in many instances organic liquids used as solvents, lubricants, and cleaning agents can be replaced with aqueous (water-based) solutions. The aqueous alternatives produce less hazardous waste, reduced disposal costs, and because of reduced flammability and toxicity, are generally less hazardous to handle.

Aqueous alternatives are being developed for metal working fluids. These fluids serve the dual function of lubrication and heat removal during machine cutting. Traditional metal working fluids are heavy petroleum fractions, oils. Although more expensive than their organic counterpart, aqueous machine fluids are offered by several manufacturers and are becoming increasingly prominent.

Aqueous alternatives are also available for degreasing operations.

3M Corporation, a leader in the waste reduction field, recently replaced an organic process fluid with an aqueous liquid. At Riker Laboratories, 3M's pharmaceutical plant in Northridge, California, medicine tablets were coated with a material dissolved in an organic solvent. This led to emission and waste problems. 3M found that the material could be applied in an aqueous solution. To make this substitution 3M had to overcome a variety of obstacles, including soggy tablets. The company ultimately saved many thousands of dollars with this substitution.

Housekeeping Improvements

This category includes many of the simplest source reduction measures; reduction of spillage, inventory controls to eliminate degradation of unused chemicals, and other materials handling changes. Education of personnel who handle hazardous materials and similar management innovations are often the easiest and most efficacious housekeeping improvements. Education programs can combine health and safety curriculum with chemical conservation curriculum.

Laboratory Wastes -- Research institutions, such as universities, use a wide variety of chemicals and produce a diverse set of waste streams. These institutions provide a model for housekeeping improvements. A pamphlet published by the American Chemical Society (ACS), Less is Better: Laboratory Chemical Management for Waste Reduction, discusses a variety of procedural changes that research institutions can implement to reduce waste generation. (This is available from the ACS Department of Governmental Relations and Science Policy, 1155 16th Street Northwest, Washington, DC 20036.) ACS published this pamphlet to help its members comply with the 1984 RCRA waste minimization requirements.

One common waste stream addressed by this publication is unused chemicals which have decayed. Purchasing departments and individual laboratories often purchase chemicals in large containers to take advantage of reduced unit costs. Typically, a portion of the chemical decays and must be disposed. Savings in purchase price are thus lost to disposal costs. The ACS pamphlet also suggests that experiments in student laboratories be done on as small a scale as possible and with the least hazardous materials possible.

A similarly valuable publication is a book from the National Research Commission, Prudent Practices for Disposal of Chemicals from Laboratories, available from the National Academy Press, 2101 Constitution Avenue Northwest, Washington, DC 20418. This book discusses hazardous waste detoxification procedures which can be used on a laboratory scale. Widely applied, such measures can greatly reduce the volume of hazardous waste transported from research institutions.

The University of California at Davis, Health and Safety Department, has a model program to minimize hazardous waste generation at the University. For more information on the Davis program: contact Gabriela Battaglia, Environmental Health and Safety TB-30, University of California, Davis, CA 95616. The core of the program is education. A member of the Health and Safety Department presents a class on chemical disposal and waste reduction to the various university departments that generate chemical waste. This class has been well received.

The first part of the class discusses the handling of hazardous wastes, regulations concerning hazardous waste management, and the disposition of wastes after they leave the laboratory. The second part of the class concerns actions individual laboratories can take to reduce their waste output. The suggestions include purchase of chemicals in smaller volumes; consideration of waste disposal in planning stages; material substitutions in nonresearch activities such as cleanup; and inter-laboratory chemical exchange and recycling.

Another feature of the program at Davis is coordinated off-site recycling of solvents. The Health and Safety Department staff person works with the purchasing department to identify large users of solvents. She then contacts those laboratories to develop a program of solvent waste collection. The collected wastes are sent to a commercial recycler.

Off-Specification Products -- In many manufacturing processes housekeeping improvements can be achieved through automation and computerization. Paint formulators are increasingly relying on computers to assist them in their work. These businesses mix stock paints to produce a product with the desired characteristics, colors, and textures for a particular application. Using computers, the formulators are able to establish the desired ratios more easily and with fewer wasted batches.

On-Site Recycling

Typically, there are three types of on-site recycling: reuse of the waste in the same process, use of the waste in a different process at the plant, and processing of the waste to produce a marketable product. In the first case it may be possible to install a feedback loop so the recycling takes place automatically.

Hydrogen Chloride Gas -- Dow Chemical in Pittsburg, California, recently installed feedback loops to recycle hydrogen chloride gas from two sources. One source was the output of a vacuum pump which was sent to a scrubber. After an investment of many thousands of dollars, the HCl is now recovered and reused at substantial savings. The second source is the residual from an HCl liquification process. This stream, containing nitrogen gas and oil as well as HCl, had also been sent to scrubbers. Dow now removes the contaminants and reuses the HCl.

Waste Ink -- In California waste from oil-based newspaper ink must be managed as a hazardous waste. Many California newspapers, including The Sacramento Bee, The Oakland Tribune, The Peninsula Times Tribune, The Los Angeles Herald Tribune, The Press Democrat, and several smaller papers, successfully recycle their ink. Recycling of newspaper ink requires filtering to remove paper dust contaminant.

Photographic Materials -- On-site recycling has long been a standard feature of the photographic processing industry. The initial impetus for processor's diligence was the cost of lost silver. Now, silver is invariably recovered from the fixer bath and is often recovered from processing baths as well. The recovered silver may be used in another process on site or sold to another plant or company.

Photographic processing companies that use ferriccyanide bleach recycle that compound. During processing the ferriccyanide is reduced to ferrocyanide. Traditionally, the ferrous ion was reoxidized with potassium persulfate. Periodically, the solution had to be wasted. There are now several preferable methods for rejuvenating the ferrocyanide for recycling. Technicolor, Inc., in North Highlands, California, uses ozonation to regenerate the ferric ion. Other techniques are also available. On-site recycling illustrates that material costs are often an important motivation for waste reduction measures.

Zinc Sludge -- The galvanization process produces waste solutions and sludges with high zinc content. These wastes can be converted to fertilizer and supplements for animal feed. At least one California galvanizer is considering processing the waste on site to be sold off site.

Waste Segregation

The recyclability of a waste stream often depends on its purity. Recyclability can be lost when two or more dissimilar wastes are combined. In waste segregation measures, waste streams with intrinsic value are isolated so that the value is not lost.

Paint Solvents -- DeSoto paints in Berkeley, California, manufactures organic solvent-based paints. The production equipment used must be cleaned with organic solvents before each change of color. The company has found that it is not necessary to dispose of the used cleaning solutions. Instead, they are segregated according to the color of the paint removed and used in later batches of paint.

Pesticide Dust -- A North Carolina pesticide manufacturer is also able to recycle segregated waste. In this case the waste is pesticide dust. The dust is collected from a gas stream. Formerly the dusts from a variety of different processes were collected in a single large bag house and disposed. The manufacturer realized that by collecting and storing the dust separately, he could recycle each dust into its original process.

CHAPTER 2
RECYCLING

A. INTRODUCTION

Companies and industries, with increasing frequency, are discovering the value of their waste. Recycling takes advantage of that value; the waste is returned to the manufacturing process or used in a separate process. Recycling of hazardous wastes not only reduces the volume of hazardous materials disposed of on land but also conserves materials and often energy.

Hazardous waste may be recycled at the place of generation or off site. In the latter case, the waste is transported to a commercial recycler or to another manufacturer. A commercial recycler processes the waste and returns it to the generator or sells it on the open market. The processing may be a purification step such as distillation or a treatment step such as oxidation.

Solvent leasing is a specialized commercial recycling service in which the solvent user never owns the solvent but instead pays a fee for its use. The solvent leasing company transports the solvent to and from the user's plant.

Incineration with heat recovery is a form of recycling useful for wastes with a large heat content. The heat released in incineration can be captured for electricity generation or for industrial use. For example, one California cement manufacturer obtains a large amount of the thermal energy needed for its processes from the incineration of hazardous waste. Hazardous waste incineration is regulated by the Federal EPA, the California Department of Health Services, and local air pollution control districts.

B. GOVERNMENT POLICIES AND REGULATIONS

Hazardous waste recycling is both regulated and promoted by government. At the federal level, RCRA specifies standards and procedures for hazardous waste recycling. The regulation is necessary to ensure careful handling of hazardous waste. RCRA also explicitly encourages recycling. The waste minimization statement that RCRA requires of hazardous waste generators obliges those generators to look for opportunities to recycle their waste or reduce generation.

State Government has a variety of policy tools with which to develop recycling within its borders. Many states, including California, actively facilitate recycling through the operation of waste exchanges, information clearing houses which link generators of recyclable hazardous waste with manufacturers who can utilize these wastes. Table 2-1 is a partial listing of state-operated waste exchanges. States can also promote recycling by facilitating the permitting process for commercial recyclers. The procedures by which recyclers and other hazardous waste facilities obtain the necessary permits is cumbersome. Several states, including California, have taken steps to ease the regulatory burden on recyclers while protecting the public health and environment.

Recycling in California

Over 322,000 tons of hazardous waste were recycled off site in California during the calendar year 1984. Table 2-2 lists some of the waste streams recycled. This information was obtained from the Department of Health Service's Hazardous Waste Information System.

TABLE 2-1

INFORMATIONAL WASTE EXCHANGES IN THE UNITED STATES

Arizona
Dr. Nicholas Hild
Western Waste Exchange
ASU Center for Environmental Studies
Tempe, Arizona 85287
(602) 965-2975

California
Robert McCormick
California Waste Exchange
Toxic Substances Control Division
Department of Health Services
714/744 P Street
Sacramento, California 95814
(916) 324-1818

Florida
Dr. Roy Herndon
Southern Waste Information Exchange
P. O. Box 6487
Florida State University
Institute of Science & Public Affairs
Tallahassee, Florida 32313
(904) 644-5516

Georgia
Clinton Hammond
Georgia Waste Exchange
Business Council of Georgia
P. O. Box 7178, Station A
Marietta, Georgia 30065
(404) 448-0242

Illinois
Margo Ferguson
Industrial Material Exchange Service
2200 Churchill Road, No. 24
Springfield, Illinois 62706
(217) 782-6762

Michigan
William Stough
Great Lakes Regional Waste Exchange
3250 Townsend Northeast
Grand Rapids, Michigan 49505
(616) 363-7367

Missouri
Clyde H. Wiseman
Midwest Industrial Waste Exchange
Ten Broadway
St. Louis, Missouri 63102
(314) 231-5555

Montana
Janelle Fallon
Montana Industrial Waste Exchange
P. O. Box 1730
Helena, Montana 59624
(406) 442-2405

New Jersey
William E. Payne
Industrial Waste Information Exchange
New Jersey Chamber of Commerce
5 Commerce Street
Newark, New Jersey 07102
(201) 623-7070

New York
Lewis Culter
Northeast Industrial Waste Exchange
90 Presidential Plaza, Suite 122
Syracuse, New York 13202
(315) 422-6572

North Carolina
Mary McDaniel
Piedmont Waste Exchange
Urban Institute
UNCC Station
Charlotte, North Carolina 28223
(704) 597-2307

Tennessee
Sharon Bell
Tennessee Waste Exchange
Tennessee Manufacturing Association
501 Union Building, Suite 601
Nashville, Tennessee 37219
(615) 256-5141

TABLE 2-2

A PARTIAL LIST OF HAZARDOUS WASTE RECYCLED OFF SITE IN CALIFORNIA (January 1, 1984 to December 31, 1984)

Data were obtained from the California State Department of Health Services' Hazardous Waste Information System.

Waste Category	Quantity (Tons)
Solvents, used or contaminated	
Halogenated solvents	10,660
Hydrocarbon solvents	22,530
Oxygenated solvents	6,360
Unspecified solvent mixture	29,010
Used or unused petroleum products	
Oil/water separation sludge	49,300
Unspecified oil-containing waste	9,900
Waste oil and mixed oil	162,340
Acid wastes (including acid solution with metals)	9,900
Alkaline wastes (including alkaline solution with metals)	1,990
Unrinsed empty containers	680
Other	
Baghouse waste	2,000
Degreasing sludge	120
Other inorganic solid waste	1,360
Paint sludge	540
PCBs and materials containing PCBs [a]	1,520
Tank bottom waste	1,150
Other organic liquid mixture	510

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[a] PCBs as such cannot legally be recycled. However, containers contaminated with PCBs and oils contaminated with PCBs can be recycled as long as the PCB contamination is removed as part of the recycling process. Thus, the waste category recycled refers to the oils or containers, not the PCBs.

California has an aggressive program to promote hazardous waste recycling. The State's hazardous waste control law explicitly authorizes and mandates California's recycling program (Table 2-3).

TABLE 2-3

RECYCLING IN CALIFORNIA
(Statute from Health and Safety Code Section 25170)

"The Department (of Health Services) shall:

-- Promote recycling and recovery of resources from hazardous wastes.

-- Investigate market potential and feasibility of use of hazardous wastes and recovery of resources from hazardous wastes.

-- Publish and distribute (1) Lists of hazardous wastes for the purpose of enabling persons to match the constituents of hazardous waste streams with needs for hazardous materials resources. (2) Directories of known and permitted commercial hazardous waste recyclers in the state.

-- Coordinate research and study in the technical and managerial aspects of management and use and recycling and recovery of resources from hazardous wastes.

-- Establish and maintain an information clearinghouse, which shall consist of a record of wastes which may be recyclable."

The provisions are administered by the resource recovery staff of the Department. California's resource recovery program is intended to be a service to industry. The activities of the resource recovery staff and California's recycling program are described below.

<u>The California Waste Exchange (CWE)</u> -- CWE is an information exchange of the sort described above. CWE's quarterly publication, the <u>Newsletter/Catalog</u>, lists hazardous wastes available and hazardous wastes wanted. The catalog is the direct implementation of the clearinghouse mandated by California statute (Table 2-3). Listings in the catalog are anonymous. A company interested in a listed waste must contact the Department and request that its name be given to the listing company.

The newsletter part of the publication is used for three purposes: to keep the waste generators, waste recyclers, and interested persons aware of changes in the hazardous waste control law and the Department regulations; to inform them of the activities of the Toxic Substances Control Division; and to promote recycling of hazardous waste by describing successful recycling efforts and recycling technologies.

CWE works with waste exchanges throughout this country and Canada to standardize and exchange listings of wastes available and wastes sought for recycling. For several years, CWE has listed recyclable wastes available or wanted outside as well as inside of California. These listings are obtained from the publications of other waste exchanges, which also list wastes from California.

<u>Directory of Industrial Recyclers</u> -- Each year the Department publishes a directory of permitted commercial recyclers servicing California industries. The recycler listings are categorized by the types of waste they accept. Currently, there are nine categories: acids, agriculturally useful materials, catalysts,

containers, distressed, surplus or expired chemicals, metals and metallic salts, oils, solvents, and miscellaneous.

The demand from industry for the Directory is high. The most recent edition has been distributed to more than 6,000 interested parties. The Department continues to receive new requests for the Directory.

Letters of Inquiry -- Department of Health Services regulations require that a generator of specified recyclable waste streams (Table 2-4) attempt to recycle those wastes. The Department has found that it is technologically and economically feasible to recycle those wastes. The Department resource recovery staff routinely checks shipment data (manifests) to determine if any of the specified wastes are being disposed at a hazardous waste facility. If so, the Department contacts the generator and inquires why the wastes are not being recycled. The regulations stipulate that the generator must respond in 30 days or less. The program has been quite successful; many generators have begun to recycle as a result of these letters.

TABLE 2-4

SELECTED RECYCLABLE HAZARDOUS WASTES
(From California Administrative Code, Section 66796)

- Unused commercial chemical products
- Halogenated solvents
- Oxygenated solvents
- Hydrocarbon solvents
- Petroleum products, including oils and hydraulic fluids
- Pickling liquor
- Unspent acids and alkalis
- Selected empty containers

Direct Technical Assistance -- Upon request, the resource recovery staff visits hazardous waste generators and commercial recyclers to provide assistance on resource recovery issues. In particular, the resource recovery staff helps to identify recycling opportunities. The staff visits recyclers regularly to determine what wastes the recycler accepts and to maintain communication. The Department's permitting and enforcement activities with recyclers are carried out by a separate unit so the resource recovery staff is free to act in a supportive manner.

Presentations/Conferences/Seminars -- The Department works closely with the University of California extension programs presenting seminars and classes on hazardous waste management. Many of these programs concern opportunities for hazardous waste recycling. Presentations are regularly given to trade associations about recycling opportunities in their particular industry. The resource recovery staff also attends recycling conferences organized by hazardous waste interest groups.

Regulatory Reform -- To enhance recycling, the Department has developed a resource recovery permitting process which is available to facilities which recycle wastes. The RCRA hazardous waste facility permit is required for companies which treat or dispose of hazardous wastes. The series "A" resource recovery permit, the most stringent, has essentially the same requirements as a hazardous waste facility permit.

However, identification as a resource recovery facility rather than as a hazardous waste facility can improve a facility's interactions with the local community and government. The series "A" permit is available to recyclers who handle hazardous and extremely hazardous wastes, including those recyclers who operate incinerators for energy recovery. The series "B" and series "C" resource recovery permits have fewer requirements than a series "A" permit and are acceptable for recyclers handling less hazardous wastes in specified manners. This variety of permits enhances recycling while assuring that recycled hazardous wastes are handled with appropriate caution.

A second area of regulatory reform involves the manifesting requirements for hazardous wastes. Ordinarily, a generator shipping hazardous waste off site for any purpose (recycling, treatment, disposal) must complete a manifest describing that waste and its eventual fate. The manifest form requires an elaborate procedure: the generator and the recipient of the waste must return copies to the Department; the recipient must return a copy to the generator; and the generator, the hauler, and the waste recipient must all retain copies. The Department has eased the manifesting requirements in cases where a single company generates, transports, and receives the waste such as solvent leasing (see below). The manifesting requirements have also been eased for shipments of batteries and shipments of waste oil.

A third area of regulatory reform involves hazardous wastes transferred between two or more facilities operated by the same person. When such transfer is for the purpose of recycling, the management of the waste is exempt from the hazardous waste control laws.

C. CLASSES OF RECYCLING AND EXAMPLES

The large variety of recyclable waste types and ultimate destinations makes each recycling application unique. The types of recycling discussed in the remainder of the chapter illustrate the diversity of off-site recycling. Other major recycling activities such as solvent recycling, oil recycling, and acid recycling are discussed in the waste stream chapters of the report.

Solvent Leasing -- Solvent leasing services are available for companies in industries such as automotive repair and dry cleaning, who generate highly recyclable organic solvent waste. The leasing companies, described more fully in Chapter 7, lease the solvent and the solvent handling equipment. The leasing company also provides transportation services and training for proper handling of the solvent. Many small generators would carelessly dispose of their wastes if a solvent leasing service were not available.

The full manifesting procedure would be prohibitive for leasing companies; a single truck typically picks up wastes from dozens of companies each day. The Department allows the hauler/leaser to submit only one manifest per truck per day. However, the leasing company is required to maintain accurate records of the volumes received from each generator and make those records available to the Department upon request.

Battery Recycling -- Large batteries such as automobile batteries contain substantial amounts of lead which can be recovered and recycled. In one process the battery recycler first crushes the batteries to separate the lead, the plastic housing, and the acid. The resulting mixture is multilayered with the lead on the bottom and the housing on the top. The lead is collected to be smelted and sold.

Until recently, spent batteries, which contain strong sulfuric acid as well as lead, had to be managed as a hazardous waste in accordance with California's hazardous waste laws. New regulations ease the requirements for the transportation and temporary storage of limited quantities of spent batteries which are to be recycled or regenerated. However, the recycling facility itself must obtain a resource recovery permit.

Drum Recycling -- Drum recycling is also a well established industry in California. Used drums that contained hazardous materials and have not been adequately rinsed must be managed in accordance with California's hazardous waste laws. Several companies (resource recovery facilities) in California offer a service of cleaning and treating the drums so that they may be reused. Most drums can be adequately cleaned by a triple-rinse procedure; the choice of rinsing solvent depends on the drum's content. When a triple-rinse procedure is not convenient, a drum recycler may employ thermal or other treatments with approval of the Department. In thermal treatment, the recycler cuts the ends off the drum and heats the drum in a specialized furnace. Specialized regulations for the transportation and recycling of used drums are being developed. These regulations will facilitate drum recycling while protecting the public health.

Mercury Recycling -- Liquid metal mercury is uniquely suited for a variety of applications, particularly pressure and temperature measurements. Unfortunately, mercury is highly toxic, is easily contaminated, and frequently requires replacement. Commercial mercury recyclers treat and purify the mercury by distillation. In the distillation process, the heavy liquid is heated in a sealed furnace under low pressure. Mercury vapor is carried away and subsequently condensed for reuse.

Because of the extreme toxicity of mercury, solids with even slight mercury contamination must be managed as a hazardous waste. The mercury can be recovered from these solids by a process similar to distillation. The solid is heated in a furnace until the mercury vaporizes and can be collected.

Quicksilver Products, a mercury recycler in California, has developed a program to recover and recycle the mercury from fluorescent light bulbs. Because of their high quantity of mercury, fluorescent bulbs should be managed as a hazardous waste. Although an exemption is made for household users, disposal of large quantities of bulbs is a significant problem for institutional users. In the recycler's process, mercury will be recovered from the glass and the aluminum ends of the tubes will be sent to an aluminum recycler.

CHAPTER 3
TREATMENT

A. INTRODUCTION

Treatment of hazardous waste may be seen as the last choice alternative to land disposal. In contrast to source reduction and recycling, treatment does nothing to conserve materials or reduce the need for further exploitation of natural resources. In many cases, however, source reduction and recycling are infeasible for economic or occupational health reasons and treatment is the only alternative to land disposal.

Treatment processes are generally designed to accomplish one of three things: (1) destruction or detoxification transforms a hazardous waste into a material safe for disposal; (2) concentration or volume reduction facilitates the safe handling and disposal of the hazardous components; and (3) immobilization isolates the hazardous components from the environment. Solidification and stabilization processes are the two most common forms of immobilization.

Many large hazardous waste generators treat their wastes on site. Smaller generators generally send their wastes to commercial or off-site treatment facilities. Increasing numbers of generators are taking advantage of transportable treatment units, which make available technologies previously restricted to very large facilities. Treatment processes for hazardous waste generally produce a hazardous residue requiring disposal. For that reason, most commercial treatment facilities are associated with disposal sites. On-site treatment facilities often send their treatment residues to commercial disposal facilities.

The distinction between treatment and recycling is often subtle. Combustion of hazardous waste, for example, may be considered recycling if a significant portion of the heat value is recovered and may be considered treatment otherwise.

B. GOVERNMENT POLICY AND REGULATIONS

Treatment of hazardous waste is extensively regulated by government at all levels. In California, hazardous waste facility permits are issued by the State under the supervision of the Environmental Protection Agency (EPA). The federal agency sets minimum standards for the facilities. The regulations include financial responsibility criteria, the site must demonstrate that it has liability insurance of at least $2 million a year; related requirements apply to closure and contingency plans. Operational regulations give technical specifications for each treatment technique conducted at the site: incineration, tank treatment, biological treatment, etc. Environmental monitoring regulations specify that possible routes of contamination must be continuously or regularly monitored.

Hazardous waste facility operators monitor the composition of the wastes they treat or dispose. This is a relatively simple matter for on-site facilities whose operators are generally familiar with the waste produced. However, commercial treatment facilities must maintain the capability to analyze each new waste stream they receive. In all cases, the operator is required to keep records of the wastes received and treated.

Hazardous waste facilities are also regulated at the local level. Hazardous waste treatment is an industrial activity. As such, it must comply with local regulations concerning land use, basic health and safety matters, and construction practices. With its permitting authority, local government has extensive ability to ensure that a hazardous waste facility operates with regard for its neighbor's concerns.

Governments can promote treatment of hazardous waste by facilitating the disposal of the treatment residues. The economic feasibility of a treatment process for hazardous waste depends on the disposal cost of the hazardous residue. Reduced disposal fees (taxes) for treatment residues improves the treatment market. Several local governments in California are sponsoring the development of disposal sites that will only accept treatment residues.

C. CLASSES OF TREATMENT TECHNOLOGIES AND EXAMPLES

Treatment technologies are commonly broken down into several categories: physical, thermal, chemical, and biological. Each of these categories is discussed below. Tables 3-1 through 3-4 list technologies in each category. The codes alongside the treatments are EPA's; waste generators and waste management facilities use these codes to comply with reporting requirements. Because several of the physical technologies have very general applicability, they are discussed here in a generic fashion. Other treatment technologies are discussed in later chapters as they apply to specific wastes.

Physical Treatment

A large class of physical technologies separate solids from liquids. Some, like flotation, are useful for removal of solids that are less dense than the surrounding fluid. Sedimentation and centrifugation on the other hand are applicable for heavier solids. Filtration is applicable in both situations.

TABLE 3-1

PHYSICAL TREATMENTS

(1) Separation of Components

Code	Treatment
T35	Centrifugation
T36	Clarification
T37	Coagulation
T38	Decanting
T39	Encapsulation
T40	Filtration
T41	Flocculation
T42	Flotation
T43	Foaming
T44	Sedimentation
T45	Thickening
T46	Ultrafiltration

(2) Removal of Specific Components

Code	Treatment
T48	Adsorption -- molecular sieve
T49	Activated carbon
T50	Blending
T51	Catalysis
T52	Crystallization
T53	Dialysis
T54	Distillation
T55	Electrodialysis
T56	Electrolysis
T57	Evaporation
T58	High gradient magnetic separation
T59	Leaching
T60	Liquid ion exchange
T61	Liquid-liquid extraction
T62	Reverse osmosis
T63	Solvent recovery
T64	Stripping
T65	Sand filter

<u>Air Flotation</u> -- Solid or liquid particles which are lighter than the surrounding liquid can be separated from that liquid by air flotation. In this process, a stream of fine air bubbles is introduced into the bottom of the flotation tank. The air bubbles adhere to the particles or droplets and carry them to the surface of the liquid.

Electroflotation processes utilize hydrogen and oxygen gases to provide the flotation. These gases are generated at the surface of electrodes inserted into the solution. The waste particles, which are often charged, migrate to the electrode and coalesce on the emerging bubbles.

Flotation processes are generally followed by drainage processes whereby the liquid is drained from underneath the flotation solids. Air flotation and electroflotation are commonly used to separate oil and latex emulsions; the residues are dried and taken to land disposal facilities.

<u>Sedimentation</u> -- Dense solids can be separated from a surrounding liquid by sedimentation. Successful sedimentation requires that the tank be sufficiently motionless to allow particle settling. The clarified liquid is decanted from above the settled solids which are subsequently collected for further treatment or disposal.

Sedimentation is often used with flocculation and chemical precipitation processes to remove dissolved heavy metal ions from a waste stream. The treatment plant at the Stringfellow Disposal Site, shown schematically in Figure 13-2, includes a combined flocculation-precipitation-sedimentation unit to remove heavy metals from contaminated groundwater.

<u>Filtration</u> -- Filtration through screen or cloth is used to remove fine solids from a liquid. Pressure differences or gravity force the liquid through the filter. The problem commonly encountered in this technique is clogging. This occurs more readily if polymeric solids are present in the solution. Chemical

conditioning or heating of the filter medium can alleviate the clogging caused by polymers.

Centrifugation -- Centrifugal forces, similar to the forces that hold water in a whirling pail, can be used to separate liquids from solid and to separate liquids of different densities. Centrifuges may also be equipped with filters to further separate finer solids from the liquid. Crystals are separated from dry-cleaning solutions and fine particles are removed from motor oil with centrifugal separators. Centrifugation is more expensive than comparable methods such as sedimentation and chemical precipitation. However, it is faster.

Distillation -- Liquids with very different volatilities can be separated by distillation. Heat is applied and the liquids are separated on the basis of their vapor pressures. The more volatile liquids vaporize are removed, and collected. Distillation is discussed extensively in Chapter 5.

Ultrafiltration and Reverse Osmosis -- These are membrane filtration processes which remove the solvent from a waste solution. Under a large hydrostatic pressure, the solvent passes across the membrane; the solute remains in the more concentrated solution. The difference between the two processes lies mainly in the size of the contaminants treatable. Ultrafiltration is applicable to large solutes and colloids (suspended solutes). Reverse osmosis is applicable to lighter molecular weight solutes.

Separation by ultrafiltration depends upon the size of the membrane. Larger pores allow larger molecules to pass through the membrane. Membranes can be fabricated in accordance with the desired particle retention size. In theory, a series of ultrafiltration membranes with different pore sizes can be employed to separate a complex mixture of chemicals.

Reverse osmosis membranes have very small pore sizes and can retain solutes as small as metal ions. Filtration or even ultrafiltration often precedes reverse osmosis to protect the membrane from fouling. Reverse osmosis is discussed in Chapter 4.

Thermal Treatment

TABLE 3-2

THERMAL TREATMENTS

T06	Liquid injection incinerator
T07	Rotary kiln incinerator
T08	Fluidized bed incinerator
T09	Multiple hearth incinerator
T10	Infrared furnace incinerator
T11	Molten salt destructor
T12	Pyrolysis
T13	Wet air oxidation
T14	Calcination
T15	Microwave discharge
T16	Cement kiln
T17	Lime kiln

Thermal treatments depend essentially on the generation of heat. Incineration, discussed in Chapter 9, is the principal thermal treatment in wide application. Some thermal treatments, such as infrared incineration, which have long histories of use in the treatment of nonhazardous wastes are now finding application in hazardous waste treatment. Other thermal treatments, such as fluid wall reactors, are at an experimental stage.

Wet air oxidation (WAO) is an established technology for the treatment of municipal wastes and hazardous wastes. WAO is often regarded as a chemical treatment rather than a thermal treatment.

Chemical Treatment

TABLE 3-3

CHEMICAL TREATMENTS

T19	Adsorption mound
T20	Adsorption field
T21	Chemical fixation
T22	Chemical oxidation
T23	Chemical precipitation
T24	Chemical reduction
T25	Chlorination
T26	Chlorinolysis
T27	Cyanide destruction
T28	Degradation
T29	Detoxification
T30	Ion Exchange
T31	Neutralization
T32	Ozonation
T33	Photolysis

This family of treatments exploit differences in chemical properties. The treatments involve chemical reactions, for example, ozone oxidation of cyanides, neutralization of acids, and precipitation of metals. Chemical treatment of waste is often followed by a physical treatment such as solids separation, absorbtion, or evaporation.

Biological Treatment

TABLE 3-4

BIOLOGICAL TREATMENTS

T67	Activated sludge
T68	Aerobic lagoon
T69	Aerobic tank
T70	Anaerobic lagoon
T71	Composting
T72	Septic tank
T73	Spray irrigation
T74	Thickening filter
T75	Trickling filter
T76	Waste stabilization pond

In biological treatment, the contaminants are absorbed and usually decomposed by living organisms. Most often, the organisms are microbes which decompose the contaminants. However, applications where the organisms accumulate the contaminants, but do not decompose them, are also common. Plants and fungi are often employed in bioaccumulation processes. Biological treatment is discussed in Chapter 6.

D. TRANSPORTABLE TREATMENT UNITS

Transportable treatment units (TTUs) will play an increasingly large role in hazardous waste management in this country. TTUs are free from the problems that plague other treatment options. While land disposal is no longer an option for many waste streams, it is very difficult and often impractical to build large treatment facilities. Attempts to site large commercial (off-site) treatment facilities generally fail because of strong local opposition. On the other hand, few companies generate a sufficiently large volume of waste to justify installation of a treatment unit on site.

In response to these difficulties, transportable versions of most treatment technologies are being developed (Table 3-5). TTUs are advantageous because they reduce the need to transport large volumes of hazardous waste. Indeed, many TTUs are exclusively volume reduction technology. For example, at least five companies operate transportable centrifuges (IT Corporation, Newpark Waste Treatment Systems, Resource Conservation, Resource Recovery of America, and Tricil). Other TTUs offer complete destruction technologies.

TABLE 3-5

EXAMPLES OF EXISTING TRANSPORTABLE TREATMENT UNITS

Rotary Kiln Incinerators
Fluidized Bed Incinerators
Chemical Dechlorination
Neutralization
Activated Carbon Adsorption
Distillation
Anaerobic Digestion
Centrifugation
Filtration

TTUs are also well suited to the cleanup of contaminated hazardous waste disposal sites. Local residents may object to the construction of permanent treatment facilities which will attract new wastes to the area after site decontamination is complete. However, the volume of contaminated soil is often too large to be transported. TTUs offer the ideal solution. (TTUs and other approaches to site mitigation are discussed in Chapters 13, 14, and 15).

TTUs present a new challenge for regulatory agencies. Because of their mobility, it is difficult for regulatory agencies to monitor TTUs and ensure that they are meeting treatment objectives. Regulatory agencies have not yet developed a uniform approach to TTUs. At the state and federal levels, proposals exist to develop a procedure to give blanket or regional permits. Under this "permit-by-rule" system, the TTU operator need demonstrate only once that the unit meets RCRA requirements; additional permits would not be required for each operation of the TTU. Local governments, however, generally want to retain the right to regulate the operation of TTUs.

The economics of TTUs units vary considerably and depend on the difficulty of setting up the particular unit. For example, six to nine months may be required to set up a sophisticated incinerator. For economical operation, that incinerator must remain at a site for several years or more. On the other hand, an activated carbon adsorption unit can be set up in two days and can be economically operated for a month or less.

Several TTUs are discussed at greater length later in this report; in particular, mobile PCB dechlorination units (Chapter 10), mobile incinerators (Chapter 9), and mobile activated carbon adsorption units (Chapter 6).

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INORGANIC WASTESTREAMS

CHAPTER 4
ACID AND METAL WASTES

A. INTRODUCTION

Acid and dissolved metal containing wastes account for at least 20 percent of the hazardous waste generated in California. Metal plating processes in a broad spectrum of industries generate a large portion of the wastes containing acids and metals. The chemical manufacturing industries are also a large source of this waste (University of California Davis, 1981).

Many of the technologies available for recycling and treating wastes containing acids and dissolved metals are relatively simple, well established processes. The application of these processes to industrial waste management problems is expanding in response to new limitations on disposal options. Many generators of acid and metal containing wastes are caught by new restrictions on both discharge to sewers and land disposal.

Regulations restricting the land disposal of specified hazardous waste went into effect on January 1, 1984. These regulations represent a dramatic change from California's almost total dependence on land disposal and favor recycling, treatment, and destruction of wastes.

The following liquid hazardous wastes were restricted from land disposal in California on January 1, 1984: (a) liquid hazardous waste with a pH less than or equal to two (2.0); and (b) liquid hazardous waste containing the following dissolved metals or other derivatives concentrations greater than or equal to those specified in Table 4-1:

TABLE 4-1

METAL WASTES RESTRICTED FROM LAND DISPOSAL

Arsenic	500 mg/l
Cadmium	100 mg/l
Chromium (Vl)	500 mg/l
Lead	500 mg/l
Mercury	20 mg/l
Nickel	134 mg/l
Selenium	100 mg/l
Thallium	130 mg/l

These regulations restrict only liquid hazardous waste; solid wastes are not subject to these land disposal restrictions. Sludges and slurries, which contain both liquids and solids, are more difficult to classify. The U. S. EPA has dealt with this question by relying on the concept of "free liquids". This approach has also been adopted by the California Department of Health Services.

Free liquids are "...liquids which readily separate from the solid portion of a waste under ambient temperature and pressure". EPA has further clarified the term "free liquid" by establishing the "paint filter test". The paint filter test protocol calls for a representative 100 ml sample of the waste to be placed in a 400 micron, conical paint filter for 5 minutes. The waste is considered a restricted hazardous waste if liquid passing through the filter in the five-minute period contains listed compounds above the specified concentrations.

California's Toxic Pit Clean-up Act of 1984 prohibits the discharge of restricted wastes into surface impoundments as of January 1, 1986. This statute also mandates that surface impoundments used for nonrestricted hazardous waste must have double liners, a leachate collection system, and a groundwater monitoring program unless an exemption is obtained.

Federal law also prohibits the use of surface impoundments for disposal of restricted wastes. Under the federal statute, surface impoundment may be used for treatment (not disposal) if the impoundment is cleaned out yearly. Because it is more stringent, the Toxic Pit Clean-up Act of 1984 supercedes federal law in California.

B. SOURCE REDUCTION AND ON-SITE RECYCLING IN THE METAL FINISHING INDUSTRY

Before a waste treatment system is selected, a generator should carefully evaluate options available for reducing or eliminating the entry of hazardous materials into the waste stream. Pollution control legislation has increased the economic penalty associated with inefficient use of raw materials. In response, manufacturers are modifying their processes to reduce raw material loss, water consumption, and sludge generation. These modifications are aimed at reclaiming dissolved metals in wastewater, thus circumventing sludge formation and disposal problems.

The costs of waste treatment and the costs of recovery are highly waste and process specific. Several considerations will help a manufacturer decide if recovery is an economical option. The first is production cost savings; including savings on the purchase of raw chemicals and in residuals handling. The second consideration is the elimination of waste treatment capacity. This applies to generators building a new plant or who have inadequate treatment facilities in the old plant. The generator may save money by avoiding the purchase of additional treatment equipment. A final consideration is the elimination of sludge generation. This must be applied judiciously because it is rarely possible to eliminate all sources of waste.

Electroplating is a metal finishing process; the object to be coated is suspended in a solution of the desired metal and is given a negative electric charge. Positively charged metal ions flow to the object's surface where they are reduced to the elemental metal, forming the desired coating. Plating solution contains not only high concentrations of the often hazardous metal, but also cyanides, strong acid, and other hazardous additives. This solution becomes a waste when high concentrations of contaminants prohibit effective plating. The electronics industry in particular has very exacting requirements for its plating solutions. Processes which remove contaminants from plating solutions greatly extend the life of those solutions. Alternatively, metals and other valuable constituents of plating solutions can be recovered from spent plating solution and added in fresh solution. Technologies applicable to both of these purposes are discussed below.

Another common waste from electroplating is rinse solution. An object removed from a bath carries liquid from that bath (this liquid is known as dragout). In order to remove all excess plating solution, the object is rinsed several times. The rinse baths eventually become contaminated beyond usefulness. As discussed below, the useful contaminants of rinse baths can be recovered and used to replenish process baths or in the formulation of new process baths.

Equipment for recovery and recycle of aqueous solutions with dissolved metals is widely available. Capital costs for recycling systems vary considerably. Small plating shops (less than $1 million per year gross income) may spend from $80,000 to $275,000 for recycling equipment. For large companies, the capital costs can be millions of dollars.

A recent EPA Technology Transfer publication, Environmental Pollution Control Alternatives: Reducing Water Pollution Control Costs in the Electroplating Industry, provides the basis for estimating the cost of resource recovery equipment for a particular installation. The unit cost of this equipment depends on the volume of waste and the extent of contamination. The EPA publication includes worksheets and sample calculations for typical plating shops. (This publication is available from EPA-Publications, Hazardous Wastes Engineering Research Lab, 26 West St. Claire Street, Cincinnati, OH 45268.)

Countercurrent rinsing is a well established waste reduction measure. Fresh water is added only to the final rinse bath, which remains relatively clean. The other baths are replenished from the subsequent bath (Figure 4-1). In this manner, only the first rinse solution becomes waste. Countercurrent rinsing greatly reduces the volume of rinse solution that becomes waste.

Many recovery processes operate on the same basic principle: they concentrate the dragout plating solution contained in the rinse water so the solution can either be returned to the processing baths, reused in another system, or sold on the open market. These recovery and recycle systems reduce or eliminate the waste load to any subsequent treatment operation, reducing the volume of sludge generated, and disposal costs.

A recovery process can provide an essentially closed system around a process bath (Figure 4-2a). Process chemicals are recovered and little, if any, rinse water is sent to downstream waste treatment facilities. Under very favorable conditions, a recovery system can achieve almost zero effluent discharge to sewers.

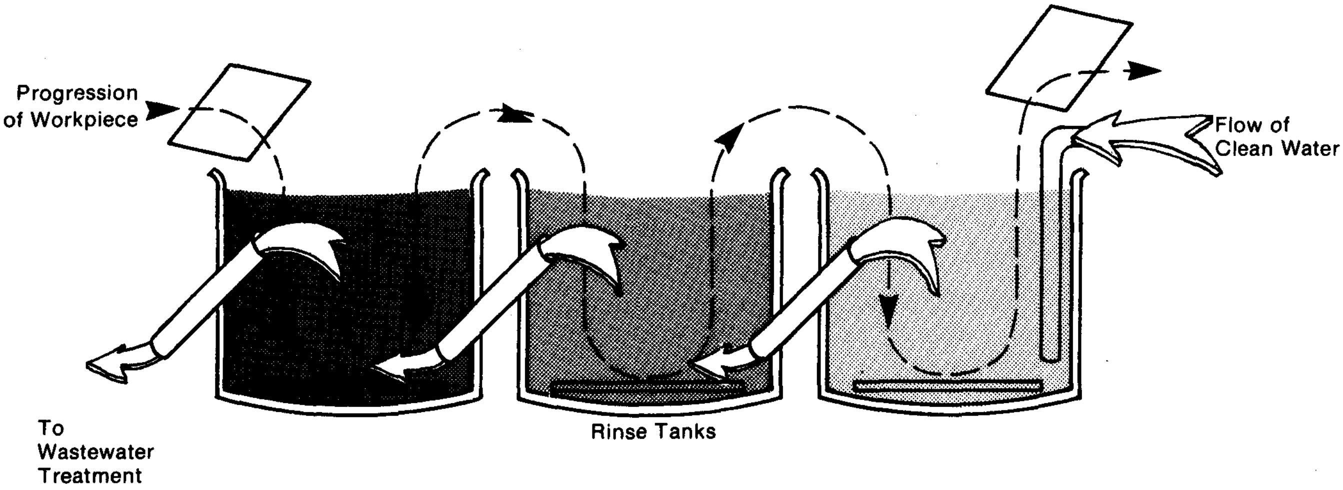
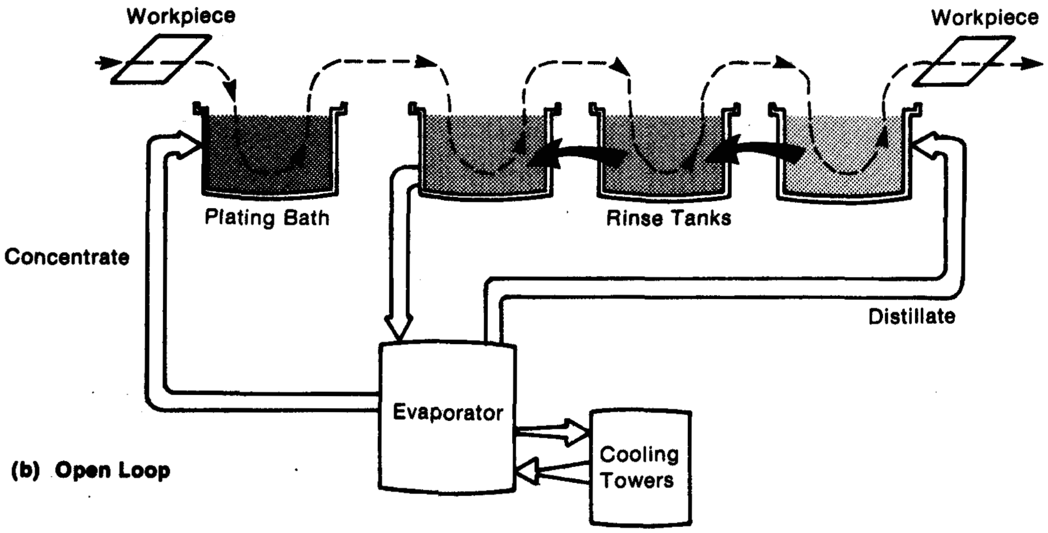


Figure 4-1 Counter-current Rinsing.
The workpiece is moved from the tank on the left to the tank on the right; rinse water flows in the opposite direction.
Source: EPA

The use of a recovery system may necessitate additional measures to reduce the build-up of contaminants. The purification system required depends on the type of process chemicals being used.

A wide variety of recovery technologies used in the metal finishing industry are discussed below. Many of the technologies are applicable to both process bath regeneration and material recovery from dragout.

(a) Closed Loop



(b) Open Loop

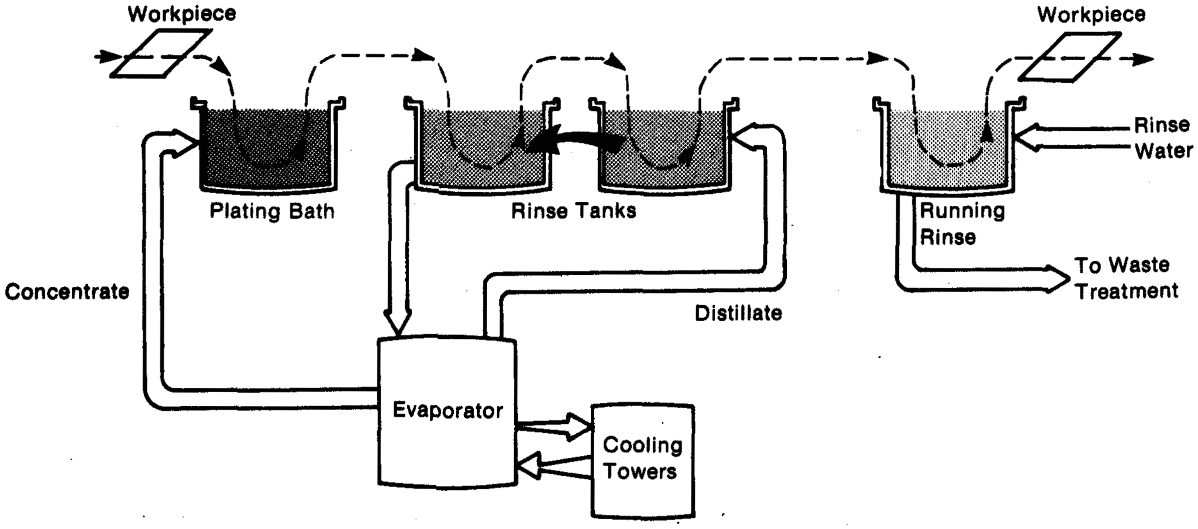


Figure 4-2 Two Electroplating Configurations.
The rinse water is circulated countercurrent to the plating process. Excess metal is recovered by evaporation.
Source: EPA

Evaporation -- Evaporators for material recovery and water reuse in the metal finishing industry are a proven technology with expanding applications. Evaporation is a simple concentration process. Water is evaporated from a solution until the chemicals remaining in the wastewater are concentrated to a level that allows their reuse in the process bath. Figure 4-2 illustrates the use of evaporation to recover metals from electroplating rinse water. Although evaporation has the highest energy requirements of the recycle alternatives, its simplicity and reliability are compensating factors.

Evaporative recovery is the method of choice for chromium plating. If a large volume of evaporated dragout is returned to the process bath, accumulated metal impurities will need to be removed by another system, such as cation exchange. The equipment costs for a chromic acid evaporative recovery unit with a capacity of 20 gallons per hour is approximately $25,000. This does not include installation, cost, or equipment costs for an ion exchange unit.

Electrolytic Metal Recovery (EMR) -- EMR is finding successful application with electroplaters, rolling mills, printed circuit board manufacturers, and metal coating firms. A static rinse with an EMR unit is usually situated downstream of the process tank to remove the bulk dragout. Solution from the static rinse tank is circulated through an electrolytic cell where the metal is removed.

In the cell, a direct current is passed through the metal-bearing solution. Electrochemical reduction of metal ions to elemental metal takes place at the cathode. Simultaneously, oxygen is evolved at the anode.

Metal deposited on the cathode is allowed to build up to a thickness of about one-half inch. The power is then shut off and the deposited metal is recovered from the cathode. Modern electrolytic cells, under favorable conditions, can recover 99 percent of the dissolved metal in rinse solutions.

Copper, tin, silver, zinc, cadmium, and precious metals can be recovered from plating and etching dragout by EMR. Because the electrolytic process maintains a low concentration of metal in the dragout tank, the amount of metal carried into the succeeding rinse tanks is minimized. This, in turn, reduces the load to the downstream waste treatment plant reducing production of sludge.

Recent advances in EMR technology make possible the recovery of metal from spent electrolysis baths and from chloride or ammonium etch solutions.

Reverse Osmosis -- In reverse osmosis, a waste solution is pumped under pressure into a chamber containing a semipermeable membrane. Only solvent (water) passes through the membrane, salts and dissolved metals remain. Two output streams are produced: one very concentrated with metals and one relatively clean. The clean water can be reused or discharged, and the concentrated solution can be used in the process bath.

Reverse osmosis has been successfully used on the rinse waters from a number of electroplating baths, including Watts nickel, nickel sulfate, copper pyrophosphate, nickel fluoroborate, zinc chloride, copper cyanide, zinc cyanide, and cadmium cyanide baths. Chromic acid and high pH cyanide baths are not easily treated with reverse osmosis.

Reverse osmosis recovers plating solution additives in addition to dissolved metals. This is a major advantage.

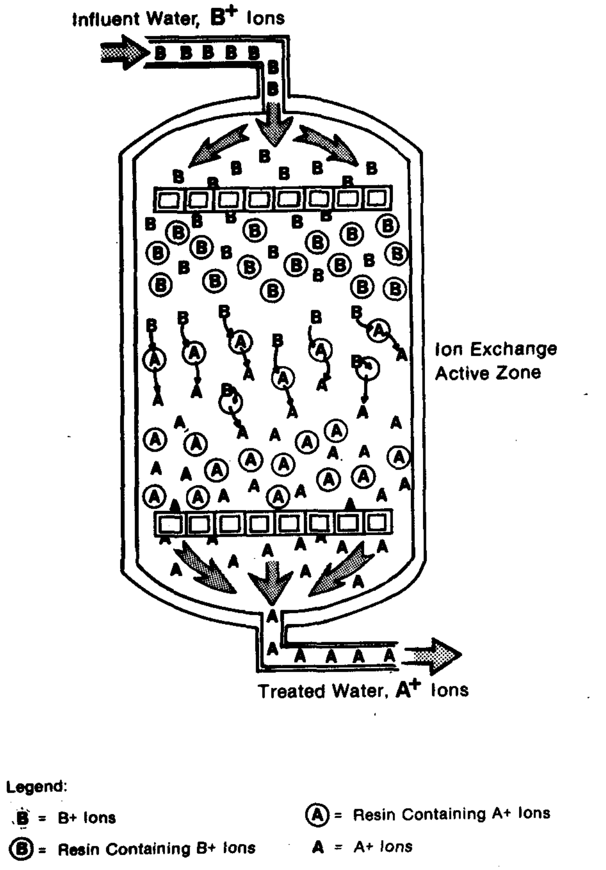


Figure 4-3 Ion Exchange Column.
B+ ions displace A+ ions from the resin. The B+ ions remain bound to the resins. In waste treatment applications B+ ions are the hazardous constituents and A+ ions are comparatively innocuous.
Source: EPA

Unfortunately, reverse osmosis units are expensive to install, maintain, and operate. The equipment cost for a reverse osmosis unit with 330 square feet of membrane is approximately $200,000. High pressure must be maintained at all times during operation leading to large operating expenses.

Ion Exchange -- Ion exchange units consist of a resin bed or beds designed to remove cations (positively charged ions) or anions (negatively charged ions) from a waste stream. The liquid waste flows through the exchange bed; hazardous ions from the waste bind to the bed material, displacing comparatively innocuous ions (Figure 4-3). A treatment system including an ion exchange unit is shown in Figure 4-4. Periodically, the resin beds must be chemically treated to remove the absorbed waste. For this reason, ion exchange units are usually installed in parallel; the waste stream is diverted through the second unit while the first one is being regenerated. The material removed from the resin beds often can be used in process baths.

Metal finishing facilities can utilize ion exchange to concentrate and purify their process baths. Ion exchange has proven effective for recovery of aluminum, arsenic, cadmium, chromium (hexavalent and trivalent), copper, cyanide, gold, iron, lead, manganese, nickel, selenium, silver, tin, and zinc.

Advantages of ion exchange are that water savings are significant, energy consumption is relatively low, and the process works well on dilute waste streams.

Disadvantages are high costs for chemicals, labor, and maintenance. In addition, capital costs are high and the process is not capable of producing a highly concentrated stream for recycling.

Crystallization -- Heavy metals can be removed from saturated solutions with crystallization. This process, like EMR, removes a portion of the metal to form a solid that can be sold, reused, or dewatered and landfilled. Crystallization is best suited for on-site treatment waste in which stream segregation is possible and metal concentrations are high, such as in an etch or strip tank.

Commonly, a portion of the process tank solution is circulated through a refrigeration unit where crystallization takes place. The newly formed crystals are separated by gravity or filtration. With proper adjustment of the system, the desired metal concentration can be maintained in the process tank.

Electrodialysis -- An electrodialysis apparatus is a series of alternating cation and anion permeable membranes between two electrodes (Figure 4-5). Wastewater passes between the parallel membranes. An electrical potential applied across the membranes causes the ions to migrate towards the electrodes. Alternate cells become either loaded with ions or depleted of them. The concentrated streams are sent to the process stream while the dilute stream goes to the rinse tank.

Electrodialysis has been shown to be an effective method for concentrating rinse waters to a high percentage of their original bath strength. Nickel, copper, chromic acid, iron, and zinc can be removed from process wastes by electrodialysis. The economic feasibility of the process depends heavily upon the life of the membranes which are susceptible to fouling and to leakage. Field repair is impractical.

Advantages of electrodialysis include low energy consumption, production of a highly concentrated stream for recovery, and good selectivity so that many undesirable impurities are eliminated.

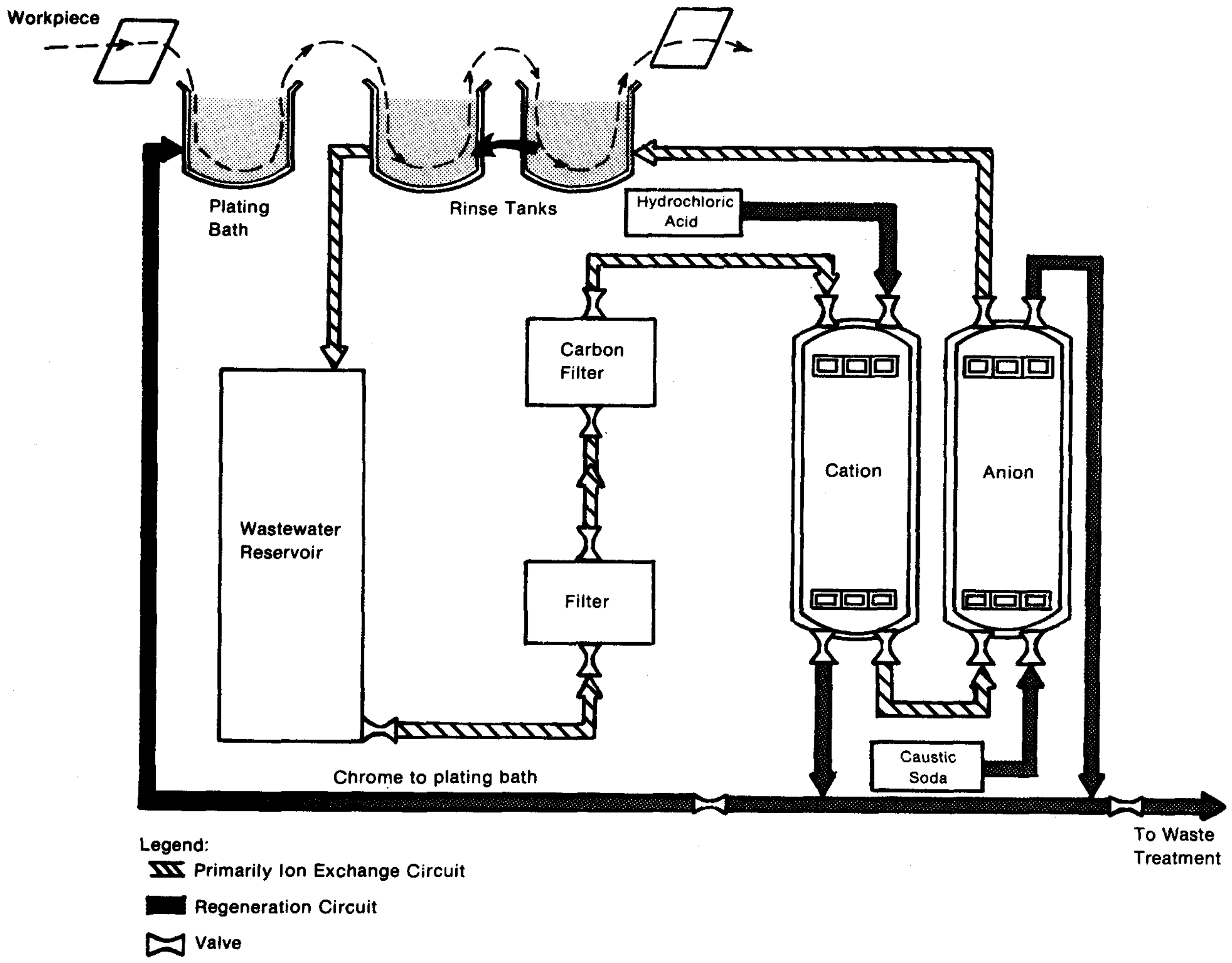


Figure 4-4 Ion Exchange for Chromic Acid Recovery.
This system includes provisions to recover the reuse and absorbed metal and water.
Source: EPA

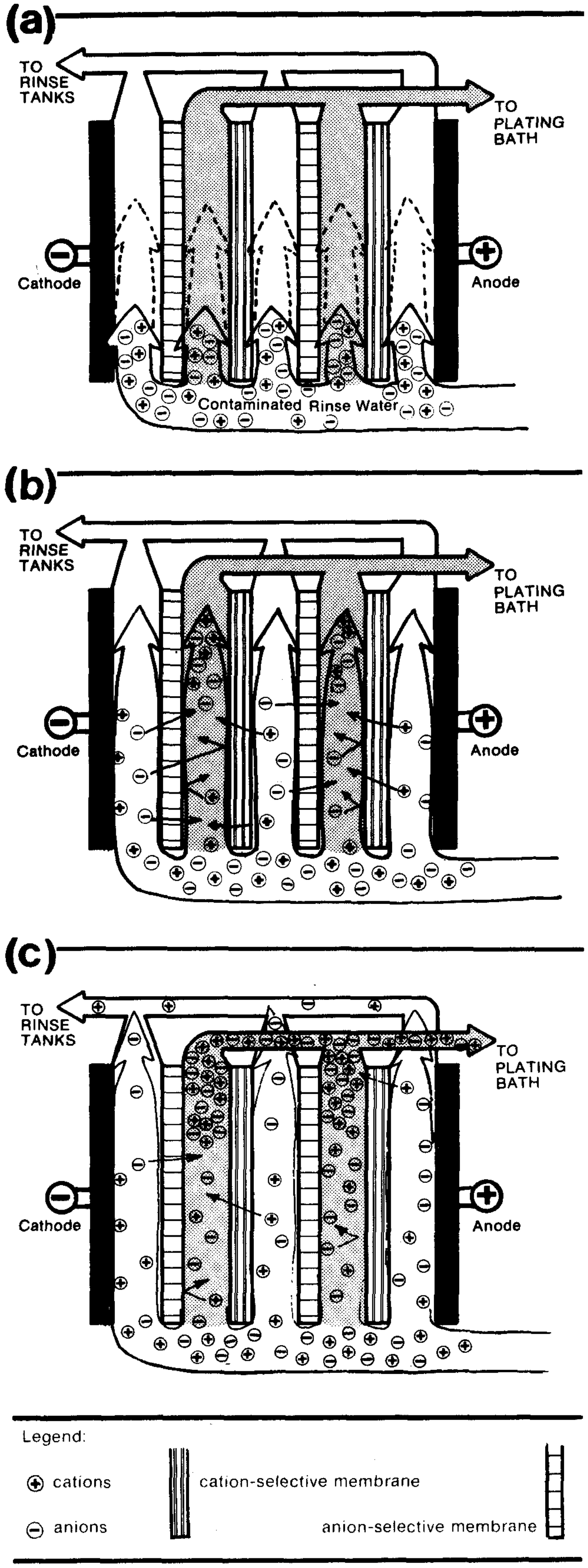


Figure 4-5 Electrodialysis Flow Schematic.

(a) As contaminated rinse water flows through the chamber, ions are attracted toward the electrodes.
(b) The ion selective membranes cause the ions to collect in alternating chambers. **(c)** The ion concentrated stream is returned to the plating bath; the ion depleated stream is used in rinse water.

Unfortunately, electrodialysis requires careful operation and periodic maintenance to avoid damage to the membranes.

C. OFF-SITE RECOVERY AND RECYCLE TECHNOLOGY OF DISSOLVED METALS

While scrap ferrous and nonferrous metals have been extensively recycled, dissolved metals are not easily reclaimed from blended waste streams. The presence of other dissolved metals and organic contaminants often make it uneconomical to recover the metal of interest from the waste, making further use of that metal impractical or impossible. In addition, the currently depressed value of raw and scrap metals further reduces the economic incentive for recovering or recycling dissolved metals in wastes.

There are notable exceptions to the general absence of off-site recycling of dissolved metal wastes. Off-spec and slightly contaminated electroplating and etching solutions from the electronics industry are often reused by metal finishing industries with less demanding requirements for their process solutions. Metal finishing wastes have also been used to provide micronutrients such as zinc in agricultural fertilizers. Precious metals are recovered by some off-site recyclers, but the volume is small.

D. RECOVERY AND RECYCLE OF ACID WASTES

Because most acid wastes also contain dissolved metals, and often other compounds, recycling such solutions is difficult. Commercially recyclable acid wastes are generally concentrated acids that contain very little dissolved metal.

Sulfuric Acid Regeneration

In 1984, over 79 billion pounds of sulfuric acid were produced in the

United States alone; far more than any other single chemical. The recycling of sulfuric acid is well established. Spent, contaminated, or dilute sulfuric acid may be regenerated in the process used to manufacture the acid from raw materials.

The recycling of sulfuric acid is exempt from many of the hazardous waste management regulations at the state and federal levels. In particular, storage of sulfuric acid prior to recycling is exempt from the 90-day time limit, and transport of sulfuric acid to recycling is exempt from manifesting requirements.

Generation of sulfur dioxide gas, the first stage of sulfuric acid manufacture, takes place in a furnace. Elemental sulfur combined with oxygen burns to produce sulfur dioxide (CO_2) and heat. Spent sulfuric acid, on the other hand, absorbs heat and decomposes to sulfur dioxide, oxygen, and water. These feedstocks are combined in the furnace. Hydrocarbon fuel is often added to maintain the high temperatures needed. The mix at any time is determined by the availability of fuels and the need for optimal operating conditions.

The sulfur dioxide (SO_2) is catalytically oxidized to sulfur trioxide (SO_3). The catalyst, vanadium pentoxide, is expensive and easily damaged by hydrogen chloride, water, and other common contaminants of the sulfur dioxide stream. Consequently, the sulfur dioxide is treated before it reaches the catalyst. The stream is washed with water to remove hydrogen chloride gas and washed with sulfuric acid to remove water.

The sulfur dioxide must be cooled before the catalytic oxidation. Gas emerges from the furnace at temperatures near 1,000°C. The oxidation must take place near 400°C. The oxidation reaction is exothermic and reheats the gas.

The final stage is adsorption of sulfuric trioxide by water to form sulfuric acid. Extensive variations are possible depending on the desired product: dilute sulfuric acid, concentrated sulfuric acid, or liquid sulfur trioxide. The sulfur oxide gases and associated products are extremely corrosive; careful design is necessary to protect the piping and equipment.

E. TREATMENT OF ACID WASTES

Waste acid solutions can be treated by neutralization. Acid wastes containing high concentrations of dissolved metals are often neutralized in the process of precipitating those metals from solution. Neutralization technology is discussed below as part of the precipitation process for dissolved metals. Several commercial treatment facilities in California offer acid neutralization services. In the fall of 1985, the cost for neutralization ranged from less than $.60 per gallon for weak acids (below ten percent) to almost $1.00 per gallon for strong acids.

F. TREATMENT OF DISSOLVED METAL WASTES

On-site treatment of dissolved metal wastes generates water to be discharged and solid waste or sludges to be disposed. On-site facilities can be installed to treat the relatively dilute wastewaters generated from rinsing operations, and to treat the much more concentrated contaminated metal finishing process solutions.

Off-site treatment facilities for dissolved metal wastes generally receive solutions with high concentrations of metals from spent or contaminated process tanks. Wastes received at off-site facilities require a prescreening and chemical analysis before mixing with other wastes. Wastes managed at off-site facilities often require pretreatment for removal of oil, cyanides, and hexavalent chromium (CrVI).

Although waste management practices and objectives may differ between on-site and off-site facilities, the treatment processes for dissolved metals are similar, differing primarily in the volumes and concentrations encountered. Conventional treatment processes for managing wastes containing dissolved metals fall into three categories: (1) treatment processes that convert dissolved metals into solids; (2) solids removal; and (3) sludge conditioning and dewatering.

Treatment Processes That Produce Solids

Solar Evaporation -- This is a simple means to convert metal containing liquid waste to a form that meets California's land disposal requirements. The dried metal salts can be buried directly in a Class I land disposal facility.

A waste stream can be fed to a surface pond and taken to dryness by solar evaporation. However, present California statute (Toxic Pit Cleanup Act of 1984) prohibits the use of impoundments for restricted wastes (Table 4-1), therefore, surface ponds may be used only for nonrestricted wastes.

Several factors must be considered when wastes are to be processed by solar evaporation. The ponds must be constructed according to RCRA specifications; proper construction of ponds is expensive. The space required must also be considered. Pond size is determined by the volume of waste input and the average evaporation rate. In most areas industrial land is too valuable to be used for evaporation ponds.

Mechanical evaporation employs an energy source other than solar heat. Many types of units are available such as flash, rising film, and single-effect evaporation. Mechanical evaporators usually do not take the waste to dryness. Where waste steam is available, it may be used as the heat source in a single-effect evaporator. In some cases, water can be condensed from an evaporator and reused as needed.

Commercial evaporators are available as "off-the-shelf" items and can be tailored to specific applications. Other firms will construct custom units as required. Although evaporation may not be practical where other processes are available, it is very useful for the treatment of some dissolved metals that do not lend themselves to conventional treatment processes. Evaporation may be the only feasible process for treatment of certain dissolved metals.

Precipitation -- Precipitation is also a common process used to convert dissolved metals to solids. Several reagents are available and are widely used, each having its advantages and disadvantages. These reagents include lime, caustic soda, soluble and slightly soluble sulfides, and sodium borohydride. Each reagent is discussed later in this section. Several precipitation systems are illustrated in Figure 4-6.

Pretreatment is usually required before precipitation methods can be used. Certain compounds in the waste solution must be chemically treated or removed. All cyanides and oils must be removed and any hexavalent chromium present must be reduced to the trivalent state. Precious metals are often removed before precipitating other metals. A full pretreatment and precipitation system including flocculation is illustrated in Figure 4-7.

Oil present in a waste can be in any of three forms: free oil, water soluble oil, and oil emulsions. Dissolved metal wastes do not commonly contain large quantities of oil, but when oil is present, it must be removed before further treatment. A variety of techniques are used to remove oil from waste: skimming, coalescing, centrifugation, ultrafiltration, carbon adsorption, and de-emulsification. Many commercial units and chemicals can be readily purchased for these tasks.

Hexavalent chromium is reduced to trivalent chromium in two steps. First, the pH of the solution is adjusted to between two and three with sulfuric acid. Secondly, a reducing agent, such as sodium bisulfite, is added until the reduction reaction is complete. Sulfur dioxide gas can be used in place of the bisulfite. This reduction is well suited to automatic control and is generally carried out with a pH controller adjusting the acid feed and an oxidation reduction potential (ORP) controller adding the reducing agent.

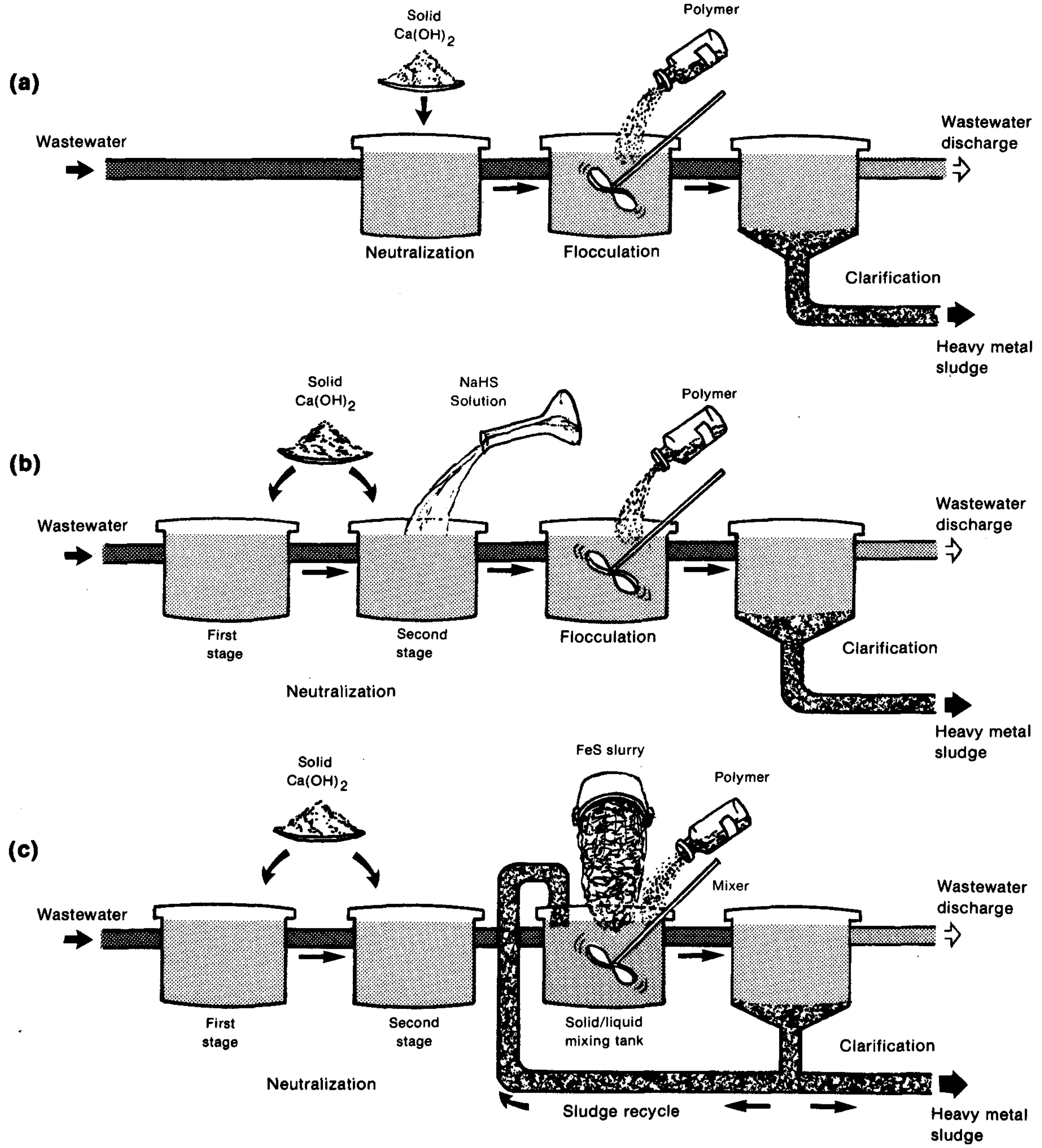


Figure 4-6 Metal Precipitation Systems.
(a) Hydroxide precipitation (b) Soluble sulfide precipitation (sulfide added in solution) and (c) Insoluble sulfide precipitation (sulfide added in a slurry).
Source: EPA

Hydroxide Precipitation With Lime, Quicklime, or Limestone -- The reagents used in this process are calcium hydrate, CA$(OH)_2$, calcium quicklime (CaO), and calcium limestone ($CaCo_3$). For the purpose of this discussion, only calcium hydrate (hydrated lime) will be considered.

Hydrated lime is usually fed to a treatment system in the form of a slurry consisting of about 10 to 15 percent solids. The slurry form facilitates automation of the reagent addition. Where large batch treatment systems are used, such as off-site facilities, bulk lime is usually added directly to the reactor in dry form. The reaction takes place almost immediately, producing large amounts of metal hydroxide precipitates. The metal hydroxides are usually then treated with a flocculating agent to promote settling (Figure 4-6a).

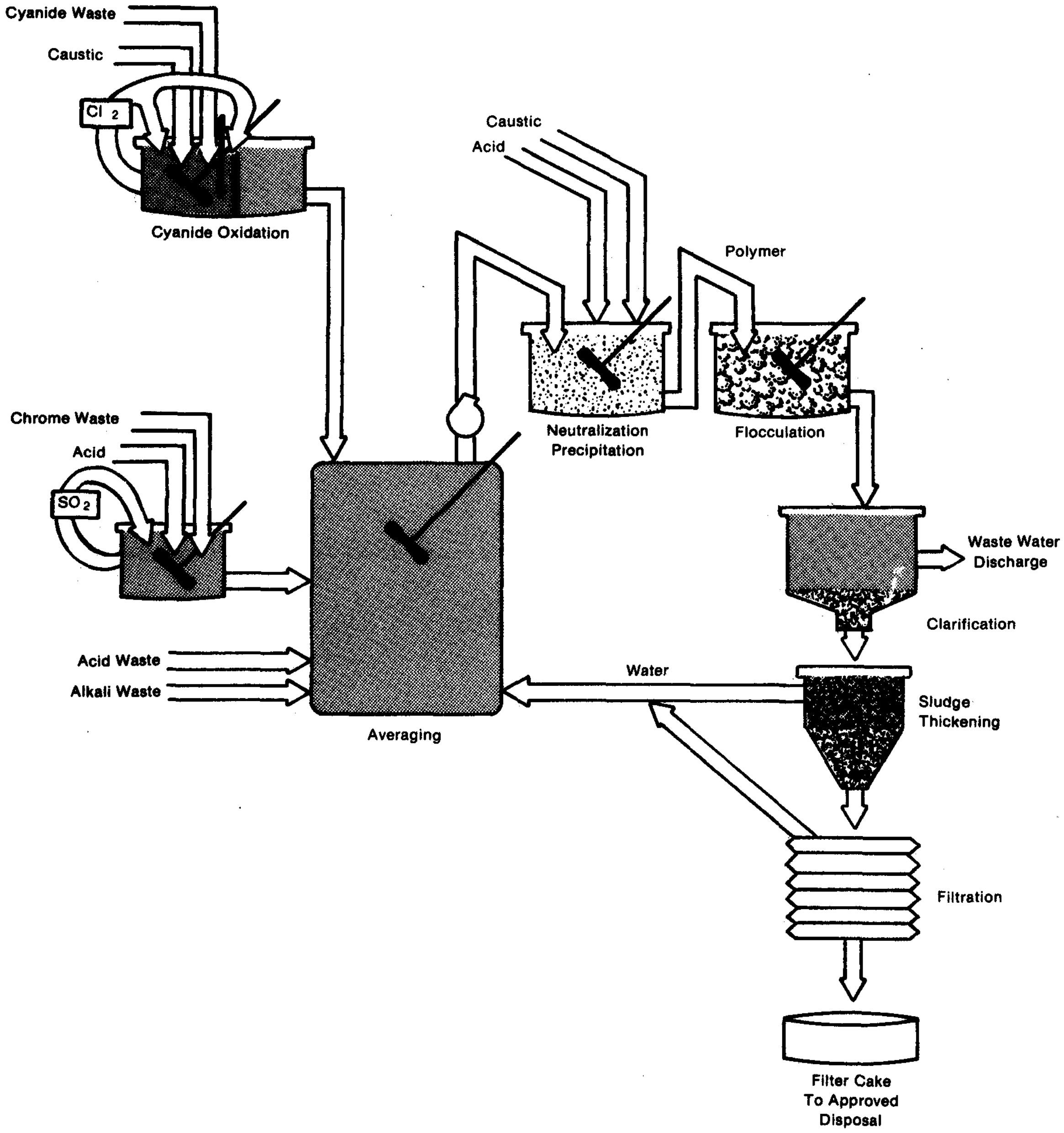


Figure 4-7 Conventional Wastewater Treatment/Precipitation System for Electroplating.
Cyanide, chrome, and acid/alkali components are treated prior to precipitation and sedimentation.
Source: EPA

One of the principal advantages of lime as a neutralizing reagent is its low cost. The use of lime for dissolved metal precipitation will usually produce a large amount of sludge to be disposed of. However, this type of sludge is easily settled and may not pose handling and disposal problems.

Disadvantages of a lime system are the large purchase and installation costs. Since in most cases the lime is handled as a slurry, a complete recirculating pumping system is required including mixing tanks, agitators, and circulation pumps. Lime slurry systems require periodic maintenance on the handling and delivery systems to ensure satisfactory operation.

Hydroxide Precipitation With Caustic Soda (NaOH) -- Caustic soda is another common reagent used to precipitate dissolved metals. This reagent is usually added as a liquid. Caustic soda does not produce the large volume of sludge typical of treatment with lime.

Caustic soda is very soluble in water making it well suited to automated systems where the material has to be pumped some distance. Because caustic soda is easily handled and does not produce much sludge, it is applicable to small systems.

The major disadvantage of caustic soda is the cost of the reagent. Although the installation cost can be considerably less than for other reagents, the operation cost can more than offset this, especially for a large system. The low volume of sludge generated is an advantage of caustic soda over lime which saves money on equipment and disposal costs.

Sulfide Precipitation -- The addition of sulfide ions effectively precipitates many dissolved metals. Metal sulfides are less soluble at high pH than are metal hydroxides, so sulfide precipitation can be used as a second or polishing step after the bulk of the dissolved metals have been removed by hydroxide treatment. This may be necessary when the effluent will be discharged to a sewer.

Two methods of sulfide precipitation are in common use (Figures 4-6b and 4-6c). The first uses a soluble sulfide such as sodium sulfide, calcium polysulfide, or sodium hydrosulfide. In this method, sulfide solution is added to a waste solution with the pH maintained above eight. Careful management of this type of system is critical, and generally the sulfide is added by an automatic controller. A well operated sulfide precipitation system can remove metals to a very low level.

The second method uses a slightly soluble sulfide such as ferrous sulfide as a source of sulfide ions. The sulfide can be added as a powder or in a slurry. Most metal sulfides are less soluble than ferrous sulfide; consequently, the metal will precipitate as the iron dissolves. Because the reaction is performed at a pH greater than eight, the iron will subsequently precipitate as iron hydroxide.

In both methods, the minimum solubilities of the dissolved metals occur over a narrow pH range. Therefore, pH control is critical in sulfide precipitation processes.

A major advantage of sulfide precipitation is that hexavalent chromium is reduced to the trivalent state and then precipitated as chromium hydroxide without an additional reagent. This eliminates the two-step reduction required where the precipitation is accomplished with hydroxides.

A disadvantage of the soluble sulfide method is that in the presence of excess sulfide, some hydrogen sulfide gas can be produced. A vacuum venting system and scrubber is needed to remove the fumes. This problem can be avoided by using solid ferrous sulfide which, because of its low solubility, does not produce an excess of free sulfide ion in solution. Use of excess of ferrous sulfide reagent should be avoided to minimize sludge production.

Precipitates formed by sulfides are usually very finely divided and hard to settle. Larger particles (flocculants) are often added to promote settling.

The cost of sulfide precipitation depends on the concentrations of the metals to be removed. It may be more economical, therefore, to remove the bulk of the dissolved metals by hydroxide precipitation and then treat with sulfide. Initial and operating costs will probably be less for ferrous sulfide systems than for soluble sulfide systems. Where sulfide precipitation follows hydroxide precipitation, it is recommended that the hydroxide sludge be removed before the sulfide reagent is added.

Sodium Borohydride Precipitation -- Sodium borohydride precipitation provides a straightforward method of removing certain soluble metals from solution. Sodium borohydride is a mild reducing agent and will cause precipitation of soluble metal cations as the insoluble elemental metal. The precipitated metals can be removed from solution by filtering or decanting. The recovered metals can be reused, landfilled, or sold. This process works well for removing lead, mercury, and nickel. Sodium borohydride can also be used to precipitate several precious metals, thus providing a method for their recovery. This reagent is generally used for on-site treatment.

Sodium borohydride is available as a free-flowing active powder or as a stabilized solution in caustic soda. The solution is more commonly used because it is easier to handle and reacts more readily with waste streams. Some metals require a narrow pH range for optimal reduction by sodium borohydride; however, most are effectively reduced at any high pH. Sodium borohydride reduction is most useful where metals are to be recovered for reuse or sold.

Solids Removal

This section covers the formation and primary thickening of sludges in preparation for final dewatering. The sludges commonly encountered in this type of treatment are those of precipitated metal hydroxides.

Sedimentation is a simple process, the result of gravitational forces acting on the floc for a given period of time. This process can be accomplished in several ways, the more common of which will be considered here.

Once precipitation has started, a coagulant or flocculant is added to produce larger, more easily removed particles. Coagulants in common use are: alum, ferrous chlorides, ferrous sulfate, ferric chloride, ferric sulfate, and lime. Some organic polymers are used as flocculating agents for specific heavy metals and produce excellent results. Flocculation can be accelerated by vibration of the mixture (Figure 4-7).

Settling Ponds and Tanks -- Some sedimentation processes can be conducted in a large pond (if waste is not restricted from land disposal) or tank. Liquid must remain in the tank long enough for the suspended solids to fall to the bottom. The clear liquid is then decanted from the top and the sludge is collected from the bottom.

Equipment used with settling ponds and tanks is simple, but often expensive to construct. Ponds must now meet RCRA requirements. Tanks themselves can be purchased at low cost, however, tanks with adequate throughput may be objectionably large. Commercial tank settlers are available in various sizes.

Slant Tube and Inclined Plate Clarifiers -- Slant tube clarifiers are an alternative device for sedimentation. A slant tube clarifier is a series of parallel tubes that are set at an angle to the surface of the liquid. The tubes are housed in a tank structure with some type of overflow weir at the top and a mechanical scraper at the bottom for sludge removal. The tubes are usually made of plastic and are generally about two inches by two inches square. In most units, the tubes are set at an angle of between 45° and 60° with the water surface.

Liquid flows upward through the clarifier. Solids removal takes place within the tube section. The floc particles have only a short vertical distance to fall before striking the lower side of the tube. The particles then slide down the lower side of the tube and into the sludge bed where they can be removed.

An inclined plate clarifier is much the same as the slant tube, except that plates are used in place of the tubes.

Both slant tube and inclined plate clarifiers have the advantage of being small in size for their throughput capability. These units are efficient and are available in sizes to handle a few gallons per minute (gpm) to several hundred gpm. Many units are off-the-shelf items and may be purchased from several different companies.

The disadvantages to both types of clarifiers are the higher cost and maintenance requirements than with settling tanks.

Air Flotation -- Air flotation is used where the floc formed has a specific gravity less than that of water, or is very finely divided. Flocs in this category would require an objectionably long residence time in either slant tube or other type of clarifier.

One of the most common variations is dissolved air flotation. In this technique, a solution super saturated with air is injected into a flotation cell where bubbles form to lift the solids and create a surface sludge blanket. This blanket can then be mechanically removed for further dewatering; the clear liquid can be decanted from the cell and sewered or returned for reprocessing.

Dispersed air flotation is also a common approach. This process is essentially the same as dissolved air flotation, except that air is bubbled directly into the flotation cell through a dispersion screen. The bubbles lift the floc to the surface where it forms a sludge blanket that can be mechanically removed.

In general, air flotation units are fast, efficient, and reliable. The units are small in size and can be adapted to many situations. Many units are available as off-the-shelf items in various sizes and capabilities.

These units have the disadvantages of being more costly to operate than sedimentation processes and require more frequent period maintenance.

Sludge Dewatering

Dewatering is the final step in preparing a metal containing sludge for land disposal. Two processes will be discussed in this section: evaporation and filtration.

Evaporation -- This is the simplest process for sludge dewatering. Sludge taken from a clarifier is deposited directly in an evaporation pond and allowed to dry. The dried sludge can then be removed to a land disposal facility.

The advantages and disadvantages for evaporating sludges are the same as for evaporating solutions, discussed above.

Vacuum Drum Filter -- In this unit the filtering takes place on the surface of a drum which is coated with appropriate filtering medium. A vacuum is applied to the inside of the drum. The drum is rotated in a trough where the filter media contacts the sludge. Clear liquid is pulled through the filter media, collects on the inside of the drum, and is conveyed through the vacuum system. A scraper removes the dewatered sludge from the outside surface. The sludge collected can be taken to a land disposal facility. Depending on the material being dewatered, a sludge cake containing between 20 percent and 40 percent solids is produced with this type of unit.

Vacuum drum filters operate on a continuous feed basis and produce good results. However, the cost of installing a vacuum system can be high. These filters are available in a variety of sizes, filter types, and designs.

Filter Press -- The filter press is one of the most common units used for sludge dewatering. The press consists of a series of plates covered by a filter media. Several plates are stacked together on rails. Sludge is pumped into the space between the plates which are then pressed together. Water is removed by the compression, leaving behind the dewatered sludge cake. The frames are then opened and the sludge is collected in a hopper or other device for transport to a disposal facility.

Filter presses are reliable and capable of producing a dry sludge cake. The solids content of the compressed sludge cake is typically between 40 and 50 percent. One disadvantage of filter presses is that they are batch-fed, and may require sludge holding facilities. Presses are available in all sizes ranging from units that are hand operated with a capacity of 0.5 feet to units of about 600 feet capacity.

Belt Filter Press -- The filter belt press is much like the filter press in that wet sludge is compressed and water removed by direct pressure. In this case, wet sludge is fed to a circular belt that pass through a series of rollers which progressively press the sludge. The solid cake is rolled off the end of the belt and collected for disposal.

Filter belt presses are well suited for continuous feed operations producing large volumes of sludge. They are capable of producing a filter cake of up to 40 percent solids. For large operations, they may be the most economical dewatering system. Belt presses have many of the same problems as filter presses, and also require frequent maintenance.

CHAPTER 5
CYANIDE WASTES

A. INTRODUCTION

Cyanide waste streams are produced by several industries in California, including ore extraction, photographic processing, synthetics manufacturing, and metal finishing.

Cyanide-containing wastes include metal finishing contaminated rinse water, spent process solutions, and accidental spills. Metal finishers use cyanide baths to hold metal ions such as zinc and cadmium in solution during the electroplating operation. Metal platers may also use cyanide in their stripping solutions.

Contaminated rinse waters generally have cyanide concentrations under 100 milligrams per litre (mg/l), and typically at about 10 mg/l to 20 mg/l. These dilute wastes are usually treated to meet municipal pretreatment requirements and are then discharged to sewers.

Spent cyanide process solutions typically have concentrations above 1,000 mg/l. Batch discharges of these spent solutions occur periodically when the quality of the solution is no longer suitable for the plating operation. The relative volumes of spent process solution wastes are not large, but the cyanide concentrations are high.

As of June 1, 1983, liquid hazardous wastes containing free cyanides at concentrations greater than or equal to 1,000 mg/l were prohibited from land disposal in California. These wastes are now being treated on site, or at one of four off-site facilities in California. Methods used by the off-site facilities are described in this chapter.

B. TREATMENT PROCESSES FOR CYANIDE WASTES

Several processes can be used to treat aqueous cyanide wastes. Treatment of aqueous cyanide typically requires chemical oxidation, or conversion to thiocyanate. Cyanide treatment processes are described below, with examples of available off-site facilities included for each process where applicable.

<u>Oxidation With Chlorine and Hypochlorites (Figure 5-1)</u> -- This has been the most widely accepted method of cyanide treatment during the past 30 years, and is still the most common method. Cyanide is first oxidized to cyanate at pH 9 to 11. Cyanate is then converted to bicarbonate and nitrogen gas at pH seven to nine. The theoretical chlorine requirement is 6.8 pounds of chlorine per pound of cyanide. The actual chlorine requirement for a given waste is always greater due to the presence of other oxidizable constituents. Additional chlorine helps to speed up the reaction.

Chlorine or hypochlorite oxidation is convenient because it can be carried out at ambient temperature and it is suitable for automatic control.

Most chlorine and hypochlorite treatment units for on-site use are designed to treat only dilute cyanide solutions and rinse waters. These batch-type units may be modified so that plating baths with cyanide concentrations up to 5,000 mg/l can be treated. Solutions with cyanide concentrations above 5,000 mg/l or solutions that are heavily complexed with iron or nickel generally require greater expertise in treatment control than the average plating shop can provide. Treatment of concentrated cyanide solutions produces a great deal of heat and undesirable side reactions can take place unless the operation is well controlled. Currently, equipment is not generally available for on-site treatment of high concentration or heavily complexed cyanide waste. High concentration cyanide wastes should be treated at a centralized facility.

Some disadvantages of cyanide oxidation with chlorine or hypochlorite include: the possible emission of volatile intermediate reaction products, and chemical interference in the treatment of mixed waste.

Improper chlorination of cyanide ion, hydrogen cyanide, or thiocyanate ion, particularly under conditions below pH ten, will result in increased evolution of cyanogen chloride, which is as hazardous as hydrogen cyanide.

The presence of nickel, cobalt, iron, silver, and gold slow the oxidation of cyanide. The reaction will take place if sufficient time is provided.

Many companies, including several listed in California, offer prepackaged and custom designed chlorine and hypochlorite oxidation units for wastewater treatment for metal finishers. Most of these are designed to both treat the cyanide wastes and to remove heavy metals from the rinse waters before discharge to municipal sewers. The sizes of these treatment units range from batch units with capacities of 100 gallons per day to continuous units which can handle hundreds of thousands of gallons per day. These units vary in complexity depending on the metal finishing process employed, the requirements of the local sewage treatment plant, and the space available for the treatment facilities.

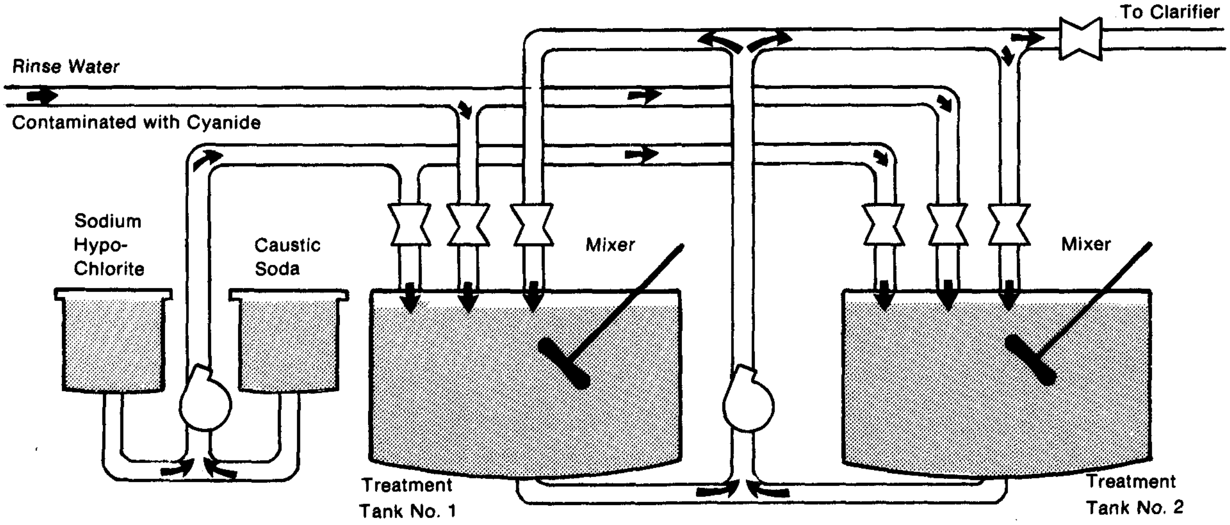


Figure 5-1 Batch Treatment of Cyanide with Sodium Hypochlorite.

Capital costs for chlorine hypochlorite treatment systems vary considerably. The minimum equipment costs for a small batch system (about 200 gallons per day) is around $10,000. Continuous flow systems which treat cyanide and remove dissolved metals range in cost from $50,000 for moderate units (around 20 gallons per minute) to hundreds of thousands of dollars for high flow custom systems. The cost to install the treatment unit can be comparable to the purchase price. Operating cost using chlorine or hypochlorite to treat cyanide ranges from $2.50 to $7 per pound of cyanide for on-site treatment. Examples of commercial chlorination units are presented in Table 5-1.

Industrial waste treatment services which exist in the eastern United States charge $3 to $4.50 (1982 dollars) per pound of cyanide for treatment. Such facilities have a much longer operating experience than similar facilities in California and may be indicative of stable costs for treatment of cyanide. The costs vary depending on the initial concentration of cyanide, interference from heavily complexed metals such as iron and nickel, and the stringency of local discharge requirements when the effluent is discharged to sewers.

TABLE 5-1

EXAMPLES OF COMMERCIALLY AVAILABLE CHLORINATION UNITS

Manufacturer	Capacity of Units	Units in Service	Cost Examples
Advanced Metal Finishing, Inc.	1,000 gallons per day to 350 gallons per minute	More than 300	20 gpm...$50,000 120 gpm..$125,000
Advanced Chemical Systems, Inc.	5 gallons per hour to 1,000 gallons per minute	50	50 gpm..$100,000

Oxidation by Hydrogen Peroxide -- A hydrogen peroxide solution with formaldehyde may be used to oxidize sodium cyanide, potassium cyanide, and cadmium cyanide. This process is usually operated at a temperature of 50°F to 60°F and at a pH between 10 and 11.5. The effluent from this process has a high biochemical oxygen demand and requires biological treatment before discharge to sewers. Effective oxidation by hydrogen peroxide may require a catalyst. This process is not usually suitable for treatment of copper plating wastes.

Similar to chlorination, oxidation with hydrogen peroxide is a simple process easily automated and which takes place at ambient conditions. Limitations of this process include: possible chemical interference, the limited shelf life of hydrogen peroxide, and incomplete oxidation of cyanide beyond the cyanate level.

Manufacturers and suppliers of hydrogen peroxide generally provide all equipment for storing and handling the hydrogen peroxide solutions. However, the generator must usually retain a specialist to design and install the treatment equipment, tanks, and control systems.

Capital and operating costs for cyanide treatment with hydrogen peroxide are comparable to those for chlorine treatment.

Ozonation -- Ozone, a molecular form of oxygen, effectively oxidizes cyanide. Commercial units are available which include on-site ozone generation. Ozonation shares many of the advantages and disadvantages with other chemical oxidation processes for cyanide. The reaction takes place at ambient temperature and is well suited to automatic control. Oxidation beyond the cyanate level is slow. Chemical interference may be a problem when mixed wastes are treated. Oxidation of strong cyanide complexes, especially iron complexes, is slow. In general, ozone oxidation of cyanides is enhanced by copper ions, high pH, and intimate contact of the cyanide with the ozone.

A small number of vendors, including west coast suppliers, offer ozone oxidation units for treating cyanide wastes on site. Ozone oxidation is probably not economical for small generators. A 50-gallon per minute unit for dilute wastes costs approximately $300,000. Operating costs are approximately half that of chlorine oxidation units.

Electrochemical Oxidation -- Electrochemical oxidation is used to treat free cyanide and cyanate at high concentrations. A direct electrical current oxidizes the cyanide to nitrogen, carbon dioxide, and ammonia. Operating temperatures are around 200°F. Effluent from electrolytic oxidation containing less than 100 mg/l of cyanide can be further treated by chlorination. Wastes containing several thousand milligrams per liter of cyanide have been treated, but the time required to destroy such high concentrations is on the order of several days.

Electrolytic treatment systems are presently available as off-the-shelf units. These systems are modular, expandable, and allow flexibility to treat high concentration cyanide wastes.

Costs for electrolytic oxidation equipment run from $15,000 for a system to treat one pound of cyanide per hour to $30,000 for a system to treat four pounds of cyanide per hour. The major cost of operation is for electricity. An estimated average operating cost is $4 per pound of cyanide removed.

Treatment With Sulfur -- Metallic cyanides react with elemental sulfur to form inorganic thiocyanates. In some cases, polysulfide compounds, calcium polysulfide, or sodium polysulfide can be substituted for elemental sulfur. The reaction is carried out in a reactor at a pH of ten. The reaction is slow, with residence times of two to six days. Thiocyanates are relatively chemically stable, are soluble in water, and are considerably less hazardous than their cyanide precursors.

There is no off-the-shelf equipment available. All equipment is custom designed and built.

Costs for this process are dependent on the availability of an inexpensive source of sulfur.

Only one off-site facility in California offers the sulfur treatment process, Chemical Waste Management, in Kettleman Hills (Table 5-2).

Hydrolysis -- The hydrolysis process provides the plating industry with a simple, effective, and economical alternative for on-site disposal of cyanide wastes. Cyanide is converted to ammonia and formate (formic acid) without expensive chemicals. In hydrolysis, the cyanide waste is placed under a pressure of 250 to 600 pounds per square inch (psi) at a temperature of 475°F to 525°F. In bench-scale tests, cyanides at concentrations of 50,000 mg/l of total cyanide have been reduced to less than 30 mg/l within 60 minutes.

The American Electroplating Society completed tests on a full-scale commercial prototype hydrolysis reactor. The size of the reactor was 150 gallons. The unit was also designed to hold a 55-gallon drum of cyanide sludge for treatment. Operation of the commercial size unit confirmed the same high efficiencies (99.99 percent) obtained in an earlier laboratory program. Although drummed inorganic cyanide sludge was successfully treated, wastes containing organic material did not readily solubilize. The hydrolysis treatment is followed by either oxidation with potassium permanganate to destroy chelating agents and allow precipitation of metal hydroxides, or by sodium sulfide addition to precipitate dissolved metals in order to produce effluent suitable for discharge to sewers.

The design is simple and no exotic equipment is needed. Complete details are available from the American Electroplaters Society, Research Project 53A, 1201 Louisiana Avenue, Winter Park, FL 32789. Their prototype hydrolysis reactor was constructed of stainless steel. However, reactors can be built locally.

The capital and installation costs for a unit to treat 300 gallons per day of wastes containing 50,000 mg/l cyanide are estimated to be as low as $20,000 to $50,000 for a unit designed to treat both liquids and sludges. Estimated overall cost of treatment of liquid cyanide waste, including posttreatment, maintenance, labor, energy, and capital cost, are from $.62 to $1.88 per pound of cyanide. For treatable sludges, the costs range from $1.07 to $1.78 per pound of cyanide.

Other Technologies for Cyanide Wastes -- Cyanide wastes can be treated by many of the techniques used to treat organic waste streams. Both waste types are generally decomposed by oxidation. Biological oxidation is routinely used to decompose dilute cyanide wastes. In the petrochemical industry, cyanide wastes up to 100 ppm are treated with activated sludge and trickling filter processes. A rotating biological contactor has been used to treat gold mine wastewaters with cyanide levels of approximately 30 ppm.

Biological oxidation of cyanides requires caution. A sudden increase in the concentration of cyanide (shock load) can kill the biomass with consequent accumulation of untreated wastes and risk of environmental contamination. Decomposing organisms often require acclimation before decomposing cyanide.

Wet air oxidation (WAO), another technique applied to organic wastes (Chapter 6), also decomposes cyanide wastes. In WAO, materials are oxidized by oxygen at elevated temperatures (350°F to 650°F). High pressures are required to prevent volatization and to increase the dissolved oxygen content in the water. The oxygen is usually supplied in the form of air.

A WAO developed by Zimpro Corporation was placed into operation at Casmalia Resources in Santa Barbara County (Table 5-2) for off-site treatment in 1983. This unit has the capability of treating cyanides and several categories of organic wastes. This unit can achieve destruction efficiencies of better than 99.5 percent; in one case, a cyanide concentration was reduced from 25,000 mg/l to 82 mg/l.

Capital costs for WAO units are from $1 to $2 million for a 10-gallon per minute unit and from $3.5 to $5 million for an 80-gallon per minute unit. The operating costs depend strongly on the waste composition.

Cyanide sludges can be treated by hydrolysis and wet-air oxidation. However, incineration is still the best available technology for the treatment of cyanide sludge, especially for sludge with a high concentration of organics. A complete description of available incineration technology may be found in Chapter 9.

TABLE 5-2

OFF-SITE TREATMENT OF CYANIDE WASTES

Operator and Location	Treatment	Storage Capacity	Treatment Capacity or Batch Size	Cost 1/
IT-Martinez	gaseous chlorine	7,500 gal	5,000 gal tank or 1,600 gal per day	specific quote only
BKK-Chula Vista	sodium hypoclorite	18,000 gal and 13 55-gal drums	up to 10,000 gal per day	$.65 to 4.00 per gallon
Casmalia Resources-Casmalia	wet air oxidation	70,000 gal	15,000 tons per year 2/	$.05 to 1.00 per gallon
Chem Waste Mgmt., Kettleman Hills	calcium polysulfide		4,600 tons year 2/	$.05 to 1.00 per gallon

Supercritical water technology, a noncombustion thermal process, can destroy cyanide wastes. Water heated above 705°F and above 3,200 psi becomes supercritical; at this point, many normally insoluble compounds become highly soluble. Under these conditions, complex molecules are decomposed to low molecular weight compounds. Oxygen, usually added as air, rapidly oxidizes the carbon and hydrogen of the newly-formed low molecular weight compounds. Under process conditions, the inorganic salts formed are almost completely insoluble; they precipitate out, and can be removed by filtration. The remaining stream of supercritical water at high temperature and pressure can be used for process heat or fed to a turbine for generating power.

The supercritical water process has generally been applied to organic wastes. A complete description of the supercritical water process is therefore presented in Chapter 9.

1/ Costs depend largely on concentration.

2/ Assumes equipment is not used for any other waste streams.

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ORGANIC WASTESTREAMS

CHAPTER 6
AQUEOUS WASTES

A. INTRODUCTION

Many hazardous wastes are aqueous (water-based) solutions of toxic compounds. The inorganic wastes discussed in Chapters 4 and 5 are primarily aqueous. In this chapter, we consider aqueous solutions of organic compounds. The petroleum, paint, and chemical industries are only a few of the industries generating large volumes of aqueous organic wastes.

Aqueous wastes may be treated by extraction processes or destruction processes. In destruction processes such as biological degradation, wet air oxidation, and chemical dechlorination, the contaminants are rendered less hazardous. In extraction processes, the contaminants are removed from the solution and thereby concentrated. The extracted materials are often reused.

The purified water resulting from an extraction or destruction process may be reused or discharged.

Most industrial wastewater has only low concentrations of hazardous components and is managed as a nonhazardous waste. The ultimate designation of a waste as hazardous or nonhazardous is based on the properties of the waste, not on its components, i.e., a waste that contains hazardous components in dilute concentration may be regarded as nonhazardous. California's criteria for the hazardous designation are given in the California Administrative Code, Title 22, Article 11. Nonhazardous wastes are regulated under different authority and often by different agencies than are hazardous wastes. The technologies described here are most suitable for hazardous waste. In many cases, however, nonhazardous industrial wastewater is treated similarly.

B. EXTRACTION PROCESSES

Extraction processes are advantageous when the contaminant has economic value. In these cases, the contaminant is either purified as product or recycled into the manufacturing process. Extraction is also the preferred method when degradation of the contaminants is not cost effective. Extraction processes include steam stripping, solvent extraction, and activated carbon adsorption.

Steam Stripping

Steam stripping drives off the volatile contaminants of an aqueous waste stream. Steam stripping takes place in a vertical column (Figure 6-1); the waste is added at

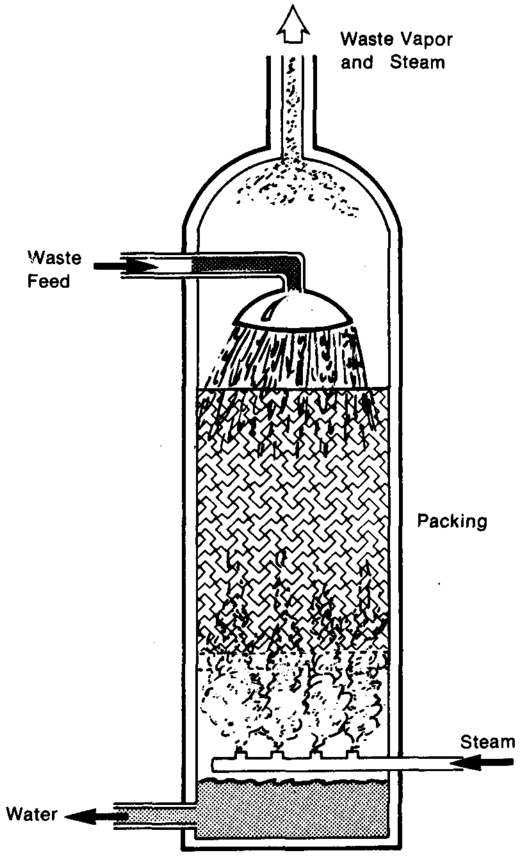

Figure 6-1 Steam Stripper.
Waste is sprayed at the top. Steam is injected at the bottom. The rising steam carries the volatile waste components out the top of the column.

the top of the column. Steam injected into the bottom of the column moves countercurrent (in the opposite direction) to the falling waste stream. The column is filled with either packing material or a series of perforated plates to ensure intimate contact between the liquid waste and the gaseous steam. The steam provides the heat and momentum necessary to carry the volatile organic components out of the solution and through the top of the column.

The vapor from the steam stripper is usually condensed and collected. The condensate, more concentrated than the initial waste, may be treated further, recycled, or disposed. Occasionally the vapor is incinerated.

Steam stripping is most efficient when the contaminant is highly volatile and only slightly soluble in water. The local price of steam is the main consideration in determining the economic feasibility of a steam stripping operation. Ideally, the steam is available from other processes at the plant. Unlike many treatment processes, steam stripping does not contribute new contaminants to the waste stream.

Romic Chemical Corporation, a commercial solvent recycler in East Palo Alto, California, uses steam stripping to recover material from waste for sale. In one application, Romic recovers methylethyl ketone from processing wastes. In a related operation, Romic recovers acetone from fiberglass waste.

For extremely volatile components, an air stripping process may be suitable. In this method the countercurrent flow is ordinary air. The contaminant may be collected by activated carbon adsorption. However, in many air stripping operations the air stream, including contaminants, is discharged to the atmosphere. Some electronic parts manufacturers use this technique to remove trace contaminants from wastewater.

Solvent Extraction

Liquid-liquid extraction or solvent extraction processes transfer a solute compound(s) from one liquid medium to another. The two liquids must be immiscible. This process is becoming increasingly prominent in chemical manufacturing and in wastewater purification. The extraction can be made quite specific through the choice of solvent.

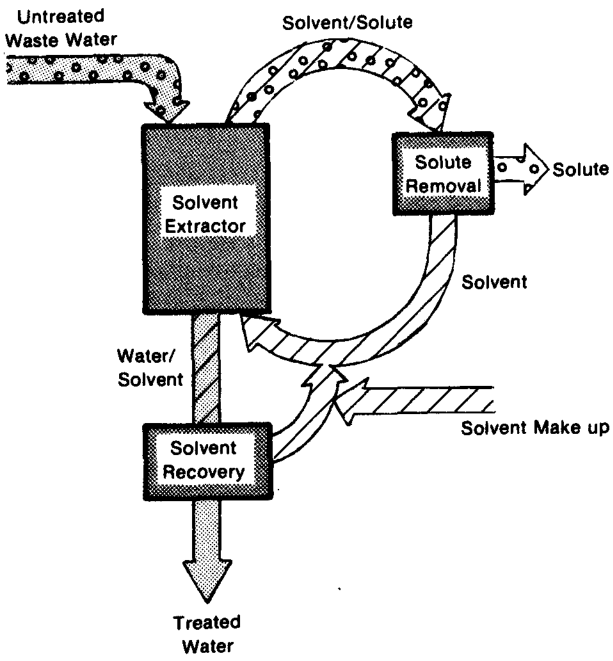

Figure 6-2 Solvent Extraction Schematic. The central extraction unit is designed to give extensive contact between the solvent and the waste. Solvent is regenerated in the solute removal step.

The essential steps of a solvent extraction process are transfer of the contaminant from the water to the solvent (purification), concentration of the contaminant (solvent regeneration), and removal of solvent from the decontaminated water (solvent recovery). Figure 6-2 illustrates the flow of liquid between these steps. In the extraction step, the waste and the solvent flow countercurrent through a device designed to ensure intimate contact of the liquids. Misting contactors and rotating disc contactors are examples of solvent extraction mixing devices.

Solvent regeneration is essential if the solvent is to be recycled or if the contaminant has any economic value. Distillation (solvent removal), adsorption (solute removal), and chemical treatment are techniques used for solvent regeneration. In some cases, the solvent solute pair may be incinerated.

The economic and technical feasibility of solvent extraction is determined by the amount of solvent required to remove the contaminant and by the energy costs of solvent recovery and regeneration. If energy costs are large, stripping or adsorption processes will be preferred over extraction.

The choice of extracting solvent is often problematic. To facilitate solvent recovery, solvents that are highly volatile and only slightly soluble in water are preferred. Unfortunately, these solvents are typically poor dissolving agents for the contaminants to be extracted; water-insoluble solvents tend to be nonpolar and, consequently, are only effective for nonpolar contaminants.

One way around this problem is to use a dual solvent system. A partially water soluble and possibly polar solvent is used to remove contaminants from the aqueous stream. Residual polar solvent is removed from the water with a volatile water-insoluble solvent.

Another approach to removing the extracting solvent from water has been developed by Resources Conservation Company (RCC). Triethyl amine, a common organic solvent, is water soluble at low temperatures and water insoluble at high temperatures (above 40°C). In the RCC process, triethyl amine is mixed with a waste sludge containing oil, water, and solids. The mixture is heated to separate the water and solvent fractions. Organic contaminants generally travel with the solvent. This technique is being applied on a trial basis to clean PCB-contaminated soil in Alabama.

There are several processes for extracting phenolic compounds (these are chemicals derived from phenol; they tend to be toxic and are common wastes) from waste. In one process, the phenol-containing waste is extracted with benzene. The phenolic compound is recovered from the benzene by extraction with sodium hydroxide. An alternate method is to extract the phenolic wastes with either butyl acetate or isopropyl ether, solvents which are easily recovered by distillation (the phenosolvan method).

Acetic acid is also commonly recovered by solvent extraction. The solvents used include alcohols, esters, and ethers of moderate size (4-10 carbons). Separation of acetic acid and solvent is accomplished by distillation.

A dual solvent system for recovery of phenolic compounds has been proposed. The primary extractant is n-butyl acetate which is recovered from aqueous solution by extraction with isobutylene.

A California chemical manufacturer is contemplating the development of a chlorinated pyridine manufacturing process that would include a solvent extraction of wastewater followed by incineration of solvent and solute.

Solvent extraction technology for the recovery of polar compounds is an active area of research in California. Professor C. J. King's laboratory at Berkeley has investigated the recovery of priority pollutants with both high and low boiling point solvents. They have identified promising solvents for removal of several priority pollutants. The estimated costs of these processes range from $4 to $10 per 1,000 gallons of water.

S-cubed, a research and development firm in La Jolla, California, is developing a solvent extraction system for organic pesticides that utilizes volatile, low-boiling point solvent. Hexane has been shown to be effective in DDT removal. S-cubed is considering building a mobile solvent extraction demonstration plant.

Activated Carbon Adsorption

Organic compounds in concentrations from a few parts per billion (ppb) up to several thousand ppm may be collected on the surfaces of granules of activated carbon. Activated carbon adsorption is an old technique which has been used in drinking water purification and as a final stage of sewage treatment for many years.

Activated carbon adsorption is becoming prominent in contaminated groundwater, hazardous waste, and industrial wastewater treatment applications. Organic compounds of moderate molecular weight are most easily adsorbed. Smaller compounds, including solvents such as methylene chloride, are adsorbed relatively slowly. Table 6-1 lists the relative adsorptivities of some organic compounds. There is wide variation in the types and properties of carbon available. Coal, petroleum-based products, and natural wood related products, such as coconut shells, are common sources for carbon. The various sources have different compositions and differ in the compounds they adsorb.

The carbon is activated at high temperatures. The activated carbon surface has pores and cracks and, consequently, a large surface area for adsorption. A particular compound's adsorptivity also depends on the size of the cracks and pores.

Activated carbon adsorption may be conducted in batch or continuous processes. Batch treatment processes utilize pulverized activated carbon. The powdered carbon is mixed intimately with the wastewater to assure contact of the carbon with the contaminant. For continuous processes, granular activated carbon is placed in lined columns; wastewater flows through the column. Usually where hazardous wastewaters are to be treated, two carbon columns are connected in series. The effluent from both columns is monitored. When the effluent from the first column exceeds the treatment objective, it is taken off-stream. The second column now becomes the first and, when fresh carbon is placed in the exhausted adsorber, it becomes the second unit.

A primary consideration when designing carbon adsorption systems is the frequency and cost of replacing and disposing of the spent carbon. The Department of Health Services considers spent adsorbents bearing hazardous wastes to be hazardous, and requires that such wastes be handled accordingly.

The carbon used in adsorption processes can be reused many times. In some cases, the carbon can be regenerated in place. In such in situ treatment, the carbon is washed with steam, solvent, or hot water. The regeneration fluids often become hazardous and must be handled accordingly.

Carbon saturated with complex mixtures may require very high temperatures to drive off or destroy the more strongly adsorbed compounds. Typical regeneration furnaces are chain-fed or rotary kilns similar to those used in the manufacture of cement. The spent carbon is roasted at 1,600°F to 2,000°F by burning an auxiliary fuel in the furnace. Air intake is controlled to preclude the oxidation of the activated carbon matrix while ensuring adequate heat to drive off organics from the carbon surface. Steam is added as a reactant to restore the activity of the carbon and to assure the formation of halogen acids, such as hydrogen chloride, produced from the decomposition of halogenated hydrocarbons. These halogen acids must be scrubbed from the exhaust stream by air pollution control equipment. At the high operating temperatures in these furnaces, desorbed organics, such as phenols, solvents, and organic acids, are converted to carbon dioxide and water vapor.

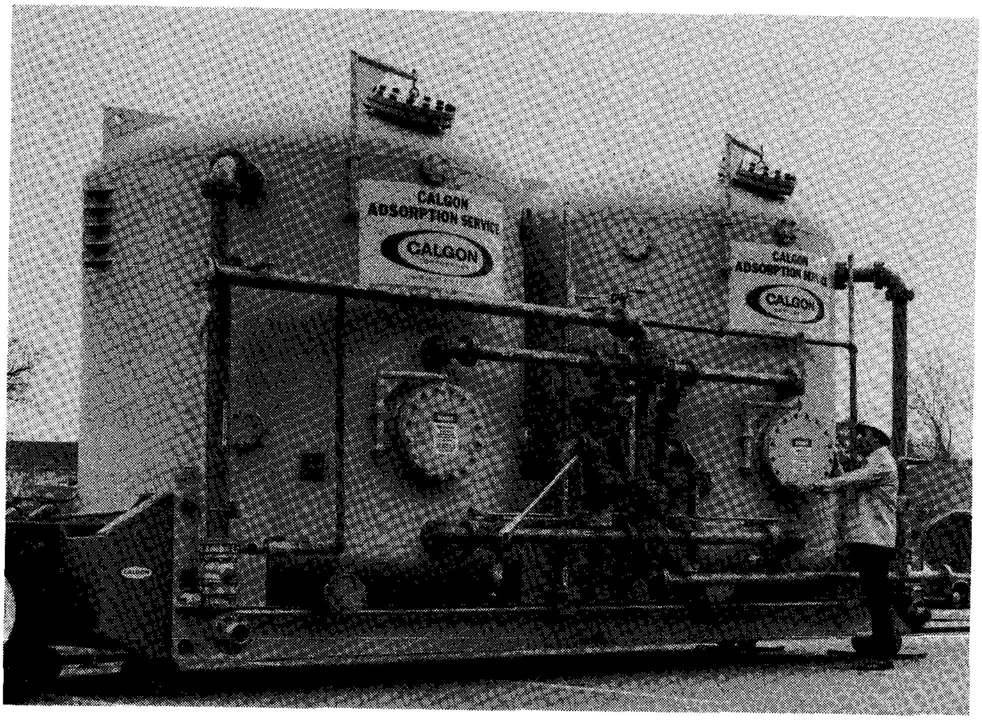

Figure 6-3 Activated Carbon Unit. This unit can be used for site clean up or industrial waste treatment

Source: Calgon Carbon Corporation

Activated carbon and the necessary process equipment are available from a number of companies. Systems are available for treating a wide range of wastes, concentrations, and flow rates. System design is preceded by bench-scale testing with the particular waste stream to estimate carbon usage rates and costs. Vendors usually market their expertise in design and operation, as well as the activated carbon.

The rate of carbon saturation and, consequently, the cost of treating a waste stream depends on the nature of the contaminants, their concentration, and the desired purity. Treatment costs include carbon purchase costs, equipment capital costs, regeneration costs, and operating costs. For most applications, treatment of an aqueous stream contaminated with 1,000 mg/l will cost from $6 to $35 per 1,000 gallons; a stream with 10 mg/l will cost from cents to $3 per 1,000 gallons.

Because carbon may be regenerated many times, the long-term costs of an adsorption process depend on regeneration costs and efficiency more than on the cost of new carbon. The charge for regenerating carbon is generally around $.50 per pound. However, a considerable amount of carbon is lost on reactivation (5 to 20 percent) and regenerated carbon has a slightly reduced adsorptive capacity.

Many grades of activated carbon are available for aqueous phase treatment. The cost for fresh activated carbon used for wastewater treatment ranges from $1 per pound to $1.50 per pound.

There are no furnaces in California permitted to regenerate activated carbon from hazardous waste treatment. Carbon recyclers transport their spent carbon as far east as Pennsylvania and Kentucky for regeneration. The added costs to comply with the more stringent air quality regulations in California are cited by the companies as the reason for the lack of regeneration furnaces in the State.

TABLE 6-1

TREATABILITY RATING OF SELECTED PRIORITY POLLUTANTS UTILIZING CARBON ADSORPTION*

Priority Pollutants	Removal Rating**	Priority Pollutants	Removal Rating**
Acenaphthene	H	Methyl bromide	L
Acrolein	L	Dichlorobromomethane	M
Acrylonitrile	L	Trichlorofluoromethane	M
Benzene	M	Dichlorodifluoromethane	L
Benzidine	H	Chlorodibromomethane	M
Carbon tetrachloride	M	Hexachlorobutadiene	H
Chlorobenzene	H	Hexachlorocyclopentadiene	H
1,2,4-trichlorobenzene	H	Isophorone	H
Hexachlorobenzene	H	Naphthalene	H
1,2-dichloroethane	M	Nitrobenzene	H
Hexachloroethane	H	2-nitrophenol	H
1,1-dichloroethane	M	2,4-dinitrophenol	H
1,1,2-trichloroethane	M	4,6-dinitro-o-cresol	H
1,1,2,2-tetrachloroethane	H	N-nitrosodimethylamine	M
Chloroethane	L	N-nitrosodiphenylamine	H
Bis(2-chloroethyl)ether	M	N-nitrosodi-n-propylamine	M
2-chloroethyl vinyl ether	L	Pentachlorophenol	H
2-chloronaphthalene	H	Phenol	M
2,4,6-trichlorophenol	H	Bis(2-ethylhexyl)phthalate	H
Parachlorometa cresol	H	Butyl benzyl phthalate	H
Chloroform (trichloromethane)	L	Di-n-butyl phthalate	H
2-chlorophenol	H	Dimethyl phthalate	H
1,2-dichlorobenzene	H	1,2-benzanthracene	H
3,3'-dichlorobenzidine	H	Benzo(a)pyrene	H
1,1-dichloroethylene	L	3,4-benzofluoranthene	H
2,4-dichlorophenol	H	11,12-benzofluoranthene	H
1,2-dichloropropane	M	Chrysene	H
1,2-dichloropropylene	M	Acenaphthylene	H
2,4-dimethylphenol	H	Anthracene	H
2,4-dinitrotoluene	H	Tetrachloroethylene	M
2,6-dinitrotoluene	H	Toluene	M
1,2-diphenylhydrazine	H	Trichloroethylene	L
Flouranthene	H	Vinyl chloride	L
Methylene chloride	L	PCB-1242 (Arochlor 1242)	H
Methyl chloride	L		

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* From EPA Treatability Manual.

** <u>NOTE</u>: The removal ratings are based on the mass of compound adsorbed per gram of carbon at equilibrium. A greater mass of a compound rated H will be adsorbed than a compound rated M and so on. The actual amount adsorbed will depend on the final concentration of compound in solution.

C. DESTRUCTION PROCESSES

Destruction processes include a number of biological treatment methods and chemical oxidations.

Biological Treatment

Biological treatment of waste involves the degradation of organic materials by microorganisms, either natural populations or microorganisms developed to act on specific compounds in the waste. Biological technologies are commonly used for treatment of municipal wasteswaters. Application of biological treatment to industrial hazardous waste, although currently limited, is an active area of research and development. The principal obstacle is that many industrial wastes are not subject to biodegradation and because of their high concentrations may disrupt biological treatment.

There are two major classes of biological treatment and a host of specific technologies. The two major classes are aerobic, with oxygen, and anaerobic, without oxygen. Specific technologies include activated sludge, aerated lagoons, facultative lagoons, trickling filters, rotating biological contactors, and anaerobic treatment. Not all biological treatment is degradation. In some cases, the organisms accumulate material but do not degrade it. Bioadsorption may be less expensive than other extraction technologies.

In aerobic treatment, microorganisms take in oxygen and organic molecules and release carbon dioxide, water, ammonia, nitrate, and sulfate. A high dissolved oxygen concentration promotes rapid metabolism and rapid degradation. A large microorganism population also leads to rapid degradation.

Anaerobic treatment takes place in the absence of oxygen. Indeed, oxygen is toxic to many anaerobic organisms. Common products of anaerobic treatment are methane, hydrogen sulfide, organic acids, and carbon dioxide. Anaerobic processes can be unpleasantly odorous.

Aerobic degradation technologies are more common than anaerobic; they are better understood, and the microbes are more easily cultured. Its disadvantages are the energy required for oxygen supply and mixing, and the large volume of sludge generated.

Volatilization can be a problem in both anaerobic and aerobic technologies. Biodegradable compounds are typically of low or moderate molecular weight and, consequently, volatile. To compound matters, biological degradation processes often cause foaming which accelerates material loss. For this reason, anaerobic processes, which produce unpleasantly odorous by-products, are operated in closed containers which isolate emissions to the atmosphere. Aerobic processes need not be enclosed but must be operated to minimize material loss through volatilization.

The industrial wastewater streams treated by biological technologies are usually nonhazardous. These streams may contain hazardous components and require special treatment, but the concentrations are small and the streams can be legally managed as nonhazardous wastes. Applications of biological processes to the treatment of hazardous waste are being developed.

The susceptibility of organic compounds to biodegradation varies considerably. The degradation of a compound involves several steps each catalyzed by a different enzyme. The degradability of a compound often depends on its similarity to naturally occurring compounds for which degradation pathways exist. Among the manmade compounds which prove biodegradable are many chlorinated and aromatic compounds.

Biological treatment systems adapt to the components of the waste stream.

The microbial populations develop an enhanced ability to digest the particular compounds in their medium. Consequently, a biological reactor is most effective when dedicated to a waste stream of fairly constant composition.

Unfortunately, biological systems often prove fragile when exposed to a sudden change in waste stream composition, concentration, or temperature. Cells carefully grown and adapted over weeks or longer can be killed in a matter of hours. Cyanide and heavy metals are two examples of the common wastes toxic to microorganisms.

Operators have several options to protect against biomass kills. First, continual monitoring of influent enables the operator to divert streams before a kill takes place. Second, sudden changes in influent, shock, can be avoided with an equalization basin. This is a final storage pond before the biological reactor. The effluent from the basin will change composition more slowly than the influent to the basin. Common pretreatments for biomass protection, such as neutralization (pH) and solids removal, can be performed in the equalization basin.

Biological treatment, especially aerobic processes, generate sludge. The disposal costs of sludge can be a significant factor in the economics of a biological reactor. Sludge disposal is especially problematic if the cells have accumulated either heavy metals or hazardous organics. Land spreading, a common sludge disposal technique, is precluded if such constituents are present. Other principal means of disposal are thermal treatments such as incineration and wet air oxidation. Incineration generally requires preliminary sludge dewatering.

Although the destruction efficiency of a biological reactor can be greater than 99 percent, many hazardous compounds are destroyed with efficiencies of less than 90 percent. In these cases, it is necessary to further treat the effluent to remove the residual hazardous materials. Activated carbon adsorption is usually employed for this purpose.

The petroleum industry, the paper industry, and the chemical manufacturing industry often employ biological treatment to degrade hazardous compounds. Another application coming into common use is the treatment of hazardous waste leachate and contaminated groundwater. Specific instances are discussed later in this chapter and in the Site Mitigation chapters.

Several areas of research hold the promise of additional applications of biotechnology to hazardous waste treatment. One technique in practice is the use of bacteria cultured in the presence of the material to be degraded. For example, soil bacteria at sites contaminated with hazardous waste are often exceptional decomposers of those contaminants. Special cultures are also prepared in commercial laboratories. These bacteria may be suited to treatment of leachate from that site.

Many researchers are attempting to use genetic engineering to produce bacteria with enhanced ability to degrade chlorinated organics and other toxic compounds. Although this research is likely to succeed, any application to hazardous waste treatment will almost certainly raise controversy about the possibility of discharge of the microbes to the environment.

A related area of research is the use of isolated enzymes to decompose hazardous organic compounds.

Activated Sludge Process -- The activated sludge process is usually a continuous-flow treatment operation. Incoming wastewater is added to an active biological sludge to form the mixed liquor. This mixed liquor is aerated and well mixed (Figure 6-4). Effluent from the aeration tank flows to a settling tank where the sludge settles. A portion of this separated sludge is returned and added to new incoming wastes (the recycle step in Figure 6-4); the remaining sludge is further processed prior to land disposal. The return of the sludge to the reactor is a key part of the activated sludge treatment because it preserves the cells which have adapted to the waste.

Many variables influence the design of activated sludge treatment systems. Among these are the influent biochemical oxygen demand (BOD), the flow rate, the desired effluent BOD, influent suspended solids content, sludge production rate, and sludge settleability.

The sequencing batch reactor, a type of activated sludge reactor, operates in a sequential fill and draw manner (the activated sludge reactor operates with a continuous flow of waste). The sequencing batch reactor is being used on a pilot scale to treat leachate from the Hyde Park landfill in Niagara Falls, New York. Occidental Chemical Company, which owns the site and is developing the technology has been treating the leachate with activated carbon adsorption. They estimate that exclusive use of carbon adsorption would cost $21 million over the next ten years. Sequencing batch reactor treatment of this waste stream would greatly reduce the total treatment costs.

Occidental has treated leachate with concentrations of greater than 2,000 mg/l total organics and 500 mg/l each of phenol, benzoic acid, and chlorobenzoic acid. The sequencing batch reactor treatment reduced the total organic carbon to 500 mg/l or less and the concentrations of the hazardous constituents to less than 10 mg/l. Although the effluent from the sequencing batch reactor still requires carbon adsorption, substantial savings result from a greatly reduced carbon replacement rate.

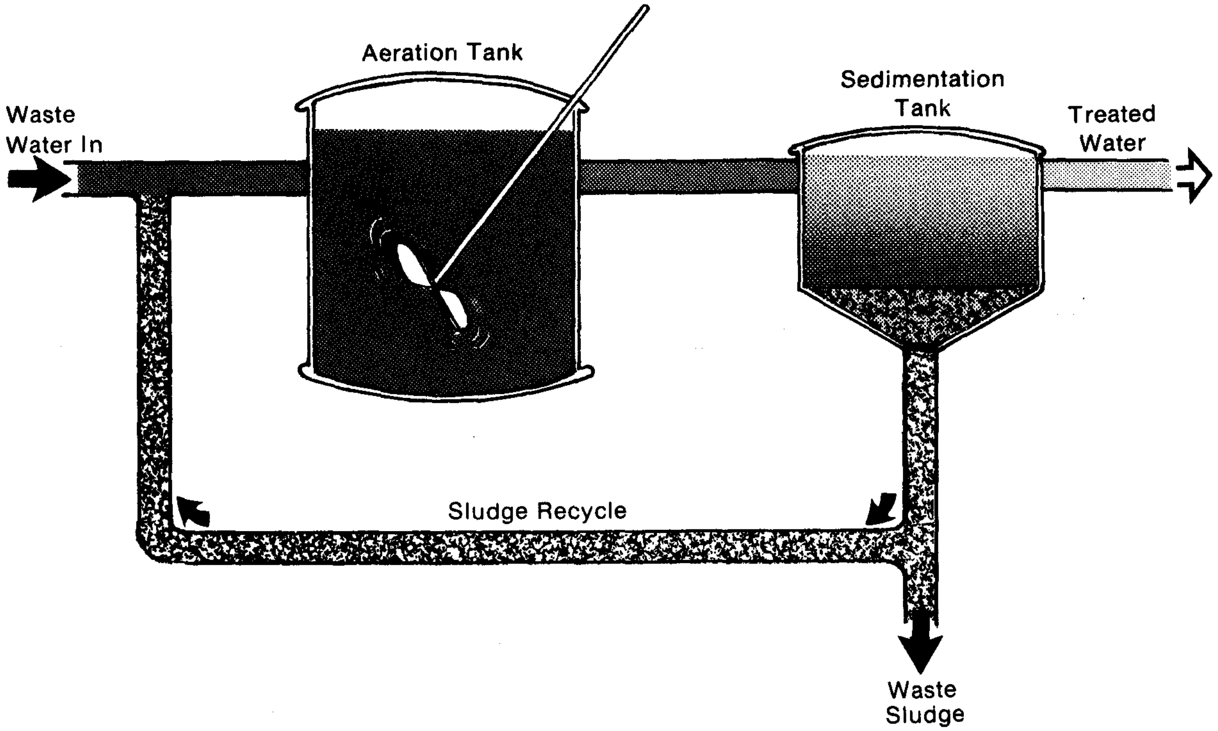
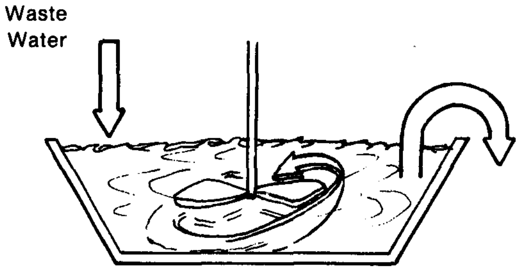
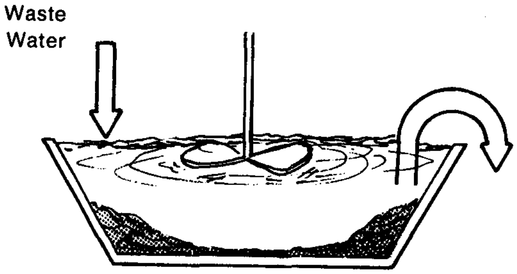


Figure 6-4 Activated Sludge Reactor.
Biodegradation takes place in the aeration tank. The propeller indicates that the tank is well stirred. The proportion of sludge that is returned varies according to operation demand.

(a) Aerobic



(b) Facultative



(c) Anerobic

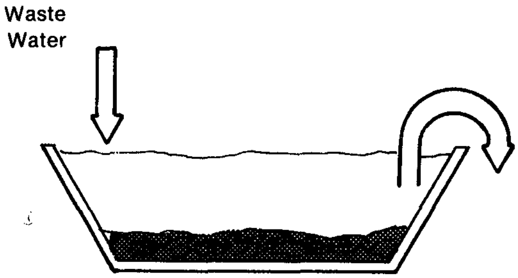


Figure 6-5 Three Ponds
The aerobic lagoon (a) is well stirred and oxygenated. The facilitative lagoon (b) is aerated only at the top. The anaerobic lagoon (c) is unstirred.

CECOS International operates a 1,900 cubic meter sequencing batch reactor at their hazardous waste treatment facility in Niagara Falls, New York.

Aerated Lagoons -- Aerated lagoons may be used for the treatment of dilute industrial and municipal wastes. Aerobic lagoons are large deep basins maintained at high oxygen concentrations and well mixed (Figure 6-5). Aerated lagoons tend to be stable, resistant to shock loadings, and relatively inexpensive to operate. The disadvantages of this technique include the large area of land required and the possibility of odor producing anaerobic digestion.

The facultative lagoon is a variation on the aerated lagoon which combines aerobic and anaerobic digestion. The facultative lagoon is operated (Figure 6-5) so that the upper portion has enough dissolved oxygen to support aerobic digestion. Anaerobic digestion takes place in the deeper sections. Combining aerobic and anaerobic processes facilitates the degradation of a wide variety of compounds. Faculative lagoons have low sludge generation rates; sludge generated by the aerobic process settles and is digested by the anaerobic organisms.

Several refineries in California use aerated or facultative lagoons to clean oil- and phenol-containing wastewaters.

Trickling Filters -- Trickling filters consist of a basin usually 3 to 15 feet deep, filled with rocks or synthetic media. Wastewater is sprayed over these solid surfaces which serve as a support for bacterial growth. Bacteria digest organic material as the wastewater is trickled through the filter. The wastewater is distributed evenly over the filter media by either rotary distribution arms, or fixed spray nozzles. An underdrain is used to convey effluent, and to provide a conduit for aeration.

Rock and synthetic plastic are the two most common types of filter media. Synthetic media, although more expensive, provide more control of void space, and allow a greater surface-to-volume ratio. Plastic media also provide greater removal efficiencies and are less prone to plugging and ventilation problems.

Trickling filters have been used for the treatment of a wide variety of dilute industrial and municipal wastes. The industrial wastes successfully treated by trickling filters include acetaldehyde, acetone, acrolein, benzene, chlorinated hydrocarbons, cyanides, formaldehyde, ketones, phenolics, nylon, and nylon intermediates.

Trickling filters tend to be expensive to build. However, although they are not applicable to intermittent waste streams, trickling filters are resistant to shock loadings and are able to treat recalcitrant organic chemicals.

Rotating Biological Contactors (RBC) -- The RBC or biological disk, is also used for the treatment of dilute industrial and municipal wastes. The RBC consists of a series of flat, parallel disks which are rotated while partially immersed in a trough of wastewater. Each disk is covered with a biological slime which absorbs colloidal and dissolved organic matter present in the wastewater.

As the disk is rotated out of the tank, it carries a film of the wastewater into the air where the oxygen is available for aerobic biological activity. Use of closely spaced parallel disks achieves a high concentration of active microorganisms over a large surface area, an advantage in the treatment of more concentrated wastes.

As excess biomass is produced, it sloughs from the disk. Such material is carried with the process effluent and must be collected in a final clarifier. The solids produced generally settle easily.

Rotating biological contactors are expensive to install and moderately expensive to operate.

Anaerobic Treatment -- Anaerobic treatment, like aerobic treatment, takes place both in bulk solution and on films (analogous to trickling filters). These reactors are simpler than their aerobic counterparts because the problems of oxygen supply and sludge disposal are not present. Anaerobic digestion decomposes a slightly different class of chemicals and may be preferable for that reason.

Powdered Activated Carbon Treatment (PACT) -- The PACT method combines activated carbon adsorption and biodegradation in a single vessel. In some applications, PACT appears to be more effective and less expensive than sequential adsorption and degradation. PACT is marketed by Zimpro, Inc.

Wet Air Oxidation

Wet air oxidation (WAO) is a process for destroying hazardous organic materials that are contained in a liquid phase. The WAO process is a method of destroying many aqueous wastes which are too dilute to incinerate economically, yet not biologically degradable in a municipal wastewater treatment facility. Wastes with concentrations from 10,000 to 100,000 mg/l can be treated by WAO.

WAO is a high temperature, high pressure process using oxygen as the oxidizing agent. The waste stream is mixed with air at temperatures from 350°C to 750°C and at pressures as high as 2,000 pounds per square inch. The high pressure increases the dissolved oxygen content and keeps the volatile organic compounds in solution.

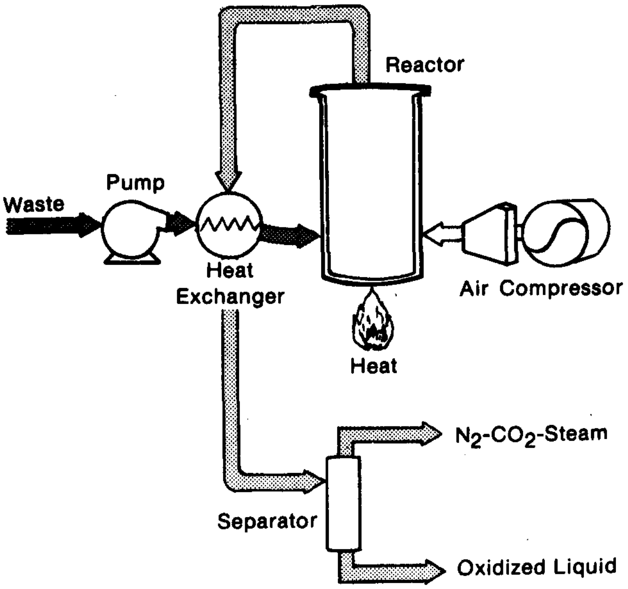


Figure 6-6 Wet Air Oxidation Schematic. Oxidation takes place in the reactor vessel. The heat exchanger recovers heat generated in the reaction. High pressure is maintained by the air compressor.

The oxidation reactions which occur in the WAO process are generally exothermic (heat releasing). Consequently, the oxidation reaction itself provides some of the heat necessary to maintain the high temperatures needed. That heat is transferred from the treated wastes to the incoming waste by the heat exchanger shown in Figure 6-6. The scrubbers, condensers, and carbon adsorption units shown in the figure are air pollution control devices. It is not practical, or necessary, to fully oxidize all organic substances in most wastewaters. Typically, 80 percent of the organic substances will be completely oxidized by the WAO process to carbon dioxide and water, while the remaining 20 percent is partially oxidized to intermediate molecular weight organic compounds.

When complete oxidation occurs; reduced organic sulfur compounds, such as sulfides and mercaptans are oxidized to inorganic sulfate. Inorganic and organic cyanides are oxidized to carbon dioxide, ammonia, or molecular nitrogen. Oxides of nitrogen are not formed.

Incomplete oxidation produces low molecular weight compounds such as acetaldehyde, acetone, low molecular weight acids, and methanol. These compounds are often volatile and are distributed between the liquid and gas phases of the treated waste stream.

The WAO process is capable of treating a wide variety of organic compounds. It is particularly well suited for nonhalogenated compounds such as mercaptans, phenols, nonhalogenated pesticides, and cyanides. Highly chlorinated compounds are usually too stable for complete oxidation. In certain instances, the use of catalysts will increase the efficiency of oxidation. Catalysts which have been used with some success include bromide, nitrate, and copper.

The main use of the WAO process has been for municipal wastewater treatment sludges. The application of WAO to industrial organic wastes has generally been limited to treating specific, homogenous waste streams, including soda pulping liquors at pulp mills, sulfite liquors, N-Nitrosodimethylamine (NDMA), and acrylonitrile wastes.

The only application of the WAO process to a varied stream of hazardous wastes is at the Casmalia Class I disposal site, located near Santa Maria, California. The WAO unit is manufactured by Zimpro, Inc. Currently, this WAO treats cyanides, phenolics, sulfides, pesticides, solvent still bottoms, and general organics.

The Zimpro unit has a treatment capacity of 10 gpm, with a compressed air flow rate of 190 standard cubic feet per minute (SCFM). The unit is designed to operate at a temperature of 550°F and a pressure of 2,000 psi.

Wastewater with chemical oxygen demand (COD) concentrations up to 75,000 mg/l can be treated with this unit.

The reactor vessel is a 600-gallon titanium clad carbon steel tank. It is heated by an 800,000 Btu/hr hot-oil heating system. Because of its excellent corrosion resistance, titanium is also used in the feed tubes and heat exchangers.

Before a particular wastewater is processed through the WAO unit, analytical tests, including processing with a bench scale wet-air oxidation unit, are performed on a sample of the waste. No candidate wastewaters are processed in the full-scale WAO unit until they have been screened.

Demonstration runs for all six categories of wastes for which the Zimpro WAO unit is currently permitted are presented in Table 6-2.

The organic sulfur and phenols in Table 6-2 were contained in a petroleum refining spent caustic waste.

The cyanide wastes in Table 6-2 were metal plating process effluent. Problems were encountered with this waste stream. Scales formed on the walls due to the precipitation of metals when soluble metal-cyanide complexes were destroyed. The process had to be periodically halted to remove scale from the system.

The general organic wastewaters were from a polyester resin manufacturing process, and contained high concentrations of propylene glycol and various mixed organic ethers and esters.

At Casmalia, some wastewaters are too dilute to be economically processed through the Zimpro WAO system. To solve this problem, Zimpro installed a PACT system. The PACT system was able to concentrate wastes onto the carbon for subsequent processing through the WAO unit.

The cost for the Zimpro WAO system to treat wastewaters at Casmalia range from $.50 to $2 per gallon, depending on the type and concentration of waste.

TABLE 6-2

RESULTS OF WAO TREATMENT OF PERMITTED WASTE CATEGORIES

Waste	Average Initial Conc. (mg/l)	Average Final Conc. (mg/l)	Percent Reduction
Organic Sulfur	3,010	180	94.0
Phenols	15,510	36	99.8
Cyanides	25,340	82	99.7
General Organic	20,830	685	96.7
Still Bottoms	15,200	7,990	47.4
Pesticides*	30	.59	98.0

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* The figures given are for carbaryl. The other pesticides tested (dinoseb, methoxychlor, malathion) all had destruction efficiencies of 99.5 percent or greater.

CHAPTER 7
SOLVENT WASTES

A. SOLVENT USE AND PROPERTIES

The term solvent is used by industry to mean an organic material used as a dissolving agent. Solvents are widely used in industry and are one of the principle contributors to groundwater pollution. The electronics industry commonly uses solvents to clean surfaces prior to processing. The petroleum industry uses solvents to extract lubricating oils and waxes during the refining process. Solvents are a component in many paints and inks. The chemical and plastics manufacturing industries depend on solvents for many of their processes. Dry cleaning and equipment cleaning, especially parts degreasing, are commonly done with solvents.

A solvent must have certain properties to be effective in these uses. It must be able to dissolve materials. It must be stable and must not react with storage containers and pipes. Often a solvent must be volatile and easily regenerated.

Unfortunately, the useful properties of solvents make solvent wastes incompatible with land disposal. Solvents act to dissolve other hazardous wastes in a land disposal site. A solvent waste can dissolve a plastic membrane landfill liner, or can extract water from a clay landfill liner; the security of the sealed landfill bottom in either case is destroyed. The stability of solvents causes them to resist natural breakdown in the environment. Most industrial solvents are toxic and flammable, worsening the hazard. Some solvents are halogenated to increase stability, or to reduce flammability. Halogenated solvents are particularly persistent and toxic in the environment. Volatile solvents may vaporize, causing an air pollution and possibly a flammability problem at disposal sites.

Many solvent wastes are subject to federal or California land disposal bans. In California, liquid wastes with halogenated organic concentration of 1,000 ppm or greater were banned from land disposal on January 1, 1985. A similar ban takes place at the federal level on July 8, 1987. EPA will also ban other specified solvents from land disposal on November 8, 1986.

The State of California has targeted solvent wastes as a waste stream whose volume can be reduced. The Department commissioned a study of opportunities for reduced generation and improved management of solvent wastes. The results are to be disseminated by publications and seminars. Solvents are also a prime target of the Department's recycling activities (Chapter 2).

B. SOLVENT WASTE REDUCTION

While some source reduction opportunities are industry specific, others apply to a variety of industries. The ink and paint industries illustrate the wide range of improvements that can be made within a single industry.

Perhaps the most important waste reduction measure in the ink and paint industries is the change from solvent-based to water-based paints and inks. Solvent-containing wastes eliminated by this product substitution include: paint sludges, tank cleaning residues, and waste inks. The transition to water-based products also eliminates the dangers associated with solvent flammability and toxicity.

The use of water-based paints and inks has increased sharply in recent years. A 1985 estimate had water-based paints accounting for 61 percent of new architectural paint. Architectural paint itself accounts for almost half the paint manufactured in the United States. One large California paint manufacturer is converting its San Carlos plant to produce water-based paints exclusively.

Water-based coatings are also finding applications outside the architectural paint industry. The Department of Defense reports that the Naval Air Work facilities in Pensacola and Jacksonville, Florida are converting to water-based primers for parts repainting. This change greatly reduces the volume of solvent necessary for cleaning and reportedly improves product quality.

The newspaper industry is also substituting water-based products for solvent-based products. Traditionally, newspapers have used an oil-based ink in letter press or lithography processes. Waste ink is generated when ink color is changed or when the presses are shut down. This waste ink contains stabilizers, preservatives, and pigments which may be toxic.

Flexography, a variation of the letter press process, allows the use of water-based inks. Ink-containing washwater, the only waste generated in this process, is easily purified by sedimentation or filtration. The filtrate water can be safely discharged to a sewer. The remaining pigment is of small volume and can be recycled.

The use of flexography for newspaper printing is not without problems. Swelling of the plates can make midrun plate changes difficult. The Long Beach Press-Telegram has recently adopted flexography. Two of the paper's eight presses are now successfully using flexography.

The flexographic process is also used by magazine and package printers. Many food and beverage containers are printed with flexography.

The development of water-based inks and coatings for other applications is an active area of research. Developing coatings with adequate gloss that do not wash or flake off has proven difficult.

Another alternative to solvent-based paints is electrostatic painting. A fine powder is sprayed and electrically applied to the surface. The coating is then baked to melt the powder into a paint like finish.

The paint industry has seen many housekeeping improvements. The development of speciality cleaning equipment has reduced material loss in cleaning operations. For example, high pressure nozzles reduce the volume of water or solvent necessary for tank cleaning. Mechanical cleaning measures such as using "squeegees" to clean tank walls or using "tennis balls" to clean pipes also reduce material loss.

On-site recycling is reducing both ink and paint wastes. Solvent-based ink waste is filtered and reused at many newspapers in California. Paint waste in the form of washings and tank residues can be collected and blended into the next batch.

The lifetime of solvents in washing and process applications can often be extended by regular filtration. A simple cloth or paper filter will remove suspended solids from the solvent. Dissolved contaminants can often be removed by filtration through "filter-aid", a granular powder that preferentially adsorbs the contaminant.

In general, improved process control is leading to reduced waste generation. Computerization is contributing to this change.

Solvent Vapor Control

A major source of solvent loss in industrial processes is solvent vapor loss. Solvent escapes at all solvent-air interfaces. Some techniques for preventing solvent loss from degreasing operations are presented in Table 7-1. The degreasing operations may be either liquid degreasing, where the object is immersed in the liquid solvent, or vapor degreasing where the object is immersed in a heavy fog of the solvent.

Solvent must also be removed from gaseous effluent of some processes. The techniques for this include wet scrubbing, incineration of the vapor, activated carbon adsorption, and the recently developed nitrogen-based recovery.

TABLE 7-1

TECHNIQUES FOR SOLVENT LOSS REDUCTION IN DEGREASING OPERATIONS

Tank Covers

Installation of automatic tank covers on open tank degreasers, which close between degreasing operations, can reduce solvent loss by 25 to 60 percent depending on the solvent and the operating conditions.

Increasing Freeboard Height

The freeboard height in a vapor degreaser is the distance between the vapor level and the top of the tank. Increasing the freeboard height from 50 percent of the tank width to 75 percent of the tank width can reduce solvent loss by 25 percent to 55 percent.

Refrigerated Chillers

Refrigeration coils installed in the freeboard area will create a cold blanket above the solvent, thus preventing escape. Installation of refrigerated chillers can reduce vapor loss by 40 to 60 percent.

Vapor Recovery/Distillation

Escaped solvent vapors are recovered by carbon adsorption, and distilled into the degreasing operation. This technique applicable to large degreasing operations, can achieve an 80 percent recovery rate.

Drag-Out Reduction

Withdrawal of the degreased pieces in a slow and smooth manner will allow better drainage of solvent back into the bath. Some pieces of equipment should be rotated while being removed.

Drain Boards

A drain board will simply capture dripping solvent and direct it back into the degreasing tank.

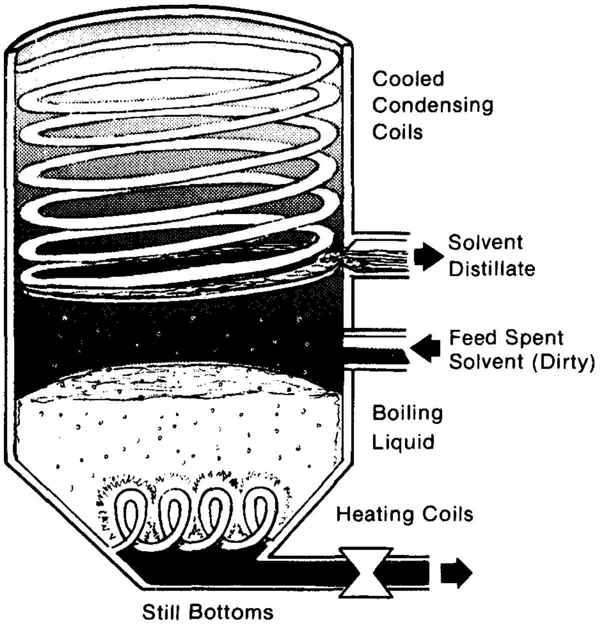

Figure 7-1 Simple Still.
Purified solvent is removed at the top of the apparatus. Periodically, heavy materials (still bottoms) must be removed from the bottom. The still can be operated in a batch or continuous manner.

C. RECYCLING OF SOLVENTS

Organic solvents are highly recyclable. However, recovered solvent may require some treatment prior to reuse. The treatment processes either remove contaminants from the solvent or separate multiple solvents. In addition to the distillation technologies discussed below, techniques used for solvent recycling include activated carbon adsorption, steam stripping, and solvent extraction (Chapter 6), ion exchange, reverse osmosis (Chapter 4), and solid removal techniques (Chapter 3).

Distillation

Distillation processes take advantage of the different volatilities of the components of a mixture. Vapor above a liquid generally has a different composition than the liquid (the two phases have the same components but in different concentrations). When the vapors are condensed, one of the components has been concentrated.

Several types of distillation processes, including simple, fractional, extraction, and vacuum distillation are discussed below. When the vapor and liquid phases have the same concentration of components, further separation of the components by distillation requires special processes. Such an inseparable mixture is called an azeotrope.

Simple Distillation -- Simple distillation is a batch process that takes place in a simple still. Heat applied to the bottom of the still causes components of the mixture to vaporize. The still is heated with steam, hot oil in coils, or electrically heated ceramic tiles. The vapors are condensed and collected in a separate pot (Figure 7-1).

Simple distillation can often produce highly purified products. Slow distillation and components with very different vapor pressures favor good separations. The still may be designed to allow part of the condensed vapors to reflux back into the still pot. Refluxing also increases the purity of the material recovered.

TABLE 7-2

EXAMPLES OF COMMERCIALLY AVAILABLE PACKAGE STILLS

Manufacturer	Types of Wastes Distilled	Ranges in Capacity Gal/Hour	Steam Usage Lb/Hour	Allowable Solids Percentage	FOB Costs Dollars
Ecolaire Heat Transfer Co.	Halogenated Oxygenated, Aliphatic Organic Solvents	20-40 up to 250-510	165 up to 1980	30	Not Avail.
Hoyt Manufacturing Company	Nonflammable Organic Solvents	35-60	240-340	60	2,600 to 4,100
Zepra Industries, Inc.	Halogenated Oxygenated, Aliphatic Organic Solvents	0.6-20		60	4,200 to 17,000

Fractional Distillation -- Fractional distillation is used to separate mixtures of compounds with similar vapor pressures. A single fractional distillation can often accomplish separations which would require hundreds of simple distillations. Fractional distillation is in common use by commercial solvent recyclers in California.

A typical fractional distillation column contains a series of evenly spaced perforated trays (Figure 7-2). Ceramic packing may be used as an alternative to trays. The waste is fed onto a tray in the fractional distillation column. The more volatile products vaporize and rise through the liquid contained on the next higher tray. The rising vapors become enriched with the more volatile components of the mixture as they pass through the liquid contained on each successive tray.

Vapor exits through the top of the column and condenses to become what is known as the overhead product. Liquid containing less volatile compounds cascades down the column enriched with the less volatile components of the vapor and becomes what is known as the bottom product.

Extractive Distillation -- Extractive distillation is one approach to separating azeotropic mixtures. This scheme utilizes a nonvolatile solvent to change the vapor liquid equilibrium of the mixture. Because the composition of the liquid and vapor are no longer identical, separation of the components is possible. The nonvolatile solvent is added near the top of the column. Extractive solvent leaves the system through the bottom of the column, goes to another distillation column for separation from the bottom product, and is subsequently recycled to the top of the extractive distillation column for a second cycle.

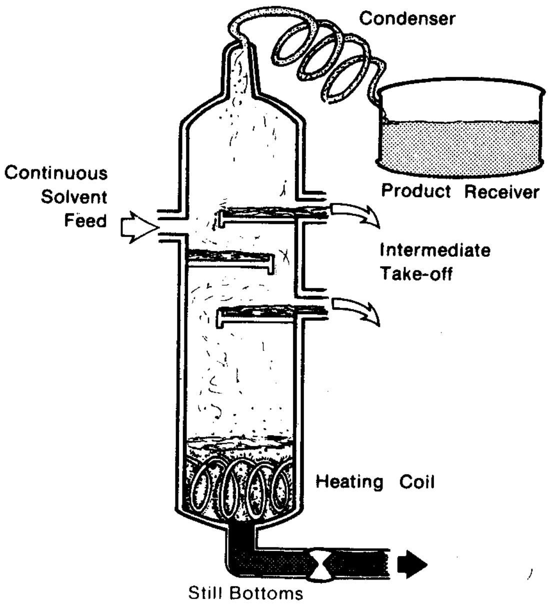

Figure 7-2 Fractional Distillation Apparatus. The trays facilitate the separation of similar compounds. Material is removed at various locations on the column.

Vacuum Distillation -- Vacuum distillation can also separate azeotropes. The distillation is conducted at reduced (below atmospheric) pressure. The process requires a vacuum pump and a specially sealed column to maintain the low pressure in the column and in the distillation pot. Changing the column pressure results in a change in composition of the vapor phase for certain azeotropes. By using two columns, one a vacuum column and the other either a pressurized or atmospheric column, a pressure sensitive azeotropic mixture can be separated.

Volatile organic compounds can be recovered from largely nonvolatile residues, such as paint residue or still bottoms, using vacuum distillation because organic compounds will vaporize more readily at the lower pressures. Direct heating of the residue by steam can enhance the vaporization of the more volatile compounds.

On-Site Distillation

A wide range of stills are available for on-site solvent purification (Table 7-2). The cost to operate a small still is often less than the fees of a commercial recycler (Table 7-3). To decide if a small still is a wise investment, a generator must consider if the distilled solvent will be pure enough for reuse and how long it will take to recoup the purchase price.

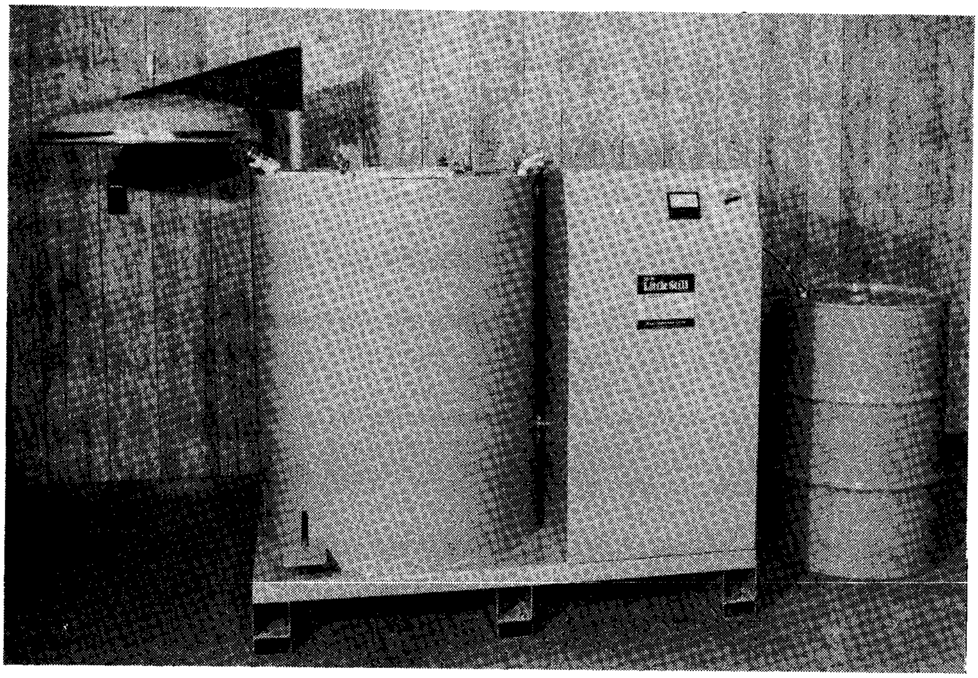

Figure 7-3 One of the Many Small Stills Commercially Available.
Source: Finish Engineering

Small quantity generators may use batch stills. The liquid to be distilled is added in discrete stages, and distillation is halted while liquid is added. Batch stills run from 1 to 55 gallons per batch.

Continuous stills are used for larger amounts. Solvent is added continuously as distillation takes place. The rate of distillation in commercial units can be higher than 500 gallons per hour.

TABLE 7-3

RECYCLING COSTS

Waste Type	Management Method	Cost 1/
Lacquer thinner	Custom recycled and returned to generator	$2 per gallon for service
Freon	Custom recycled and returned to generator	$10-$11 per gallon for service
Chlorinated organics	Custom recycled and returned to generator	$1.80-$2.50 per gallon for service
Methanol	Received by recycler	$.20-.30 per gallon
Valuable nonchlorinated organic, relatively clean	Purchased by recycler	$1-$4 per gallon

TABLE 7-4

APPROXIMATE LAND DISPOSAL COSTS

Waste Type	Management Method	Cost 2/
Bulk liquids	Solar evaporation	$0.35 per gallon
Bulk liquids	Stabilization and landfill	$1.15
Drummed solids	Landfill	$30.00 per drum
Drummed liquids	Stabilization and landfill	$65.00 per drum
Empty drum	Crushing and landfill	$40.00 per drum
Bulk solids	Landfill	$85.00 per cubic yard

1/ Telephone quotes by Romic Chemical Corporation, East Palo Alto, CA, September 19, 1985.

2/ Telephone quotes by Chemical Waste Management, Santa Clara, CA, September 19, 1985. These numbers are not comparable to the recycling costs <u>unless</u> you supply solvent cost information.

TABLE 7-5

SOLVENT LEASING COSTS*

Frequency of Collection	Capacity of Tank 10 Gallon	16 Gallon	20 Gallon	30 Gallon
Once/1 week		$1.95		$1.58
Once/4 weeks		$2.40		$1.80
Once/8 weeks		$2.89		$2.07
Anytime, using customer's tank (Includes equipment rental)	$3.50		$2.45	$2.37

---

* Safety-Kleen, Rancho Cordova, California, October 4, 1985.

Off-Site Recycling

Commercial solvent recyclers purify a waste and return it to the generator or distill a blend of waste solvents and sell the product on an open market. For the latter purpose, some California solvent recyclers have very large stills. Solvent recycling is generally less expensive than land disposal although the costs are comparable (Tables 7-3 and 7-4). The price of land disposal will continue to increase as disposal bans and other regulations take effect. Other concerns such as liability favor recycling. Figure 7-4 shows one of California's largest recyclers. Commercial recycling is also discussed in Chapter 2.

Solvent leasing is available for some industries such as automobile service shops. The leaser provides fresh solvent, a solvent tank, and degreasing equipment. In this arrangement, the solvent user never owns the solvent and is presumably not liable for any costs resulting from mishandling after it leaves his possession. Costs for solvent leasing are based on the size of the tank and the frequency of collection (Table 7-5). In California, solvent leasing is available for the parts degreasing and dry cleaning industries.

Perhaps the most important end use for waste solvents is as fuel. Incineration of hazardous waste is discussed in Chapter 9. Waste solvent too contaminated for purification makes up a large fraction of the organic waste suitable for incineration. Residue from distillation apparatus (tank bottoms) is also well suited for incineration.

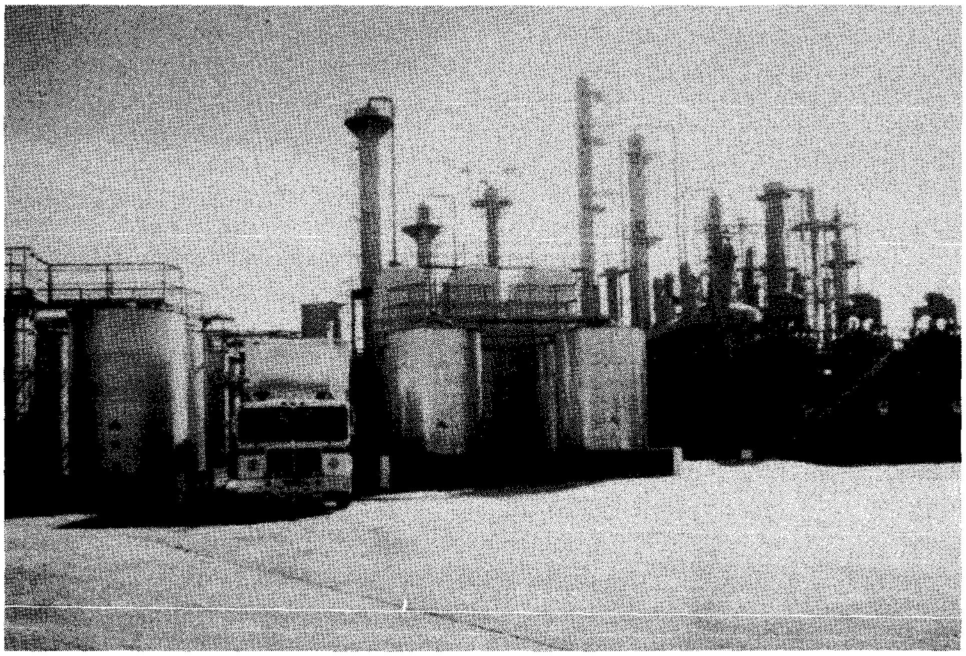

Figure 7-4 Stills at a Large California Solvent Recycler.
Source: Romic Chemical Corporation.

CHAPTER 8
USED OIL

A. INTRODUCTION

In California, used oil is regulated as a hazardous waste. Most used oil is soiled lubricating oil. The principal hazardous contaminants of waste oil are heavy metals such as lead, barium, cadmium, arsenic, chromium and zinc; and halogenated organics, such as PCBs and solvents.

Used oil recycling was reviewed by the California Waste Management Board (CWMB) in 1983. According to that report and more recent Department data, over 100 million gallons of used oil are generated in California annually. The single largest source of that oil is the automobile engine. Other important sources of waste oil are industrial lubricants, industrial engine oils, and oils for metal working.

The management of used oil is regulated by CWMB and by the Department. The Department of Health Services regulates waste oil as a hazardous waste and administers manifesting and permitting requirements. CWMB maintains and enforces recording requirements for recyclers and has an active public information program concerning recycling opportunities.

An important change in used oil management occurred at the federal level in 1985. New EPA regulations mandate that incineration of used oil be regulated under RCRA. The new regulations also establish criteria for used oil burned in nonindustrial boilers.

Approximately 60 percent of the waste oil shipped off site in California is recycled. The primary use of recycled oil is as fuel. (A 1985 report by the California Air Resources Board reviewed incineration of used oil.) A small amount of recycled oil is purchased for lubricant. Recycling of used oil is becoming more economical as disposal costs rise and as recycling technology improves. The costs of recycling a particular stream of used oil depends on the contaminants.

An unknown amount of lubricating oil is recycled on site. This oil is often purified by filtration sedimentation and simple heat treatment.

B. TECHNOLOGIES FOR USED OIL RECYCLING

On-Site Filtration

Lubricating oil eventually becomes soiled with metal fines, water, and microorganisms. Several corporations produce oil purification systems that allow on-site treatment and reduce the rate of generation of waste oil. These systems generally utilize thermal dehydration and filtration. Treatment systems, such as those produced by Traiger Energy Systems, a California company, are available both for permanent installation and for mobile use. Traiger's units have multiple stages. The oil is first allowed to settle and is then subjected to screen filtration. In the next stage, water and low molecular weight hydrocarbons are removed by distillation. The final stages are sequential filtration processes.

Traiger reports high demand for their mobile treatment units. Large machine part and tool manufacturers are typical customers who make use of the mobile systems. An average batch size is 5,000 gallons. Traiger has also sold equipment to companies wishing to extend the life of vehicle engine oil.

Distillation

Distillation processes serve several purposes in oil recycling. The most common use is to remove water and low molecular weight hydrocarbon. Both fractional and flash distillation are employed. As discussed in Chapter 7, fractional distillation slowly removes the lighter components. In flash distillation, first the material is heated under pressure until equilibrium is reached. The lighter fractions are then quickly removed. See Chapter 7 for a more complete description of distillation processes.

For specialized purposes, the oil itself may be volatilized and collected. This is done in a vacuum fractional distillation. Oil refined in this fashion is generally used as lubricant.

Chemical Treatment

In these processes, the oil is chemically treated to desolubilize metals and other contaminants. The traditional method is treatment with sulfuric acid and clay. However, this process generates acidic sludge and hazardous air emissions.

The Phillips Refined Oil Process (PROP) employs an aqueous solution of diammonium phosphates in the removal of metals from oil. The metallic phosphates formed are insoluble in both water and oil. After filtration and decantation, the oil is heated to remove water and small organic molecules. This type of treatment costs $.40 per gallon for a 10-million gallons per year installation. A number of variations of this process exist.

Solvent Treatment

Solvent processes for used oil recycling generally have three stages. The oil is first dehydrated by flash distillation or other method. The solvent extraction itself is the second step. Finally, the oil is "polished" with a solids removal step, such as filtration, and a second flash distillation to remove water and light hydrocarbons.

Early versions of this process employed methylethyl ketone as the solvent and were used to remove lead from oils. Improvements in the process have led to the use of more complicated solvents and an expansion of the range of contaminants that can be removed.

It is estimated that a 10-million gallon per year facility would cost at least $2.5 million to build with operating costs of $.10 per gallon.

An interesting adaption of this process is the use of super critical ethane as solvent; the extraction step is conducted at 42°C and 100 atmospheres pressure. A packed column aids the separation of oil and solvent. The product of this process is usually adequate for fuel, but not for some lubrication processes.

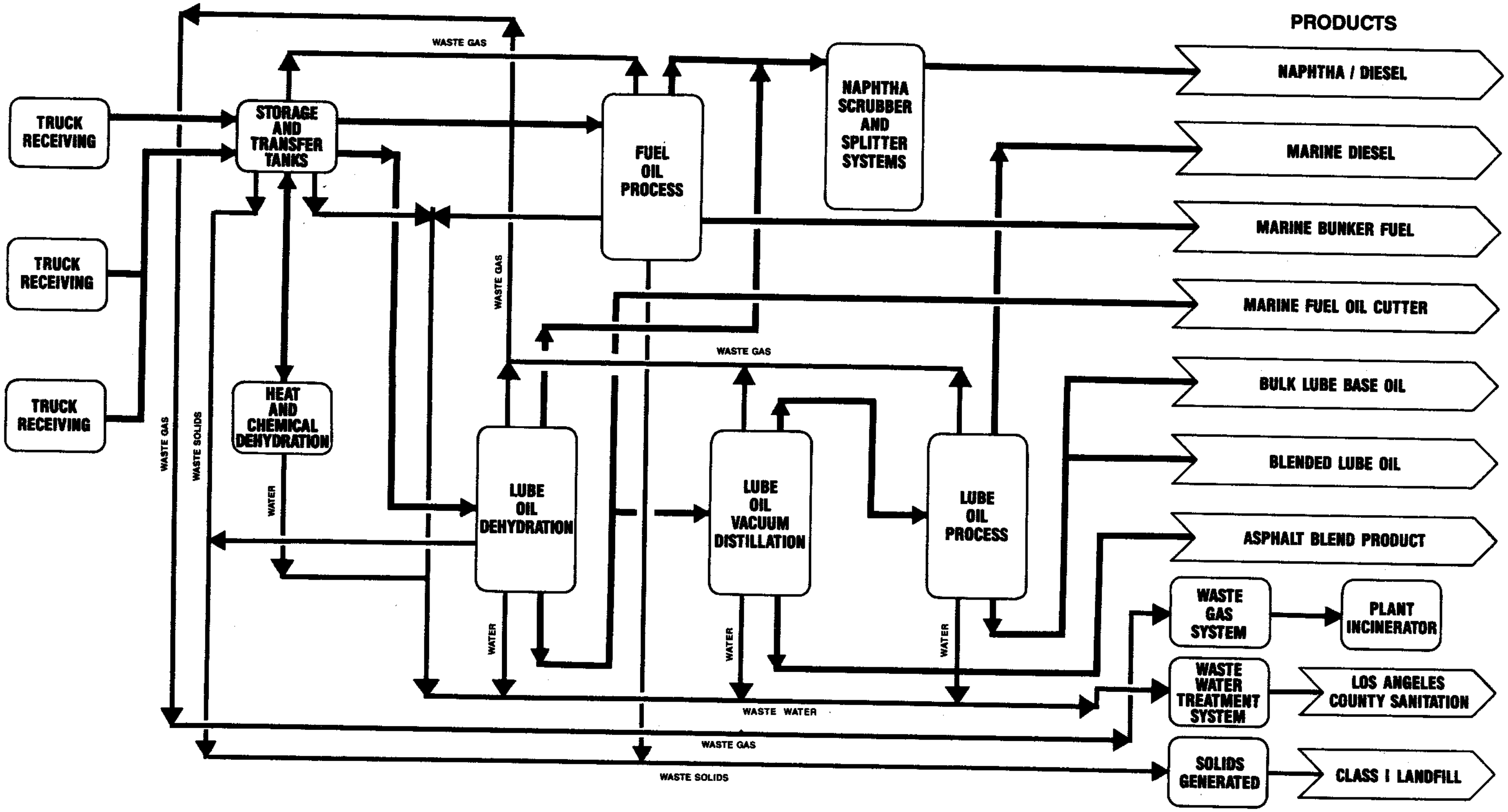

Figure 8-1 Process Program for a Large California Oil Recycler
Source: Demenno-Kerdoon

C. OFF-SITE OIL RECYCLING IN CALIFORNIA

Several large installations in California offer off-site purification of oil. Demenno/Kerdoon is a large oil recycler in California. This company runs a large thermal refining plant (see Figure 8-1). Incoming oil is subject to settling, dehydration, and several thermal steps. Demenno/Kerdoon products include diesel fuel, marine bunker fuel, various lube oils, and asphalt blend products.

Other California installations use simple technologies or acid separation clay treatment for oil treatment.

CHAPTER 9
INCINERABLE ORGANIC WASTES

A. INTRODUCTION

Wastes with combustible heat contents greater than 5,000 Btu per pound are generally considered "incinerable". However, burning wastes with lower Btu values may be a feasible option if the wastes are blended with high Btu wastes or if the thermal destruction process has a very efficient heat recovery system.

In California, Senate Bill 509 of 1985 requires the destruction or detoxification of certain incinerable organic wastes. The law will be implemented in two phases. The first phase takes effect on January 1, 1988 and requires hazardous wastes whose heating values are greater than 3,000 Btu per pound to be destroyed or detoxified. The second phase requires wastes whose concentrations of volatile, organic compounds are above a certain limit value (yet to be determined by the Department of Health Services) to be similarly incinerated or treated. The second phase takes effect January 1, 1990.

At present, EPA allows hazardous wastes having heating values greater than 5,000 Btu per pound to be burned as supplementary fuels in on-site boilers. Hazardous wastes with high Btu content may also be burned in state permitted off-site incinerators (resource recovery). To encourage resource recovery, these incinerators are partially exempt from EPA's RCRA regulations.

Off-site incineration of hazardous wastes having heating values lower than 5,000 Btu per pound require an EPA Hazardous Waste Facility Permit. The California Air Resources Board has issued guidelines, which reflect EPA and the Department incineration requirements for use by the local air pollution control districts.

B. INCINERATORS FOR ORGANIC WASTES

To date, incineration is the most widespread thermal destruction technology for hazardous wastes. This technology is an engineered process that uses thermal decomposition and air oxidation to destroy organic waste material. The operating conditions of an incinerator such as temperature, turbulence, and residence time must be optimized to minimize hazardous emissions. Air pollution control equipment is usually required to meet the local, state, and federal regulations for allowable emissions.

Incineration is an ultimate destruction technology. Any residual hazardous material has small volume and is easily managed. Consequently, incineration frees the hazardous waste generator from the liability risks of disposal. Incineration has the additional advantage of allowing heat recovery.

A variety of incinerator types have proven their long-term reliability to destroy hazardous organic compounds. These include, fixed hearth, liquid injection, rotary kiln, fluidized bed, and multiple hearth. The following sections describe these types of incinerators and discuss the status of hazardous waste incineration in California.

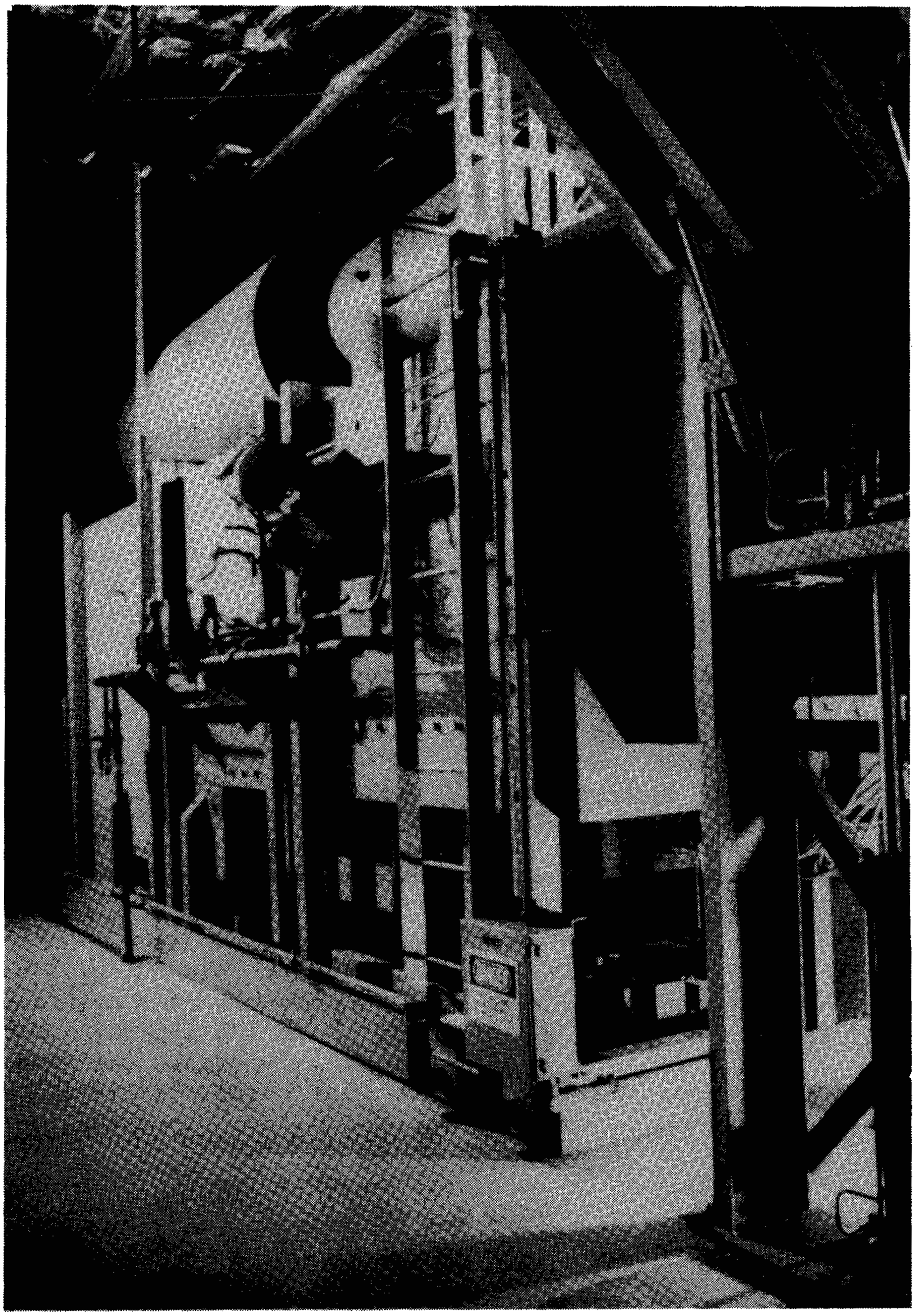

Figure 9-1 A Fixed Hearth Incinerator Used for Infectious Waste.
Source: American Environmental Corporation

Fixed Hearth Incineration

Fixed hearth-type incinerators are usually of small capacity and can handle both liquid and solid wastes. Fixed hearths are relatively simple and are seldom custom designed. The incinerator typically consists of two chambers: a primary combustion chamber, and a secondary combustion chamber. The first chamber operates in a starved air mode (not enough air is present for complete combustion). Vortex-type burners inject liquid waste mixed with air into this chamber, solids can be added by grates. Combustion products from the first chamber proceed to the second chamber where more air is added to complete combustion.

Mixed wastes, including waste solvents and combustible solids, can be handled by fixed hearth incinerators with feed rates of up to one ton per hour. These incinerators have relatively low waste throughput and limited ability to destroy more stable compounds such as chlorinated liquid wastes. Figure 9-1 shows a fixed hearth incinerator used for infectious waste incineration.

FIXED HEARTH INCINERATOR

Typical Operation Parameters

Combustion Temperatures: primary chamber (600°F to 1,600°F) and afterburner (1,200°F to 1,800°F).

Gas Residence Time: up to one second.

Air Pollution Control Equipment: usually none.

Costs: vary with waste type and throughput. Operational costs may range up to $150 per ton for simple combustible wastes.

Example of an Operating Unit

Manufacturer: Therm Tech Corp.

Location of Unit: Sacramento, CA

Waste Feed Rate: 800 pounds per hour.

Heat Input: 4 million Btu per hour.

Age of Unit: 6 months.

Type of Waste Feed: boxed infectious waste.

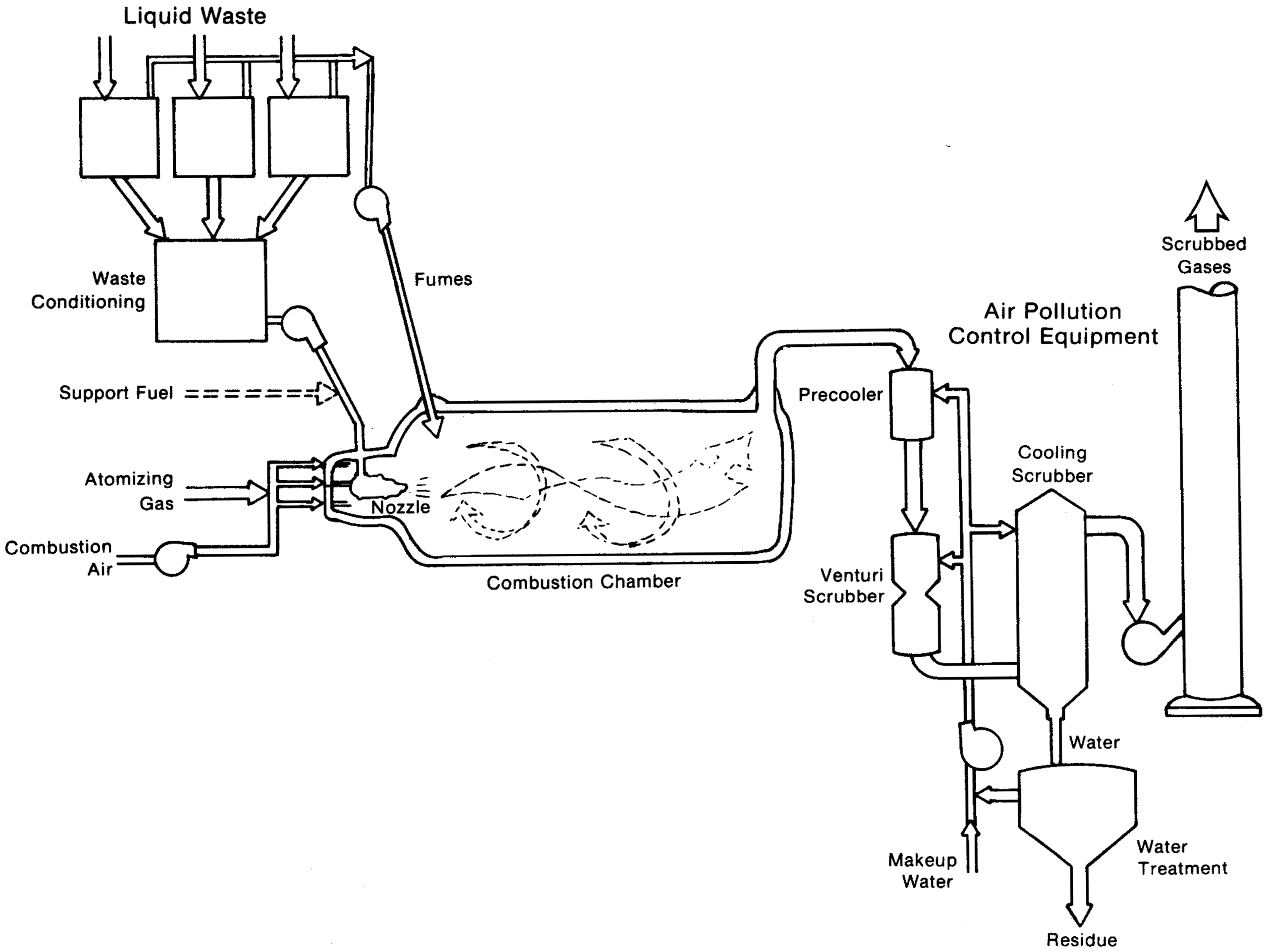

Figure 9-2 Liquid Injection Incinerator.
The equipment on the far right is used for air pollution control.
Source: Hitchcock, D. A. *Chemical Engineering* 5/21/79

Liquid Injection Incineration for Facilities on Land

Liquid injection incinerations can be used to dispose of combustible liquid or slurried waste. The liquid waste is usually blended and filtered before it is injected into the incinerated (Figure 9-3). Burning takes place in the combustion chamber where the fuel and air are mixed with a rotating cup, a pressurized fuel-atomization system, or by combination gas-fuel mixing nozzles using pressured air or dry steam.

The waste feed to the incinerator is limited to pumpable liquids and slurries that can be readily atomized. Feed rates of up to 2,400 gallons per hour (about 10 tons per hour) can be handled. Liquid halogenated hydrocarbons can be successfully destroyed at temperatures above 1,800°F.

LAND-BASED LIQUID INJECTION INCINERATOR

Typical Operation Parameters

Combustion Temperatures: 1,200°F to 2,400°F.

Gas Residence Time: 0.5 to 2 seconds.

Air Pollution Control Equipment: electrostatic precipitators and scrubbers.

Costs: vary with waste type, throughput, and air pollution equipment required. Operation costs may range up to $300 per ton of chlorinated solvents.

Example of an Operating Unit

Manufacturer: Thorpe Custom.

Location of Unit: Dominguez, CA

Waste Feed Rate: 300 gallons per hour.

Heat Input: 100 million Btu per hour.

Age of Unit: 30 years.

Type of Waste Feed: organic solvent still-bottoms.

Liquid Injection Incineration on Ships

Liquid injection incinerators have been installed on ocean-going vessels for the destruction of hazardous organic wastes at sea. In these incinerators, rotary cup (vortex type) burners inject hazardous liquid wastes and air into dual, vertically mounted, refractory lined, fixed combustion chambers. An automatic system shuts off the waste fed to the incinerators if the combustion zone temperature falls below 2,300°F.

Liquid PCB and Agent Orange have been burned on ocean-going incineration ships off the Gulf Coast. Air emission analysis has shown that these compounds are destroyed with greater than 99.995 percent efficiency. The analysis was confirmed by the EPA.

The EPA had scheduled a test burn for Chemical Waste Management's Vulcanus II for Spring 1986. This test burn, which was to take place off the North Atlantic Coast, created a storm of controversy. In June 1986, EPA announced that it will not issue a permit for a test burn at sea until it (EPA) has promulgated regulations for at-sea incineration.

SEA-BASED LIQUID INJECTION INCINERATOR

Typical Operation Parameters

Combustion Temperature: 2,300°F to 2,400°F.

Gas Residence Time: greater than two seconds.

Air Pollution Control Equipment: none required.

Cost: total cost of incineration system and ship is about $50,000,000. Service cost is $200 per ton for PCB waste.

Example of an Operating Unit

Manufacturer: Chemical Waste Management, Incorporated.

The incinerator ship Vulcanus burned 700,000 gallons (approximately 3,100 tons) of PCB-contaminated transformer oil in December 1981 off the Gulf Coast. PCB destruction efficiency was 99.999 percent. Another burn was made of 800,000 gallons in August 1982 with similar results.

Rotary Kiln Incineration

A typical rotary kiln has a cylindrical, refractory-lined shell mounted at a slight incline from horizontal. Rotation of the shell enhances mixing of solid wastes with the combustion air and provides for transport of the waste through the kiln. Rotary kilns usually have a secondary combustion chamber following the kiln.

Most organic wastes, including solids, sludges, and slurries can be burned in rotary kilns. Liquids and gases are injected through auxiliary nozzles. At present, the rotary kiln is the most versatile type of incinerator for hazardous wastes. Feed rates of up to ten tons per hour can be handled. Cement kilns, universally designed as rotary types, have successfully destroyed chlorinated organic compounds in Sweden, Canada, and the United States. The General Portland Cement Kiln, in Lebec, California, is discussed in Section C of this chapter.

ROTARY KILN INCINERATOR

Typical Operation Parameters

Combustion Temperature: 1,500°F to 2,900°F.

Gas Residence Time: two to five seconds.

Air Pollution Control Equipment: baghouses or electrostatic precipitators and scrubbers.

Costs: vary greatly with the type of waste feed processed, throughput, and type of air pollution equipment required. Operational costs range up to $600 per ton of waste.

Example of Operating Units

Manufacturer: Vulcan Iron Works.

Location of Unit: Alabama.

Feed Rate: 60 gallons per hour.

Heat Input: 10 million Btu per hour.

Age of Unit: 10 years.

Type of Waste Feed: broad spectrum of hazardous wastes.

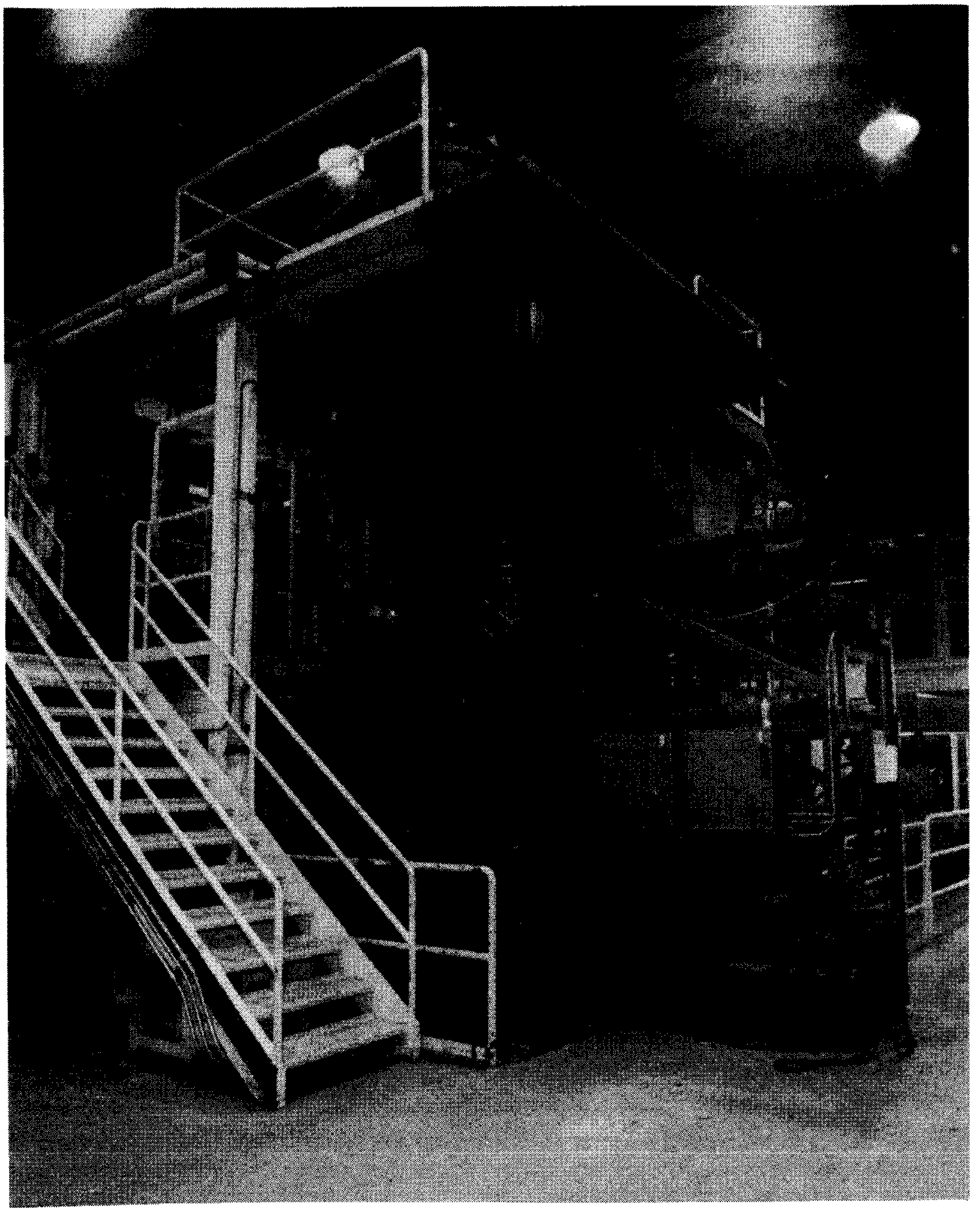

Figure 9-3 Circulating Fluidized Bed Incinerator.
Source: GA Technology

Fluidized Bed Systems

A fluidized bed incinerator is a refractory-lined vessel containing inert granular material. Combustion air is blown through the bed to make a "fluid" of the granular material. Waste feed enters the reactor either above or within the bed. The bed is preheated by an auxiliary burner. Solid combustible materials remain in the bed until they become small and light enough to be carried off with the flue gas as particulate to be recovered by air pollution control equipment. Lime or limestone can be added to neutralize acidic gases. A modified fluidized bed incinerator employs a circulating bed which enhances heat transfer (Figure 9-3).

The most common applications of fluidized bed incinerators are in the petroleum, paper, and sewage disposal industries. Fluidized bed incinerators can accept a wide variety of wastes, including solid wastes which are presized and preheated before feeding.

FLUIDIZED BED INCINERATOR

Typical Operation Parameters

Combustion Temperature: 900°F to 2,300°F.

Gas Residence Time: 0.8 to 2.5 seconds.

Air Pollution Control Equipment: baghouse or electrostatic precipitators for fly ash collection.

Costs: vary with waste type, throughput, and air pollution control equipment. Operational costs compare favorably with other available types of incinerators.

Example of an Operating Unit

Manufacturer: Dorr-Oliver.

Location of Unit: Indiana.

Feed Rate: 15 tons per hour.

Heat Input: 70 million Btu per hour.

Age of Unit: 11 years.

Type of Waste Feed: oil refinery sludges.

Multiple Hearth

A typical multiple hearth furnace includes a refractory-lined steel shell, a vertical central rotating shaft, a series of vertically stacked flat hearths, and a series of rabble arms which plow the waste material successively across the hearths. Waste enters the top of the unit and ash is discharged at the bottom. Additional liquid and gaseous wastes can be injected through side ports.

Multiple hearth furnaces can incinerate gases and liquids as well as sludges and solid wastes. They have been used mainly for sewage sludges and municipal wastes.

MULTIPLE HEARTH INCINERATOR

Typical Operating Parameters

Combustion Temperatures: 1,400°F to 1,750°F.

Gas Residence Time: up to two seconds.

Air Pollution Control Equipment: baghouse or electrostatic precipitators.

Example of an Operating Unit

Manufacturer: Lurgi Corporation

Location: California

Municipal sludge up to 1,000 pounds per hour (dry weight basis) is burned.

C. INCINERATORS OPERATING IN CALIFORNIA

On-Site Incinerator

Approximately 400,000 tons of organic hazardous wastes amenable to incineration are generated annually in California. Only one-fifth, or about 84,000 tons, of such wastes are currently incinerated and of these about 48,000 tons per year are burned in "on-site" incinerators. Twelve on-site combustion units incinerate a broad spectrum of wastes as follows:

- Two units burn vapors only.
- Five units burn dilute mixtures of simple organics in water.
- Two units burn aqueous waste mixtures having concentrations of organics in excess of 50 percent. Only one of these units reports burning chlorinated compounds wherein its "thermal oxidizer" is part of the manufacturing process.
- Three units burn various solids ranging from organic sludge through pathogens to obsolete munitions.

The above 12 installations accept only their own, on-site generated wastes. Most of the units are of simple fixed hearth design with or without liquid injection capability. Heating capacities range from a few million Btu per hour to about 200 million Btu per hour. Most of the units recover heat as steam. One company, Dow Chemical of Pittsburg, is seeking federal and state permits to expand its capacity to incinerate similar wastes, from its other installations within California, in a new rotary kiln.

Table 9-1 shows comparison of the 12 existing on-site units.

Off-Site Incineration

Currently, there is only one operating off-site hazardous waste incinerator in California. A cement manufacturing company, General Portland, Inc., of Lebec, California, is permitted to burn hazardous waste. Allowable wastes are limited to a maximum 5 percent chlorine content and a heating value of 10,000 Btu per pound or greater. No PCBs are accepted. The company is in the process of receiving a long-term (five year) permit from the Department of Health Services to continue to burn waste solvents as supplementary fuel. The waste throughput is limited to 36,000 tons per year which is equivalent to 25 percent of the kiln's heating requirement. Thus, use of the waste solvents account for a major reduction in fuel costs.

Trial burn tests conducted in August 1984, at the company's Los Robles plant, confirmed destruction and removal efficiencies (DRE) of 99.99 percent or greater for selected principal organic hazardous constituents (POHCs) which are selected, highly halogenated compounds (e.g., freon-113). These compounds are as difficult or more difficult to destroy than any other compounds likely to be received by the plant for incineration. High temperature (2,600°F), long gas residence time (greater than 5 seconds), and the inherent ability of the kiln's raw materials to neutralize acid gases contribute to this kiln's success.

Two other existing facilities have undergone trial burns to determine their capabilities to utilize off-site industrial waste organics. One facility, a sulfuric acid decomposition furnace, owned by Stauffer Chemical Company in Dominguez, obtained a short-term permit to burn synthetic wastes containing selected compounds such as pentachlorophenol and freon-113. Use of synthetic waste allowed the trial burn to be exempt from EPA requirements. Test results in February/March 1985 showed that DREs of 99.99 percent were attainable. The decomposition furnace operates at 1,800°F, has a gas residence time greater than 4 seconds, and has high gas turbulence which is expected to give acceptable DREs for actual wastes. The company is in the process of obtaining state and local permits to burn commercial waste solvents having heating values greater than 5,000 Btu per pound with a throughput up to 75,000 tons per year. Stauffer is also seeking EPA permits to burn hazardous wastes at its Martinez facility.

The second existing facility seeking federal and state permits to burn off-site hazardous waste is G. A. Technologies, Inc. (GAT) in La Jolla. This company plans to use its La Jolla pilot plant as a demonstration facility to show the applicability of a circulating bed combustor (Figure 9-3) to burn liquid and solid wastes. A preliminary test performed with synthetic solvents in 1983 indicated acceptable DREs for selected surrogate POHCs. The pilot plant has also successfully detoxified PCB-contaminated dirt under a Toxic Substances Control Act (TSCA) permit. GAT is in the process of obtaining a research and development and demonstration permit to burn limited quantities of RCRA organic wastes at its pilot plant. GAT plans to show the feasibility of transferring this technology to on-site use.

Proposals for New Off-Site Incinerators

Five proposals for constructing new off-site hazardous waste incinerators have proceeded beyond the idea stage. However, siting issues, regulatory requirements, public resistance, or financing concerns have impeded these projects. One of these companies, Security Environmental Systems, is in the process of having its operation plan and its preliminary risk analysis reviewed by several agencies.

Table 9-1

ON-SITE INCINERATORS IN CALIFORNIA

FEBRUARY 1986

Company	Type	Heat Rating Million Btu/ Hour	Manufacturer	Temp. (Degree Fahr)	Waste Types	Air Pollution Control Equipment	Heat Recovery
Alpha Resins (Perris)	Liquid & Vapor Injection	3	Hirt Combustion	1,450	Aldehyde vapors aqueous phenol Liquid	None	Boiler
Ashland Chemical (Los Angeles)	Liquid Injection	5	Hirt Combustion	1,450	Resin rinse waters	None	Boiler
Cargill (Lynwood)	Liquid Injection	6	Hirt Combustion	1,450	Resin rinse waters	None	Boiler
Chevron-Ortho (Richmond)	Liquid Injection	158	Thorpe Custom	2,600	90% organics in water	Scrubber and mist eliminator	None
Dow Chemical (Pittsburg)	Thermal Oxidizer	5	Own Design*	2,300	Chlorinated still-bottoms	Catalytic De-NOx	None
Rohm & Haas (Redwood City)	Fixed Hearth	12	North American	1,600	Organic vapors only (vinyl HCs)	None	None
IT Vine Hill (Martinez)	Liquid & Vapor Injection	18	Trane Thermal	1,800	Organic liquids and vapors incl. chlorinated HC	None	Boiler
Koppers Chemical (Oxnard)	Liquid & Vapor Injection	7	Hirt Combustion	1,600	5% Glycols in water and vapors	None	Boiler
Lawrence Livermore (Livermore)	Fixed Hearth	4	Environmental Control Products	2,200	Liquid solvents and solid pathologicals	None	None
PPG (Torrance)	Liquid Injection	8	Hirt Combustion	1,450	Organic vapors only (alcohols, ketones)	Venturi scrubber	Boiler
Shell (Martinez)	Liquid Injection (Co Boilers)	3 at 180 each	Alcorn	1,800	1% HC liquid and 2% organic sludge	Electrostatic precipitator	Boiler
Sierra Army Depot (Herlong)	"Popping" Furnace	3	Custom (In-house)	400	Small arms	Cyclone and baghouse	None

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* In-house process unit for decomposing chlorinated organics.

D. MOBILE THERMAL DESTRUCTION UNITS

The discussion below contrasts four types of thermal destruction systems applicable to site cleanup operations. Each of the processes can readily destroy waste oils and solvent residues. The rotary kiln (incinerator), the infrared incinerator, and the electric reactor (pyrolyzer) can detoxify contaminated soils. The rotary kiln and supercritical (solubilizer) units can detoxify wastewaters. Table 9-2 gives a comparison of the operating features of three of the transportable thermal destructors.

Rotary Kiln Units

EPA has developed a transportable incineration system for on-site thermal destruction of hazardous materials at remote spill or disposal sites. The system can be broken down into three sections: (1) the waste shredder and rotary kiln; (2) the afterburner with venturi gas squelch unit; and (3) the scrubber with sound suppressor and fold-down stack. The sections are transported on semitrailers (Figure 9-4).

This system can detoxify up to 2 tons per hour of contaminated dirt (about 15,000 tons per year) or up to 60 gallons per hour of liquid waste oil. Successful trial burns of heavily chlorinated wastes (e.g., dioxins) were conducted at Times Beach, Missouri in 1985 with destruction removal efficiencies of 99.999 percent or better. Operating costs for the mobile incinerator range from $300 to $1,000 per ton depending on waste characteristics.

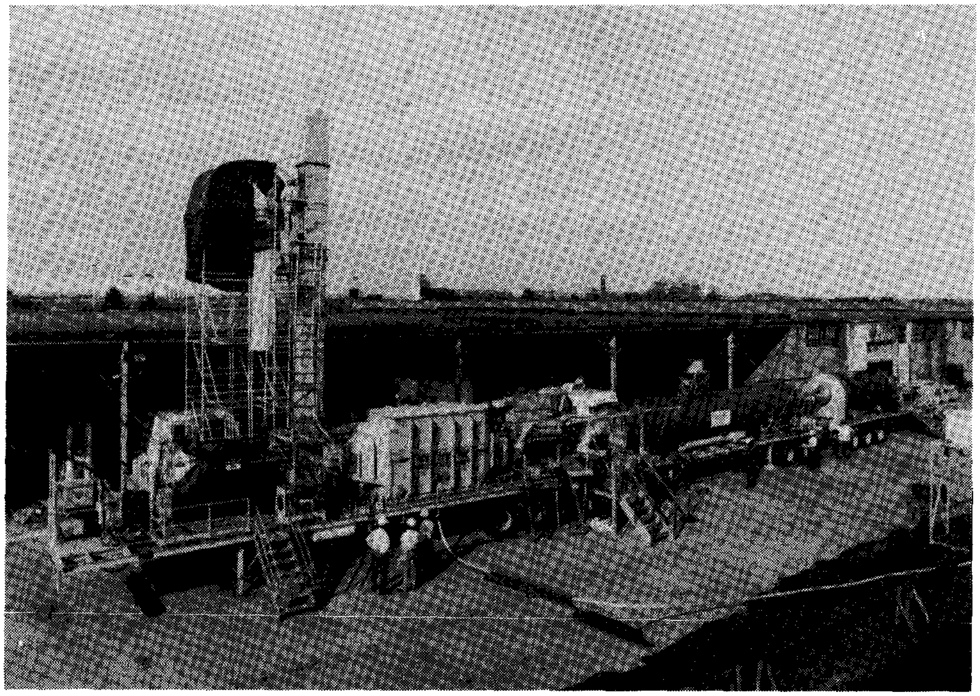

Figure 9-4 EPA Mobile Incinerator. (The "Blue Goose') The three trailers are easily mobile.
Source: EPA

Consequently, these wastes can be disposed of on site. Design specifications for the EPA mobile incinerator are available nationwide to assist federal and state personnel for Superfund cleanup projects. A few private companies have constructed rotary kiln incinerators. Several have been permitted by EPA and are operating in other states. For example, Ensco Environmental Services (Little Rock, Arkansas), offers a mobile (7 trailers) unit that can simultaneously incinerate up to 4 tons per day of contaminated solid material together with 150 gallons per hour (about 4,000 GPD) of liquid hazardous wastes (Table 9-2). Ensco rotary kiln units have been operating in Florida for on-site cleanups. Operating costs are in the range of $300 to $400 per ton of contaminated dirt treated.

Infrared Incinerators

This comparatively new technology offers tremendous flexibility for the decomposition of solid hazardous wastes. In a typical infrared incinerator, a woven metal conveyor belt carries the wastes under infrared heating elements equally spaced along the length of the insulated furnace. At the end of the furnace, ash residue is discharged to a hopper; off-gasses are sent to a secondary burner where they are destroyed by a propane burner. The flexibility of this technology comes from the operator's ability to vary the residence time (the belt speed), the temperature (the intensity of the heating elements), and the aeration. The infrared furnace's capability to operate with very low air flows is a particular advantage. The process can be operated to minimize emissions of volatile organic compounds and particulates.

Infrared incinerators can be constructed as a mobile unit. Shirco Infrared Systems of Dallas, Texas, is manufacturing several mobile units expressly for contaminated site cleanup applications. One Shirco unit is employed at a fixed location for hazardous waste treatment; several other units are used for activated carbon regeneration. Shirco reports that their units can achieve greater than 99.9999 percent DRE of PCBs and dioxin. A mobile unit with a capacity of 100 tons per day costs approximately $2,500,000.

Advanced Electrical Reactor (AER)

The AER unit uses infrared radiation to pyrolytically destroy incoming wastes. The reactor consists of a tubular core surrounded by an annular radiant zone. A porous sleeve separates the two zones. Electrodes housed in the (outer) annular space heat reactants to 4,000°F (Table 9-2).

A radiation-transparent gas (nitrogen) flows through the core's sleeve preventing the deposition of the reactants or their products on the hot surfaces. The nitrogen flow is known as a fluid wall. The reaction products are inert gases and salts.

Radioactive wastes have been treated by the AER and transformed into nonleachable glass granules. Additives help form the glass substance. Iron oxide added to wastes containing hexavalent chromium forms inert, nonleachable ferrochrome beads. Limestone added to wastes with reactive components such as chlorine, forms nonleachable salts. The AER unit will accept liquids, solids, and sludges but the nonliquid wastes must be reduced to 100 mesh size.

The Huber Corporation of Borger, Texas has developed an AER for destruction of hazardous waste. This reactor is permitted by the EPA. Granulized, contaminated material falls through a hollow cylinder containing a vertical mounted inner graphite tube. The contaminated solids or liquids are exposed to heat radiated from special electrodes spaced around the periphery of the graphite tube. A three inch diameter reactor mounted on a trailer, successfully detoxified contaminated soil (containing dioxins), at Times Beach, Missouri. Destruction removal efficiencies obtained were 99.999 or greater. The company operates a 12-inch diameter unit as a pilot plant in Texas and has also developed an 18-inch unit expected to process about 4 tons per day of contaminated soil or about 250 gallons per hour of waste oil. Operating costs for AER are in the range of $300 to $400 per ton of waste.

Supercritical Water

The supercritical water process is an emerging technology utilizing high pressure to convert organic wastes into superheated steam, innocuous gases, and salts. Water heated above 705°F at sufficiently high pressures (supercritical region) acts as an excellent solvent and decomposition agent. Aqueous mixtures or slurries are mixed with oxygen and heated to the supercritical region to chemically oxidize wastes with greater than 99.999 percent efficiency.

This process can treat dilute organic or inorganic wastes which may be liquids, slurries, or sludges which may contain reactive ions, metals, or inorganic salts. The process generates steam which can be used to make electricity or can serve as process steam.

The Modar Company of Natick, Massachusetts has developed a supercritical water reactor to solubilize and oxidize hazardous wastes. Their pilot plant, in New York State, rated at 1,000 gallons per day, obtained better than 99.999 percent destruction removal efficiencies for highly chlorinated compounds. The company offers a skid-mounted unit capable of detoxifying up to 30,000 gallons per day of wastewaters (calculated at 5 percent organic content) (Table 9-2). The supercritical water process requires cyclones or other dust collectors as air pollution control equipment. Preliminary analysis suggest that supercritical water is less expensive to operate than many high temperature incinerators.

TABLE 9-2

TRANSPORTABLE THERMAL DESTRUCTORS

Type	Rotary Kiln	Electric Reactor	Supercritical Water
Developer	Ensco Corp.	Huber Corp.	Modar, Inc.
Availability	Upon Request	Upon Request	Near Commercial
Method	High Temperature Oxidation	High Temperature Pyrolysis	High Pressure Solubilization/Oxidation
Reaction Zone Temperature (°F)	2,200	4,000	700
Residence Time			
Solids (minutes)	60	1	Not Applicable
Liquids (minutes)	1	1	1
Gases (seconds)	4	5-10	60
Feedrates			
Contaminated Soil (tons per day)	100	100	Not Applicable
	(and)	(or)	
Waste Oil or Solvents (gallons per day)	4,000	6,000	1,500
	(or)		(or)
Waste-Water (GPD)	14,000	Not applicable	30,000 at 5% organics.
Electricity Generation			
Electrical Power (Kilowatt)	200	1,000	500

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CHAPTER 10
PCBs

A. INTRODUCTION

Polychlorinated biphenyls, commonly called PCBs, are a group of chlorinated organic compounds in wide use as coolants and insulation fluids. PCBs were produced in the United States from 1929 to 1979. Concern over PCBs arose because of their extreme toxicity and their stability in the environment.

Although no longer produced, PCBs remain in active use. PCBs and PCB-containing oils are used in: hydraulic and heat-transfer systems, roofing tar, asphalt, "carbonless" carbon paper, lubricants, paints, plastics, televisions, air conditioners, and fluorescent and mercury vapor lights. Because of their thermal stability and low electrical conductivity, PCBs have been widely used in electrical transformers and capacitors. It is estimated that there are 90 million pounds of utility capacitators and 8,500 utility transformers in California; each contains PCBs which will eventually require disposal.

Numerous laboratory studies have suggested a link between PCBs and reproductive failures, birth defects, gastric disorders, skin lesions, swollen limbs, cancers, tumors, eye problems, liver disorders, and other health problems.

In 1968, approximately 1,300 people in Yusho, Japan, used rice oil accidently contaminated with PCBs. Five people died from this incident, the remaining victims developed a variety of ailments characterized as "Yusho Disease": skin lesions, eye discharges, abdominal pain, menstrual irregularity, fatigue, cough, disorders of the nervous system, and hyperpigmentation of the skin, nails, and mucous membranes.

The health threat from PCB's stability and toxicity is compounded by bioaccumulation of PCBs. Many microorganisms tolerate PCBs and concentrate them internally. Animals accumulate PCBs in adipose tissue. Thus, organisms highest in the food chain may consume considerable concentrations of PCBs in their diets.

PCBs are regulated under the Federal TSCA and not under RCRA. In California, liquids containing PCBs are regulated as hazardous down to 5 mg/l; the corresponding federal cutoff is 50 mg/l. Recycling of PCBs is strictly prohibited by TSCA.

The California land disposal ban applies to liquids containing PCBs in concentrations of 50 ppm or greater. This will be extended nationwide on July 8, 1987. Currently, land disposal of liquids containing up to 500 ppm PCBs is allowed by the EPA. In California, land disposal of liquids containing 50 ppm PCB or less and PCB-containing solids is allowed at approved sites.

B. TREATMENT TECHNOLOGIES FOR PCB WASTES

Chemical Dechlorination

The most widely used PCB-dechlorination technique was developed by Goodyear Tire and Rubber Company. This process uses a metallic sodium reagent (sodium napthalene tetrahydrofuran) to strip away chlorine atoms from the stable PCB molecule, thus reducing its toxicity.

Goodyear Company has made the details of this dechlorination process public. Several companies are developing similar processes that do not employ a napthalene-based compound. This substitution is necessary because EPA has classified napthalene as a restricted compound. The equipment required for these dechlorination processes is generally mobile, and can be transported on semitrailers.

In California, commercial use of chemical dechlorination of PCBs has been dominated by two companies, Sunohio and Exceltech. These are the only companies with the necessary permits to treat liquid PCB wastes above 50 ppm in California.

Sunohio, Incorporated, Canton, Ohio

Sunohio has developed what they call the "PCBX" process. A schematic of the PCB process is shown in Figure 10-1. The PCBX process replaces the napthalene used in the original Goodyear Company process with a proprietary compound. The Sunohio mobile PCBX unit is a self-contained, continuous-flow unit. Designed and equipped to treat transformer oil by removing moisture, acids, and other contaminants, it also removes and destroys PCBs. The mobile processing unit is permitted to decontaminate 600 gallons per hour of transformer oil containing up to 2,600 ppm of PCBs. The EPA requires that residual PCB concentrations be below two ppm.

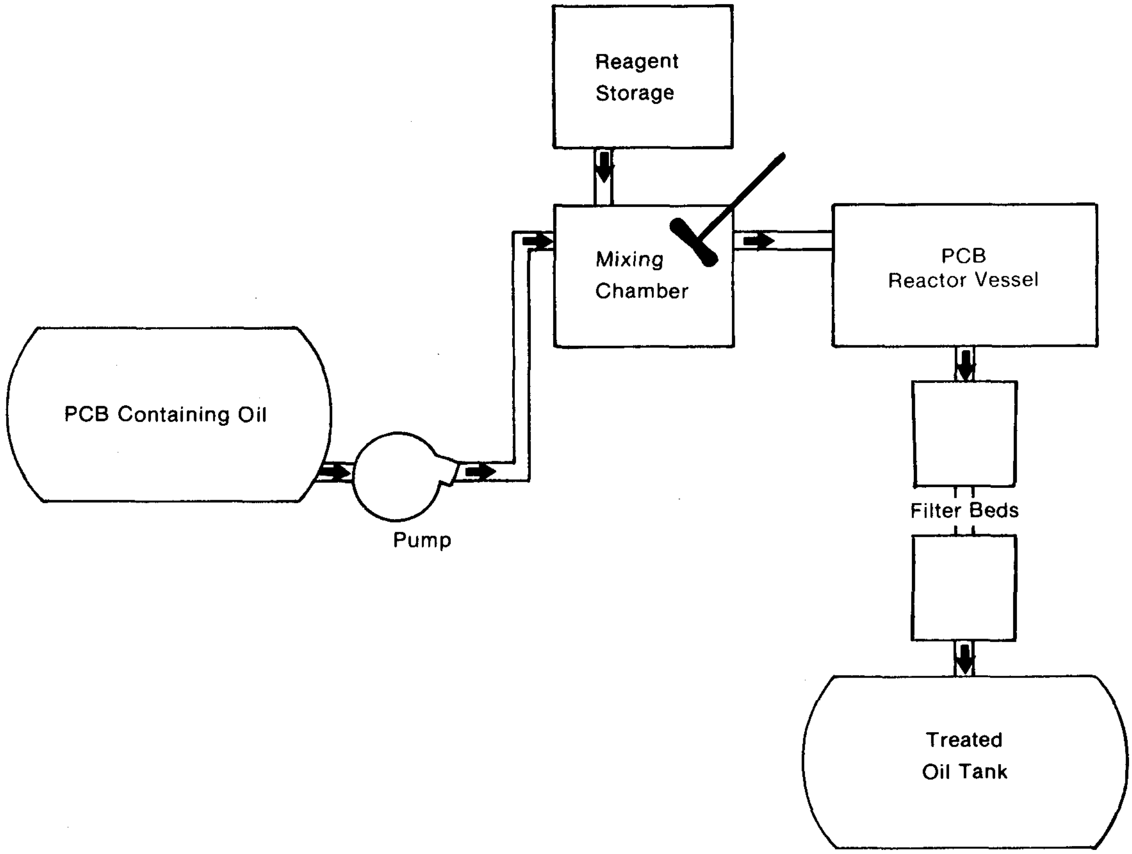


Figure 10-1 SunOhio Mobile PCBX Unit Schematic.
The PCB containing oil is reacted with metallic sodium and a proprietary compound.
Source: SunOhio

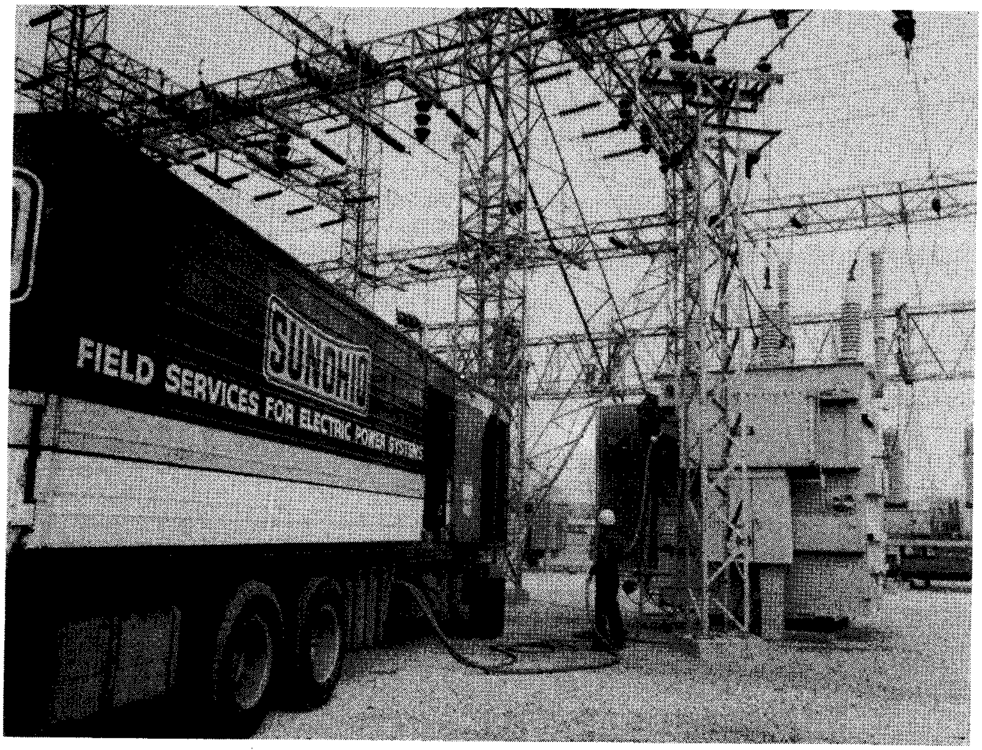
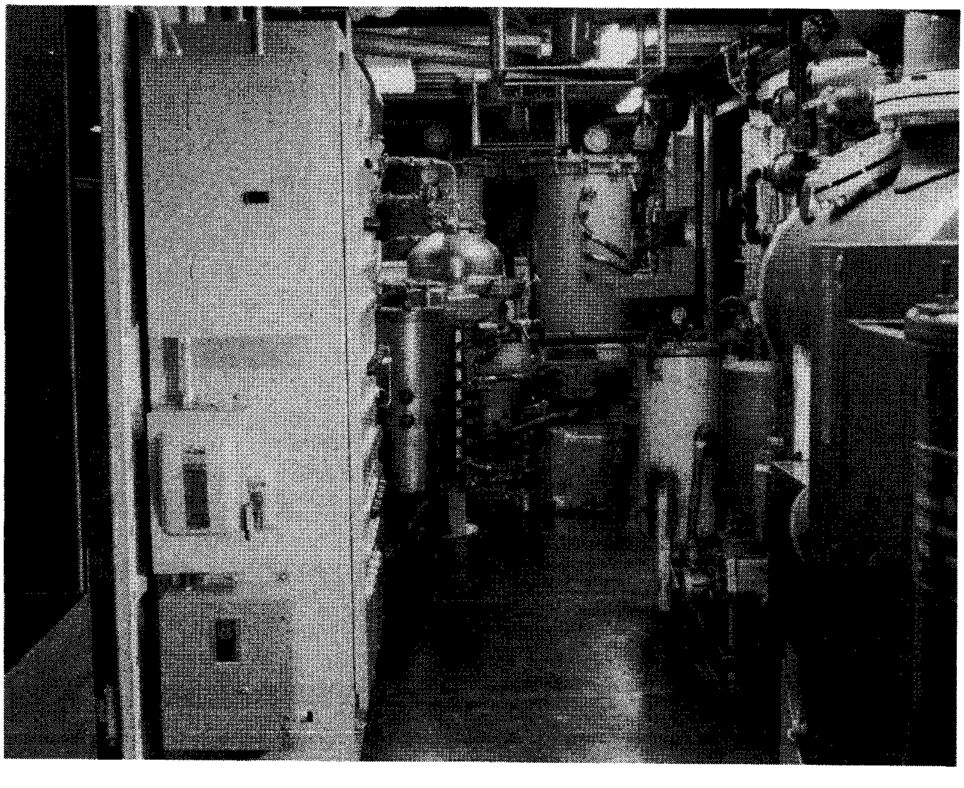


Figure 10-2 The Sunohio Treatment Unit. (a) Transformer oil is replaced without moving the transformer.



(b) Inside the trailer.
Source: Sunohio

TABLE 10-1

SUNOHIO JOBS IN CALIFORNIA

Site	Date	Processed PBC Oil Volume (Gallons)	Initial PBC Conc. (ppm)
Long Beach, Long Beach Naval Station	May 1983	3,000	90-700
San Diego, Maxwell Laboratories	November 1983	163,000	39-188
Benicia, Exxon USA	June 1984	15,000	400
Santa Clara, Owens-Corning Fiberglass	December 1984	2,914	260
Benicia, Exxon USA	December 1984	575	610
El Segundo, Chevron	January 1985	1,500	650
Carson, ARCO	January 1985	4,700	100-1,500
North Hollywood, Los Angeles Department of Water and Power	January 1985	25,000	500
North Hollywood, Los Angeles Department of Water and Power	March 1985	25,000	500
Irvine, University of California	March 1985	5,000	55
North Hollywood, Los Angeles Department of Water and Power	April 1985	25,000	500
North Hollywood, Los Angeles Deparment of Water and Power	May 1985	25,000	500
Carson, ARCO	June 1985	12,000	50-2,000
North Hollywood, Los Angeles Department of Water and Power	October 1985	125,000	500

Exceltech, Incorporated, Fremont, California

Exceltech, Inc., purchased the California rights to the Acurex process, also a liquid-sodium based process. The Exceltech unit is mobile and is used to treat PCBs on site. As PCB-contaminated oil enters the system, it is filtered and partitioned into batches. The active reagent is added. The mixture is allowed to react until complete destruction of PCBs is confirmed by chemical analysis. After complete destruction of PCBs, the excess reagent is destroyed. The treated oil is filtered and then returned to the customer. Although not suitable for reuse in transformers, the filtered oil can be burned as a supplemental fuel source.

Exceltech uses several process controls to prevent undesirable by-products from forming. The PCB destruction process takes place under an inert nitrogen atmosphere to prevent the formation of undesired oxidation products. All reactions are performed at ambient temperatures, thereby preventing thermally-induced breaking of the biphenyl bond to form benzene and its chlorinated derivatives.

The Exceltech process was given an "Approval to Operate" by EPA in November 1982.

Incineration

Another process for PCB destruction is high-temperature incineration. A detailed description of incineration technology is presented in Chapter 9. The incineration of PCBs is regulated under TSCA and is subject to very stringent performance standards. To receive a permit, the operator of a PCB incinerator must conduct a trial burn with a DRE of 99.9999 or greater. TSCA also mandates minimum temperatures and residence times for PCB incinerators; 1,200°F and 2 seconds or 1,600°F and 1.5 seconds.

At present, California has no incinerators permitted for disposal of PCBs in concentrations greater than 50 ppm. However, GA Technologies, (GAT) located in La Jolla, California, is conducting tests of their circulating-bed incinerator to demonstrate its ability to incinerate soil contaminated with PCBs. The highest concentration of PCBs tested was soil spiked to 10,000 ppm PCBs. The results indicate that this incinerator technology is capable of meeting 99.9999 percent DRE. Consequently, in March 1986, the EPA issued GAT a permit to burn PCB containing soils.

A number of incinerators elsewhere throughout the United States are permitted to burn PCBs. EPA has issued permits to two off-site rotary kilns, four on-site rotary kilns, and several power generation boilers for PCB incineration. Steam-powered electric utilities in Maryland and Washington, D.C., have obtained EPA permits to burn their own low-level (50 ppm to 500 ppm) PCB-contaminated fuel mixtures. Permitted incinerator facilities are listed in Table 10-2.

The Rollins Environmental Company (Texas) and the Energy Systems Company (Arkansas) have been permitted by EPA to burn high-level (over 500 ppm) PCB liquids in rotary kilns since March 1981. The PCB destruction efficiency of these incinerators has been tested and found to be greater than 99.9999 percent.

A rotary cement kiln in Sweden has operated successfully to burn PCB-contaminated oils. Waste oils containing up to 16 percent chlorine (as PCBs) were burned with destruction efficiencies greater than 99.9999 percent in a slurry-fed kiln. Cement manufacturers in Ontario, Canada and in Michigan have also had successful test burns with liquid fuels containing up to 50 percent PCBs. Cement quality was not impaired, and the hydrogen chloride gases generated were neutralized by alkaline dust in the kilns.

TABLE 10-2

PCB INCINERATORS

Company	Address	Capacity
ENSCO	P.O. Box 1975 Eldorado, AR 71730 (501) 863-7173	45 tons/day (as pure PCB)
EPA Mobile Incinerator	Woodbridge Avenue Raritan Depot, Building 10 Edison, NJ 08837 (201) 321-6635	1.5 tons/hrs./gal.
Rollins	P.O. Box 609 Deer Park, TX 77536 (713) 479-6001	80 tons/day (as pure PCB)
General Electric	1000 Woodlawn Avenue Pittsfield, MA 01201 (413) 494-3729	2.2 gal./mins.
SCA Chemical Services	1000 E. 111th St., 10th Fl. Chicago, IL 60628 (312) 660-7200	170 tons/day

Currently, PCB-contaminated solids and sludges can only be treated at approved incineration facilities meeting the criteria described above. No such incinerators are currently available in California.

Biological Treatment

Biodegradation has not been applied on a commercial basis for the treatment of PCBs; however, biological treatment of soils contaminated with PCBs is an active area of research and development. General Electric (GE) has isolated 14 strains of microorganisms capable of degrading one or more of the various PCB molecules. GE has studied the rate of biodegradation and the effects on biodegradation of surfactants used to remove PCBs from soils. A more detailed description of biological treatment technology is presented in Chapter 6.

Emerging Technologies

There are several different emerging technologies for the destruction of PCBs which are in the research and development stages, or are proven technologies which have not found commercial use because of economic or other reasons. Included in these emerging technologies are:

A. Chemical Treatments

1. Potassium Hydroxide/Polyethylene Glycol Dechlorination -- This process is similar to the dechlorination process described earlier. However, potassium hydroxide is used rather than metallic sodium.

2. Chlorinolysis -- In this process, PCBs are reacted with excess chlorine under high temperature and pressure to form carbon tetrachloride, hydrogen gas, and small amounts of hydrogen chloride.

B. Thermal Treatments

1. High temperature fluid wall reactors and supercritical water are promising technologies described elsewhere in this report.

2. Microwave plasma and plasma arc incineration are two technologies still in the development stage.

CHAPTER 11

DIOXIN-CONTAINING WASTES

A. INTRODUCTION

Dioxin is the short name for a family of molecules known as chlorinated dibenzodioxins (CDDs). Dioxins are well known because of their acute animal toxicity. The compounds, 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is the most well known and the most toxic of the more than 70 dioxin compounds. The polychlorinated dibenzofurans (CDFs) are a related family of molecules also acutely toxic and often found in combination with CDDs.

CDDs and CDFs are by-products of many common industrial processes. 2,3,7,8-TCDD gained notoriety because it is a contaminant of Agent Orange, the defoliant used by the United States in Vietnam. This dioxin is also found in several other herbicides including 2,4,5 T, Silvex, hexachlorophene, and erbon. CDDs are also found in wood treating compounds containing pentachlorophenol and as contaminants of PCBs. CDFs and CDDs are by-products of many incineration reactions and are found in the flue gas and in the fly ash of municipal and industrial waste incinerators.

The concentrations of dioxins in these materials is usually very small, (parts per trillion). However, because of the extreme toxicity of CDD- and CDF-containing wastes, the presence of these compounds is an issue of great importance.

B. TOXICITY

Dioxins are acutely toxic in many animal species. Sensitivity to dioxins varies widely from species to species. Table 11-1 below lists the amount of 2,3,7,8-TCDD required to cause death in a variety of animal species (for each species the dose listed was lethal in 50 percent of the animals tested). The lethal dose is characterized by progressive weight loss; death takes place after several weeks. Dioxins appear to be less acutely toxic in humans than in other species.

TABLE 11-1

DIOXIN'S LETHAL DOSE IN A VARIETY OF SPECIES

Animal	LD50 (ug per kg body weight)
Guinea pig	1
Rat (male)	22
Rat (female)	45
Monkey	70
Rabbit	115
Mouse	114
Dog	300
Bullfrog	500
Hamster	5,000

Source: Poland and Knutson, Annual Review of Pharmacology and Toxicology, 1982

The toxicity of TCDD in humans has not been firmly established. There have been indications that it is a human carcinogen and that it has toxic effects on humans. The symptoms in humans of chronic exposure to dioxins include weakness and pain with nerve condition abnormalities, emotional disorders, neuropsychiatric syndromes, eye irritation, cutaneous hyperpigmentation, and chloracne.

Other sublethal effects of dioxins have been observed in animals including reduction of body weight and tissue; loss of tissue in adipose in the thymus, spleen and lymph nodes; enlarged liver accompanied by various lesions, chloracne, and other epidermal changes; and gastric lesions.

Fetotoxicity has also been associated with TCDD in mice and rats. The problems observed in the embryos included: cleft palates, kidney abnomalies, intestinal hemorrhages and edema, and prenatal mortality.

C. GOVERNMENT POLICY AND REGULATIONS

In January of 1985, EPA exercised its authority under RCRA and designated certain dioxin-containing wastes and selected chlorinated phenols as acute hazardous wastes. The phenols were designated because they often contain CDDs and CDFs.

EPA also proposed to list as acute hazardous wastes, process wastes from the manufacture of polychlorinated benzenes under alkaline conditions and wastes from the production and manufacturing use of polychlorinated phenols and chlorophenoxy derivatives. It has been also proposed to list all wastes produced by equipment previously used for such operations.

EPA has specifically identified all dioxin-containing wastes as candidates for restriction from land disposal by November 8, 1986. Meanwhile, EPA has specified additional management standards relating to land disposal of these wastes that take effect immediately. EPA has also imposed a requirement that incineration of dioxin-containing wastes be conducted with a DRE of 99.9999 percent or greater.

The State of California will adopt EPA's dioxin rules or more stringent standards in its Administrative Code.

D. TECHNOLOGIES FOR TREATING DIOXIN-CONTAINING WASTES

Research on treatment technologies applicable to dioxin wastes looks very promising. Existing treatment technologies are being evaluated and new technologies are being developed. Some of these treatments are listed below:

1. Technologies Under Evaluation

   - Mobil incineration;
   - High temperature, fluid wall, advanced electric reactor (Huber process);
   - Ultraviolet (UV) photolysis;
   - Underground surface mines as repositories for dioxin-contaminated soils;
   - Marconi chemical detoxification process;
   - Thermal desorption of 2,3,7,8-TCDD from contaminated soils; and
   - Degradation by white rot fungus (Phanerochaet chyrsosportium).

2. Current Research

   - Extraction of 2,3,7,8-TCDD from soils by water, methanol, and toluene;
   - Biodegradation research; and
   - In situ stabilization techniques.

3. Technologies in Conceptual or Development Phase

- In situ vitrification;
- Fluidized bed and recirculating fluidized bed incineration;
- Chemically modified clays;
- Infrared heating;
- Catalytic UV (ozone) oxidation;
- Supercritical water oxidation and
- At-sea incineration.

Complete evaluations and data on these treatment technologies are not yet available. These technologies are being investigated by private sector organizations, governmental agencies, and universities. EPA provides financial support for much of this research. The State of California also provides grants for research in this area. Federal and state agencies are gathering data and information on other emerging technologies to evaluate their potential.

Incineration holds great promise as a dioxin destruction technique. EPA's dioxin rule states that incinerators burning the listed CDD- and CDF-containing wastes must achieve a DRE of 99.9999 percent. The current RCRA standard for incinerating hazardous wastes, other than dioxin- and PCB-containing wastes, is a DRE of 99.99 percent. EPA has a mobil incinerator stationed in Missouri with an adequate DRE for burning dioxin-containing wastes. However, this unit is not presently permitted to operate in California.

A Texas-based incinerator operator is expected to receive certification in the first half of 1986 to incinerate dioxin-containing wastes.

E. DIOXIN DESTRUCTION TECHNOLOGY

Catalyzed wet oxidation and photochemical reduction processes are among the technologies that have been investigated. Dioxin destruction rates of greater than 99 percent have been achieved in preliminary laboratory experiments. An extraction and photolysis process for destroying TCDD in a hazardous waste was investigated in a laboratory and full-scale plant operation. About 7 kg of dioxin were destroyed with 99.94 percent efficiency. This process takes place in two steps. First, the dioxin is extracted from the majority of the waste components by a suitable solvent. Second, carbon-halogen bonds in the dioxin molecules are photolytically dissociated.

The ability to separate dioxin from other chlorinated waste compounds is highly solvent dependent. Solvents such as hexane, tetrachloroethylene, and o-xylene are commonly used. Hexane proved to be the best among the three in laboratory experiments. Greater than 99.9 percent extraction efficiency was achieved by successive batch extraction.

Photolytic dissociation of aromatic halides occurs under the influence of sunlight or UV light. Sunlight or simulated sunlight degrades chlorodioxins in the presence of hydrogen donors. Pure TCDD in methanol decomposed 50 percent in 4 to 8 hours when exposed to simulated sunlight. Di- and trichlorodibenzo-dioxins degrade faster than TCDD. CDFs are also reduced by dechlorination and polymer formation. Photolysis rates can be affected by light-absorbing impurities, radical inhibitors and, of course, fouling of the light sources.

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STABILIZATION TECHNOLOGIES

CHAPTER 12
STABILIZATION TECHNOLOGIES

A. INTRODUCTION

Chemical stabilization and solidification processes are intended to isolate hazardous wastes without destroying the hazardous constituents. Depending upon the particular process, the final product can range from a loose, soil-like material to hard, plastic-encased molded solids. The treated waste generally has higher strength, lower permeability, and lower leachability than the untreated wastes.

Concern about the long-term integrity and leachability of chemically stabilized and solidified wastes has delayed the acceptance of this technology as an ultimate disposal option for hazardous wastes. In addition, considerable uncertainty exists about the viability of this technology for wastes having a significant organic content.

Stabilization processes achieve the treatment objectives by limiting the solubility or mobility of the constituents of concern in a waste. Adjustment of the pH of a solution followed by addition of a flocculating agent to promote the formation of metal hydroxide precipitates is a simple example of a chemical stabilization process.

Solidification processes achieve the treatment objectives by enclosing the waste in a solid or soil-like material. In the solidified waste, the hazardous components are isolated from the surrounding environment. An example of a solidification process is the incorporation of precipitated metal hydroxides into a cement-based mixture to produce a high-strength monolithic block. Setting and curing agents are usually added to control the rate and extent of solidification. The final consistency of the treated end product can be varied at the discretion of the operator.

The details of a stabilization or solidification process vary depending upon the waste being treated. In turn, the physical and chemical properties of the treated waste vary according to:

1. The characteristics of the waste;
2. The types of solidification agents;
3. Weather conditions; and
4. The time allowed for curing.

Most of the currently available chemical stabilization and solidification processes were developed for treating inorganic wastes, primarily those containing dissolved metals. Organic compounds generally interfere with the setting and curing action of bulk solidifying agents. Also, organic constituents may interfere with the action of polymeric additives included in most solidification processes.

Many wastes require extensive pretreatment prior to stabilization or solidification. A variety of waste constituents and associated pretreatment requirements are listed below:

- Acidic waste streams must be neutralized.

- Waste with a high concentration of dissolved solids will require relatively little solidifying reagent.

- Metals must be in the relatively insoluble hydroxide form prior to solidification.

- High concentrations of sulfates or chlorides may interfere with the curing of the solidified product.

- High concentrations of soluble or insoluble organic compounds also may interfere with the curing of the solidified product.

- When toxic organic compounds are present in the waste, special attention must be given to the leachability of those compounds in the solidified waste.

- Waste containing moderate to high concentrations of reduced nitrogen (ammonia, amines) will generate ammonia gas upon the addition of lime, cement, or other alkaline reagent.

- Any cyanide must be removed from the waste prior to solidification or stabilization.

- Materials containing hexavalent chromium must be pretreated before the waste can be solidified.

B. REGULATIONS CONCERNING DISPOSAL OF CHEMICALLY STABILIZED AND SOLIDIFIED HAZARDOUS WASTES

The end products and by-products of a hazardous waste treatment process are considered hazardous until shown otherwise. The operator of a waste treatment process must test the treated waste according to methods approved by the Department of Health Services (the Department) to determine if it is a hazardous waste. If a chemically stabilized and solidified hazardous waste is found to be hazardous, it must be disposed of at a permitted hazardous waste land disposal facility, unless a variance is granted for disposal at an unpermitted site.

To have a waste designated nonhazardous (delisted), the generator must demonstrate that the hazardous constituents of the untreated waste cannot be leached from the treated product at concentrations which would still be considered hazardous. The Department has adopted a test protocol known as the Waste Extraction Test (WET) for determining if a solid waste is hazardous. The extraction solution consists of 0.2 M sodium citrate adjusted to pH 5.0 ± 0.1, and the extraction period is 48 hours. This is a stronger metal complexing agent and will generally leach more metals from a solidified waste than the acetic acid solution specified by EPA's extraction procedure (EP) toxicity test.

The conditions under which extraction tests are carried out are intended to simulate the environments to which wastes might be exposed after disposal in a biologically active landfill or other area. However, because of concerns over the long-term integrity of solidified wastes following disposal, EPA requires multiple extraction tests of the solidified wastes as part of the federal delisting process.

C. STABILIZATION AND SOLIDIFICATION PROCESSES

Several chemical stabilization and solidification processes have been evaluated for their suitabilities as treatments for hazardous wastes. The stabilization and solidification processes discussed herein include:

- Cement-based processes;

- Pozzolanic processes;

- Thermoplastic techniques;
- Organic polymer techniques;
- Surface encapsulation techniques;
- Self-cementing; and
- Glassification.

While all of the above categories have been investigated, the cement-based and pozzolanic processes are the most developed processes. The cement-based and pozzolanic processes have been employed at off-site solidification facilities in Continental Europe, Great Britian, Japan, and Canada.

Solidification facilities have been proposed in New Hampshire, Illinois, and Michigan. The treated waste products expected to be produced at these facilities are being considered for delisting by EPA.

<u>Cement-Based Processes</u> -- When mixed with slurried inorganic hazardous wastes, common cement forms a solid material. Particulates of the waste are incorporated into the matrix of the solidified end product. The high pH of the cement mixture favors precipitation of dissolved metals. Organic polymers are added to the cement/waste mixture to control and improve the curing process. The final product consistency, ranging from loose, soil-like material to solid, monolithic blocks, can be adjusted with the organic polymers.

Cement-based processes are primarily used to solidify inorganic wastes. The simplicity of the operation and the wide availability of the raw materials allow cement-based processes to be managed without specialized machinery or labor.

In general, large amounts of cement are necessary for solidfying industrial wastes. The weights and volumes of wastes solidified by cement-based processes may be double those of the raw wastes, possibly increasing disposal costs.

<u>Pozzolanic Processes</u> -- Fine-grained siliceous (pozzolanic) materials such as fly ash, ground furnace slag, and cement kiln dust can be mixed with lime and water to form a concrete-like solid when cured. Curing agents, often proprietary compounds, are added to this well-known reaction to make it more suitable for the solidification of hazardous waste.

Pozzolanic processes are most commonly applied to inorganic wastes; however, they have also been used to treat municipal sewage sludge and paint sludge. Pozzolanic processes are often used to solidify flue gas desulfurization sludge.

Pozzolanic materials such as fly ash and cement kiln dust are themselves considered to be wastes and are available in large quantities. Pozzolanic processes may thus allow the generator to dispose of two wastes simultaneously.

Other advantages and disadvantages of pozzolanic processes are similar to those of cement-based processes. Some hybrid solidification systems incorporate cement, lime, and siliceous material into a single solidification mixture. The proportions are adjusted to optimize the containment of the particular waste while holding down costs. Such systems not only reduce the cost of materials, but produce solidified end products with minimized weight and volume increases. A process of this sort is used at Chemical Waste Management's facility in Kettleman Hills, California.

<u>Thermoplastic Techniques</u> -- Several types of thermoplastic materials, such as bitumen and polyethylene, have been investigated as solidifying agents for industrial wastes.

Solidifying wastes in an organic matrix effectively isolates the wastes from the surrounding environment.

Molten thermoplastic materials blended with dried wastes at high temperature (260°F to 450°F) form matrices that entrap wastes upon cooling. This process is not suited to wastes that will dissolve the thermoplastic material or that decompose at the high reaction temperatures.

Thermoplastic solidification processes require specialized equipment and labor, making such processes very expensive. Materials treated by thermoplastic solidification often crack during curing or through exposure to the environment. These cracks greatly increase the leachability of the enclosed waste.

Organic Polymer Processes -- These processes incorporate wastes into polymer matrices, trapping the hazardous constituents. To begin the process, the wastes are combined with monomer (polymer subunits) and catalyst; the mixture is allowed to solidify. This solidification technique has been most thoroughly tested using a urea-formaldehyde system, though polyester systems have also been investigated.

Organic polymer processes generally require less solidifying agent per weight of waste than do other solidification systems, and they produce a less dense material to be disposed. Unfortunately, the long-term containment of such solidified waste cannot be guaranteed because the polymerized material may degrade under environmental stress. Shrinkage of the polymerized material with age will promote cracking and accelerated leaching. Some cured polymers are readily biodegradable, and are therefore, unsuitable for land disposal.

Self-Cementing -- Flue gas desulfurization sludges that contain high concentrations of calcium sulfite or calcium sulfate can be treated in a self-cementing process. A small portion of the waste is heated almost to melting (calcined) to produce a binder. The binder is mixed with the remainder of the waste producing a plastic-like material.

Glassification -- Wastes that are very stable at high temperatures can be fused into glass or ceramics. The process is not suited to organics and has been applied primarily to radioactive wastes.

Surface Encapsulation Process -- Once wastes have been solidified or stabilized, a second level of containment can be imposed by coating the solidified waste with a layer of some protective, impermeable material. Encapsulation systems include those processes in which dried solid wastes are molded into a specified form and coated, thereby isolating the waste from the environment. The encapsulating material is usually an organic polymer. Binding between the molded waste and the surface encapsulating material may be achieved at elevated temperatures.

Although surface encapsulation processes produce treated wastes which are physically isolated from the environment, such processes are very expensive.

The necessary material, equipment and skilled labor are expensive and the energy requirements for drying, fusing, and encapsulating are high.

D. AVAILABILITY

Hazardous chemicals and wastes which can be stabilized and solidified effectively include:

- Electroplating wastes;
- Spent pickle liquors;
- Spent acids;
- Alkaline cleaners;
- Inorganic pigment wastes;

- Leather tanning and finishing wastes;
- Petroleum refining tank bottom sludge;
- Brine wastes;
- Air pollution control residues;
- Wastewater treatment sludges; and
- Aqueous wastes containing soluble toxic organics.

Very little information is available on the performance of stabilization/solidification process. Most of the research and field work have been performed by the private sector. Results and details of the stabilization schemes are considered to be proprietary. Table 12-1 is a summary of stabilization processes for treating hazardous wastes.

TABLE 12-1

EXISTING STABILIZATION TECHNOLOGIES

Type of Process	Company (Process Name)	Waste Treated	Reagents
Cement-based	Chemfix	Inorganics	Cement/Sodium Silicate
	Chem-Technics (CFS)	Inorganics	Various Siliceous Compounds
	Stablex (Sealosoft)	Inorganics	Cement, Fly ash
	Stabatrol (Tema-Tite)	Inorganics	Cement, Additives
Pozzolanic	Chemical Waste Management, Inc. (Chem-Source)	Low Concentration organics	Lime Cement Kiln Dust
	Dravo Lime (Calcilox)	FGD Sludges	Lime, Additives
	International Mill Service	Metal Sludges	Lime
	IU Conversion System (Poz-O-Tec)	FDG Sludges	Lime, Fly ash
	Soil Recovery Systems	Misc.	Lime
	Sludgemaster	Misc.	Lime, Additives
Thermoplastic Techniques	Werner and Pfleiderer	Misc.	Asphalt
	Southwest Research Institute (Sulfex)	Misc.	Sulfur, Modifiers
Organic Polymer	Dow Chemical	Radioactive	Polyesters, Polyvinyls
Surface Encapsulation	Environmental Protection	Metal Sludge	Polyolefins
	Polymers	Organic Sludge	
	TRW System	Misc.	High Density Polyethylene
Self-Cementing	Sludge Fixation Technology (Tewa-Crete)	FGD Sludges	Calcium Sulfite or Sulfate

E. APPLICATION IN CALIFORNIA

As a result of EPA's ban on the land disposal of bulk liquid, stabilization/solidification technology is playing an increasingly important role in the disposal of hazardous waste. Chemical Waste Management, Incorporated's facility at Kettlemen Hills, California, has a permit for stabilization/solidification process. Wastes received at the facility are solidified before burial in their Class I landfill site.

Nonhazardous end products may be disposed of at sites other than Class I landfill. Currently, a waste generator who would like his treated waste delisted for disposal in California must apply both to the EPA and the State of California. The Department has been approached by at least two firms either requesting delisting procedures or proposing site cleanup with stabilization/solidification.

SITE
MITIGATION

CHAPTER 13
HAZARDOUS WASTE LEACHATE TREATMENT

A. INTRODUCTION

Hazardous waste leachate is an increasingly important source of hazardous waste and a significant threat to groundwater quality. Leachate is formed as rainwater or surface flows of water percolate through a waste disposal site. The resultant liquid, the leachate, is a solution of the waste constituents and their decomposition products. Leachate enters the soil and may ultimately contaminate groundwater. The term "hazardous waste leachate" refers to leachate from hazardous waste disposal sites; however, leachate from municipal waste disposal sites can also be quite hazardous.

Federal and state regulations require that waste disposal sites be outfitted to prevent leachate from leaving the site. In practice, this means the disposal site must be lined with "impermeable" material, usually plastic or clay; and that there be facilities to collect the leachate. Following collection, the leachate is treated to remove the pollutants.

These requirements were enacted in response to the severe groundwater pollution resulting from leachate leakage at many abandoned hazardous waste dumps and landfills. The potential contamination of the water supply of Glen Avon, California, by leachate from the Stringfellow site, is a well-known example of problems caused by uncontrolled hazardous waste leachate.

Analysis and treatment of hazardous waste leachate is in its infancy. Many of the technologies discussed in this chapter have not been commercially applied in leachate treatment. Methods for the treatment of leachate have been extrapolated from experience; treating leachate from municipal landfills and from the treatment of industrial wastes. Bench scale testing of leachate samples and pilot plant operations are often used to develop efficient processes for the treatment of specific leachates. Often a sequence of treatments is required to remove the contaminants from leachate; this sequence is known as a process train.

Leachate flow rates from hazardous waste disposal facilities and sanitary landfills may be reduced by treatment of the waste and by several landfill management techniques. Smaller volumes of leachate are more easily collected and treated. A common approach to reducing the rate of leachate generation is to reduce the volume of water entering the disposal area. Clay caps and other surface diversion techniques prevent runoff and rainfall from entering the disposal site. Older sites can be retrofitted with barriers; unfortunately, the retrofitted devices are usually not as effective as devices used in new landfill construction. New landfill sites are legally required to have liners or other hydraulic barriers. These isolation measures are important because some leachate generation is inevitable.

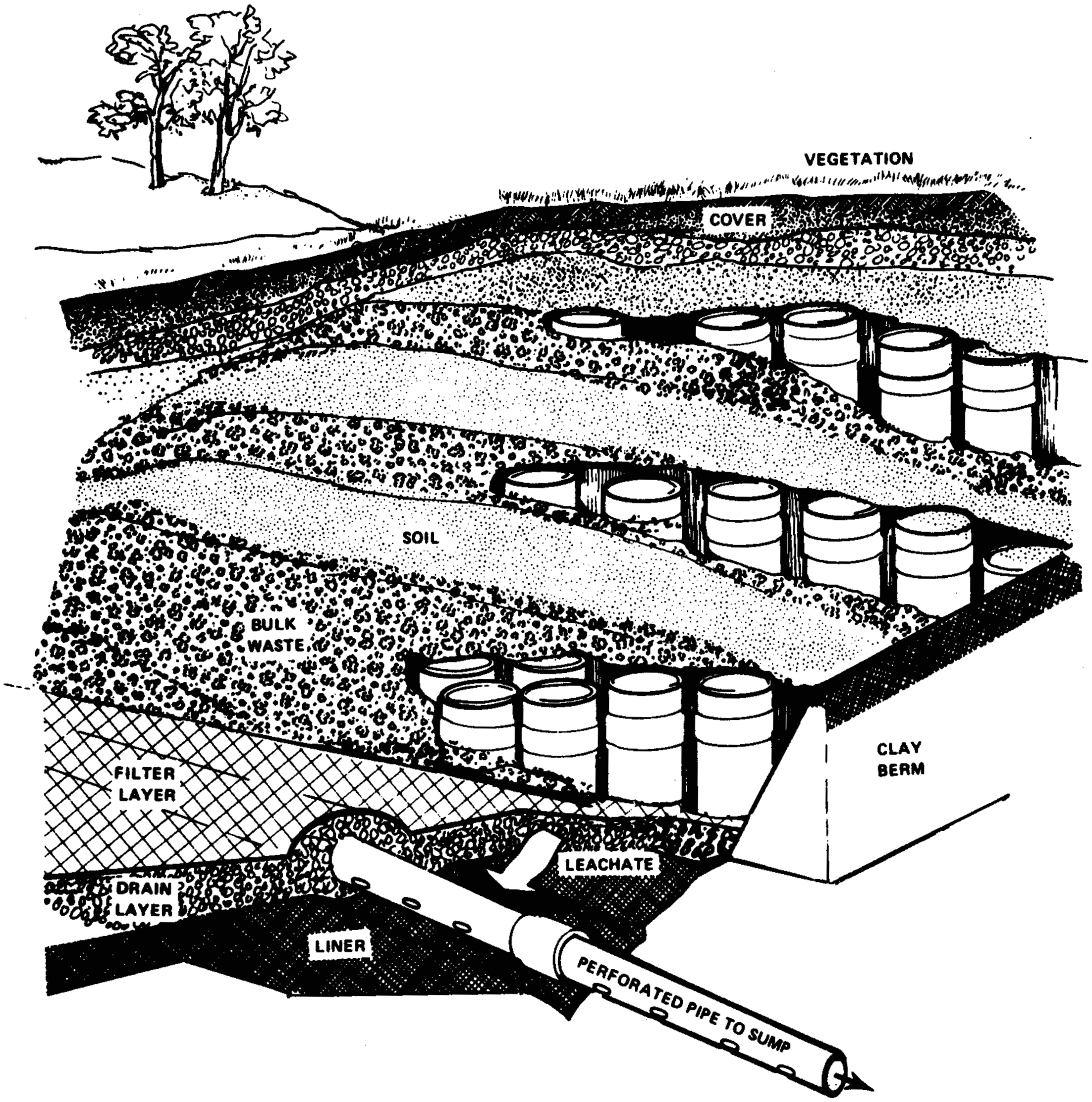


Figure 13-1 Leachate Collection System.
As leachate percolates through the ground it is collected by the perforated pipe.

The landfill operators' other option to reduce leachate generation is to treat the waste prior to disposal. Solidification and stabilization techniques bind the hazardous contaminants to solid particles. Bound contaminants are not easily leached. Detoxification of waste prior to disposal also reduces the hazard associated with the leachate.

B. LEACHATE COLLECTION SYSTEMS

Hazardous waste leachate collection systems are similar in design to those already in use at sanitary landfills. Landfill floors are sloped; liquids drain into a collection sump from which leachate can be pumped. French drains are widely used collection systems at hazardous waste sites, applicable to both new and old sites. A French drain (Figure 13-1) is a gravel filled trench containing perforated pipe. Surface runoff and shallow underground flows are intercepted by the trench, liquid percolates through the gravel, enters the pipeline, and flows to the sump. The leachate is then pumped to storage or treatment.

Reliability is of central importance to the effectiveness of hazardous waste leachate collection systems. Clogging of the perforated pipe or pipe breakage can lead to leachate buildup on the landfill liner. This can cause liner failure and increase the likelihood of groundwater contamination. Such failure is often difficult to repair. Replacement of failed liners is undesirable because it would necessitate excavating hazardous wastes. Experience with agricultural and industrial leachate collection systems has shown that proper design can largely prevent failure of such systems.

The importance of collection system reliability is illustrated by existing problems at the Stringfellow hazardous waste site (Figure 13-2). Located in a box canyon, this site has steep hillsides surrounding a slightly sloped valley floor. In an early effort to reduce water flow through the contaminated site, a French drain was installed to intercept two active hillside seeps. Recently, however, it was noticed that excessive water continues to flow through the site. Perforations in the drain pipe may have become clogged with biological growth interfering with collection. In laboratory tests, leachate taken directly from the acid pits at Stringfellow has been shown to sponsor vigorous microbiological growth. Further research is needed on methods to prevent biological clogging of leachate drains.

C. LEACHATE TREATMENT

Hazardous waste leachate may be treated on site or transported to an off-site treatment facility. On-site treatment usually involves pretreatment prior to discharge to sewer or receiving waters (ocean, river, etc.) to conventional sewage treatment or discharge directly to receiving waters. Another possibility is to recycle the leachate through the landfill, as discussed in Chapter 15.

The wide range of constituents found in hazardous waste landfill leachates, and their often unique properties, pose a complex treatment problem. Biological and chemical treatments are often combined in the treatment of hazardous waste leachates.

Biological Treatment

Biological methods hold great promise in the treatment of hazardous waste leachate. Biodegradation processes are the most cost-effective treatment of municipal and industrial wastewaters; similar results are expected from their application to hazardous waste leachate. Aerobic processes (activated sludge, trickling filters, and aerated lagoons) and anaerobic processes (lagoons and anaerobic filters) have been used in leachate treatment.

The composition of a hazardous waste leachate uniquely reflects the composition of the wastes from which it is generated. Because microorganisms can acclimate to different waste mixtures, they are able to destroy a wide variety of hazardous waste streams. A month or longer may be required for the microbial population to acclimate and develop optimal degradation capabilities. Hazardous waste leachates generally contain enough biodegradable substrate to sustain a biological treatment system. In contrast, contaminated groundwater usually does not contain enough biodegradable substrate for proper system operation. Fluctuations in waste load concentrations can be a problem in microbial treatment of hazardous wastes. In addition, heavy metals and certain organic compounds are toxic to microorganisms and must be removed prior to biological treatment. Examples of pretreatment of hazardous waste leachate are listed below:

- Heavy metals can be removed through chemical precipitation.
- Suspended solids can be removed by filtration settling, and related processes.
- Organic compounds toxic to microorganisms can be removed by carbon adsorption, ultrafiltration, reverse osmosis, and other processes.
- The pH and other chemical parameters can be adjusted to optimize the conditions for microbial growth.

Activated Carbon Adsorption

Carbon adsorption is a well-known treatment technology frequently incorporated into process trains for hazardous waste leachate treatment. This technology is particularly well suited to the removal of low concentrations of nonbiodegradable compounds. A common hazardous waste leachate treatment involves biological degradation to remove most of the contamination followed by activated carbon adsorption to remove residual organic contamination (under some circumstances this order can be reversed). This process train extends the life of the carbon, and is economical because of the high costs of carbon regeneration.

Interestingly, biodegradation and carbon adsorption complement each other. Carbon adsorption does not easily remove highly soluble, low molecular weight organic compounds which are often highly biodegradable. Conversely, biodegradation is not well suited to the treatment of dilute waste streams that are economically purified by carbon adsorption treatment.

Other treatment technologies may precede carbon adsorption to improve the operation of that unit. Suspended solids must be removed from the leachate in order to prevent clogging of the carbon. Consequently, filtration units often precede carbon adsorption. Precipitation/coagulation may precede carbon adsorption to remove dissolved metal ions.

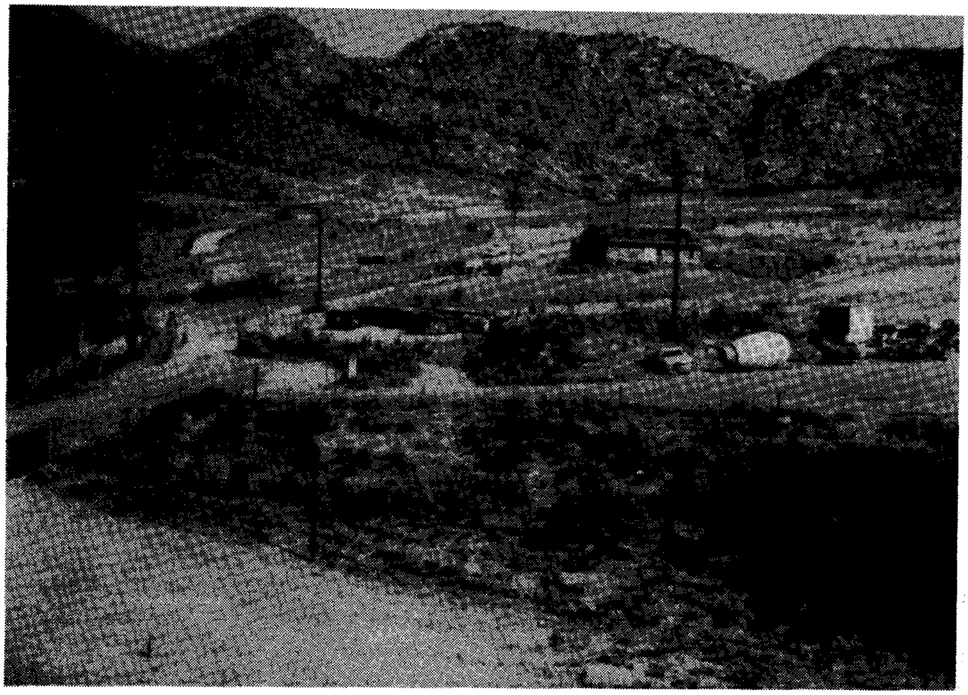
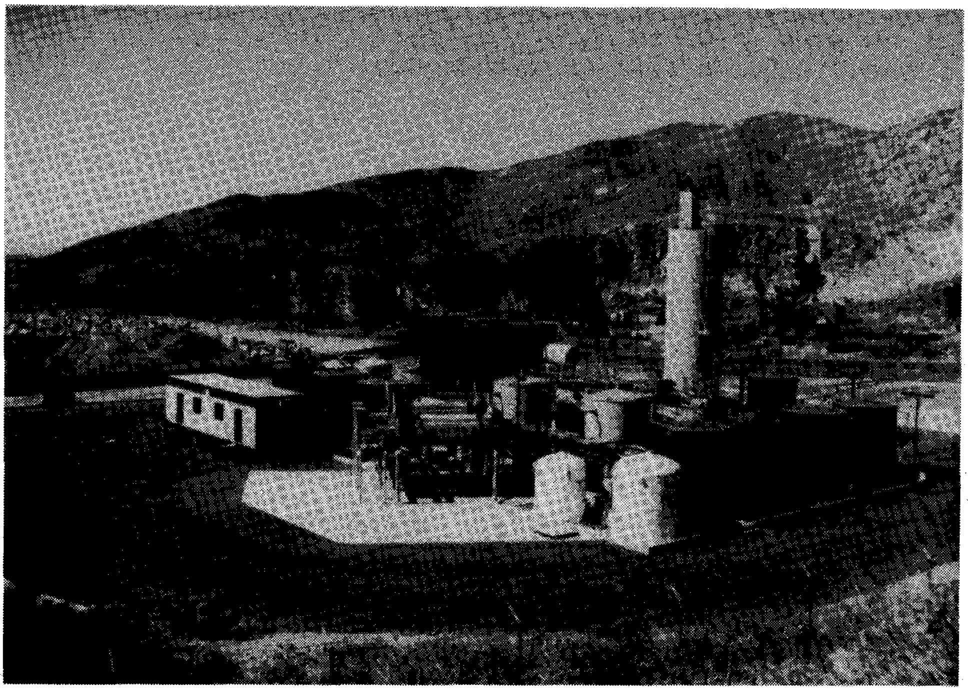


Figure 13-2 Stringfellow Disposal Site. (a) The location of the former disposal site.



(b) The treatment plant.

D. CASE STUDY: STRINGFELLOW HAZARDOUS SITE

Mitigation of contamination at the now abandoned Stringfellow Disposal Site involves many of the techniques discussed in this and the subsequent chapters. Hazardous flows are collected at two locations in the vicinity of the disposal site (Figure 13-2). Stream A, a leachate stream, is pumped from a well on the old disposal site and is similar in composition to metal finishing wastewaters. Stream B is a contaminated groundwater stream collected approximately half a mile down the canyon.

Groundwater carries the contaminants from underneath the old disposal site to the Stream B wells. In this sense, Stream B is said to be downgradient of the disposal site. Stream B has a very low concentration of metals. The metals appear to be adsorbed by the soils during the groundwater flow.

As shown in Figure 13-3, the highly contaminated Stream A is treated and combined with Stream B for further treatment.

The first step on Stream A is chemical treatment. Caustic lime is added to precipitate metal hydroxides; organic polymers are added to enhance flocculation. Circular sedimentation tanks, known as clarifiers, provide effective sedimentation. The settled hydroxide sludge is dewatered in a filter press and stored in tanks until transported by trucks to a Class I landfill.

After precipitation, the liquid stream is combined with Stream B for further treatment. EPA priority pollutants account for one percent of the combined stream, which is treated by carbon adsorption. Multiple treatment tanks allow a continuous process; when carbon in one tank becomes saturated, the flow is switched to the second tank. Spent carbon is sent off site for regeneration. The treated effluent is transported by truck to a nearby regional sewer.

Operating costs (at peak flow) of the 187,000 gallons per day activated carbon adsorption unit are approximately $1,700 per day, amounting to 75 percent of the total plant costs. Because of the high costs of the carbon adsorption unit, other technologies are being considered, including reverse osmosis, air stripping, and biodegradation.

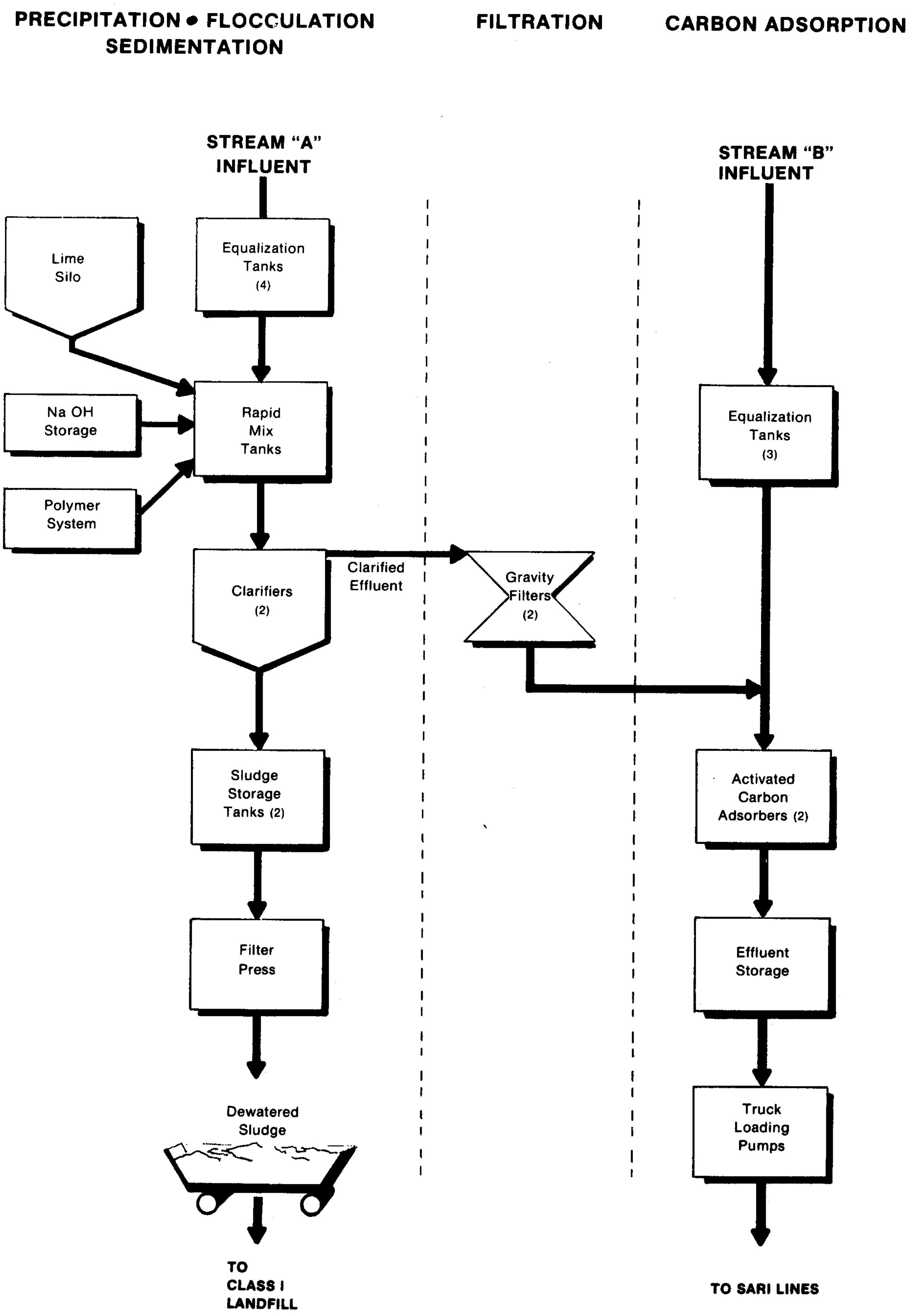


Figure 13-3 Stringfellow Leachate Treatment Processes.
Streams A and B are collected from different wells and have different compositions. Stream A is extensively treated before being added to Stream B. The combined streams are treated by activated carbon absorption.

CHAPTER 14
GROUNDWATER TREATMENT

A. INTRODUCTION

Approximately half of California's drinking water is taken from groundwater supplies; in the State's rural areas, this figure reaches 90 percent. Historically, groundwater was viewed as an almost limitless underground ocean, protected from contamination by the filtering action of soil and geological strata. Although some heavy metal pollutants are adsorbed by the ground, other pollutants, including many toxic organic compounds, easily migrate into groundwater supplies (Figure 14-1). Negligent disposal practices, leaking underground storage tanks, and the widespread application of pesticides to agricultural lands have resulted in the contamination of many aquifers. (Aquifers are underground bodies of water.)

At many locations around the State, groundwater contamination has reached active drinking water supplies rendering the water from local wells unpotable. If these wells were simply shut down, the contamination plume would be free to expand, possibly contaminating other drinking water supplies. To prevent this occurrence, it is the policy of the Department of Health Services to continue pumping from contaminated wells; the pumped water is treated to remove the contaminants and to prevent the contaminants from reentering the environment.

Treatment technologies applicable to contaminated groundwater are similar to those used to treat industrial process waste streams. However, contaminated groundwater poses unique problems that influence the choice of treatment methods. Most groundwater treatment projects are conducted aboveground; the contaminated groundwater is pumped to the surface. Because pollutant concentrations change over the project life, the treatment system must be able to respond to these variations in concentration and flow.

B. TREATMENT FOR ORGANIC CONTAMINANTS

Hazardous materials that migrate through the ground and reach an aquifer may do one of three things: the contaminant(s) may float on the aquifer, sink to lower levels, or dissolve in the aquifer. A different treatment technology is used for each of these cases.

Pure Compound Recovery

Contaminants floating on an aquifer or settled at its bottom are usually pure compounds that have entered the ground as a result of spills or leaks. To form a separate layer, these compounds must be relatively insoluble in water and have a density either significantly less than or significantly greater than water. Compounds encountered floating on an aquifer are usually petroleum products; those that sink are usually chlorinated organic compounds.

The method usually used for the recovery of pure compounds floating on the aquifer employs a pump whose inlet is placed within the aquifer well below the contaminant. Pumping causes the formation of a shallow cone of depression in the water table

(Figure 14-2). The floating pure compound flows to the inlet of a smaller pump where it is collected with an oil-water separation system.

Compounds that have sunk to the bottom of an aquifer can be located with electrical conductivity measurements. Whereas water is highly conductive, only negligible electrical current will flow in the organic layer. A probe containing two electrodes is immersed in the well. The cessation of current announces the organic layer and triggers the pure compound pump. Conductivity-based removal technologies are the only known way to remove compounds such as chlorinated organics that have sunk to the bottom of an aquifer.

These methods have been used on a great many cleanup projects and the devices, built by several manufacturers, are easily obtainable. Pure component recovery systems are very cost-effective cleanup technologies.

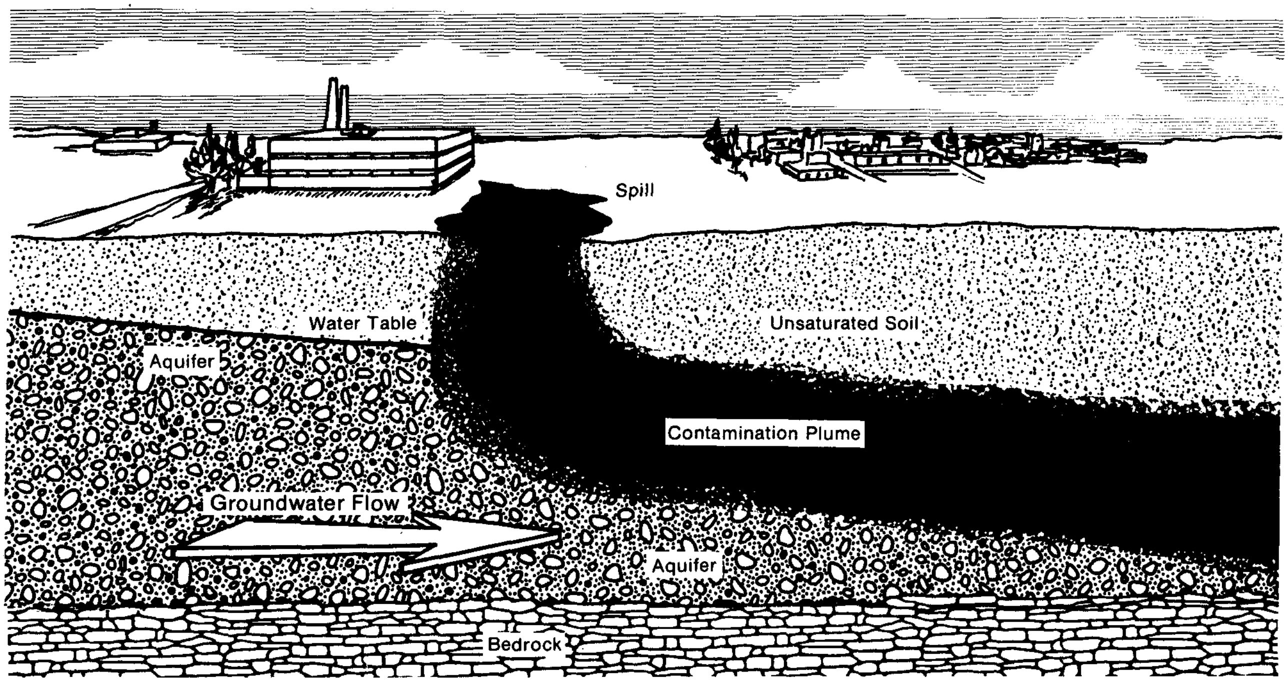


Figure 14-1 Typical Contamination of an Aquifer.
Depending on its composition the contamination plume may dissolve in the aquifer, float on the aquifer or sink to its bottom.
Source: Myer, Evan K. 1985

Treatment of Groundwater Containing Dissolved Organic Compounds

Contaminated groundwater usually contains only low concentrations (less than one percent) of organic chemicals. Air (or steam) stripping and activated carbon adsorption are cost-effective methods of cleaning dilute groundwater solutions. These methods can be effectively used for both single and multiple component waste solutions. For multicomponent solutions, air stripping and carbon adsorption units are often used in succession. Biological methods are also coming into prominence for the treatment of groundwater.

Air Stripping -- Air stripping (packed tower aeration) is widely applied to treat groundwater contaminated by volatile organic compounds. Simplicity in operation, low cost, easy installation, high mobility, and the ability to achieve very low levels of contaminants in treated groundwater, are among the advantages of air stripping.

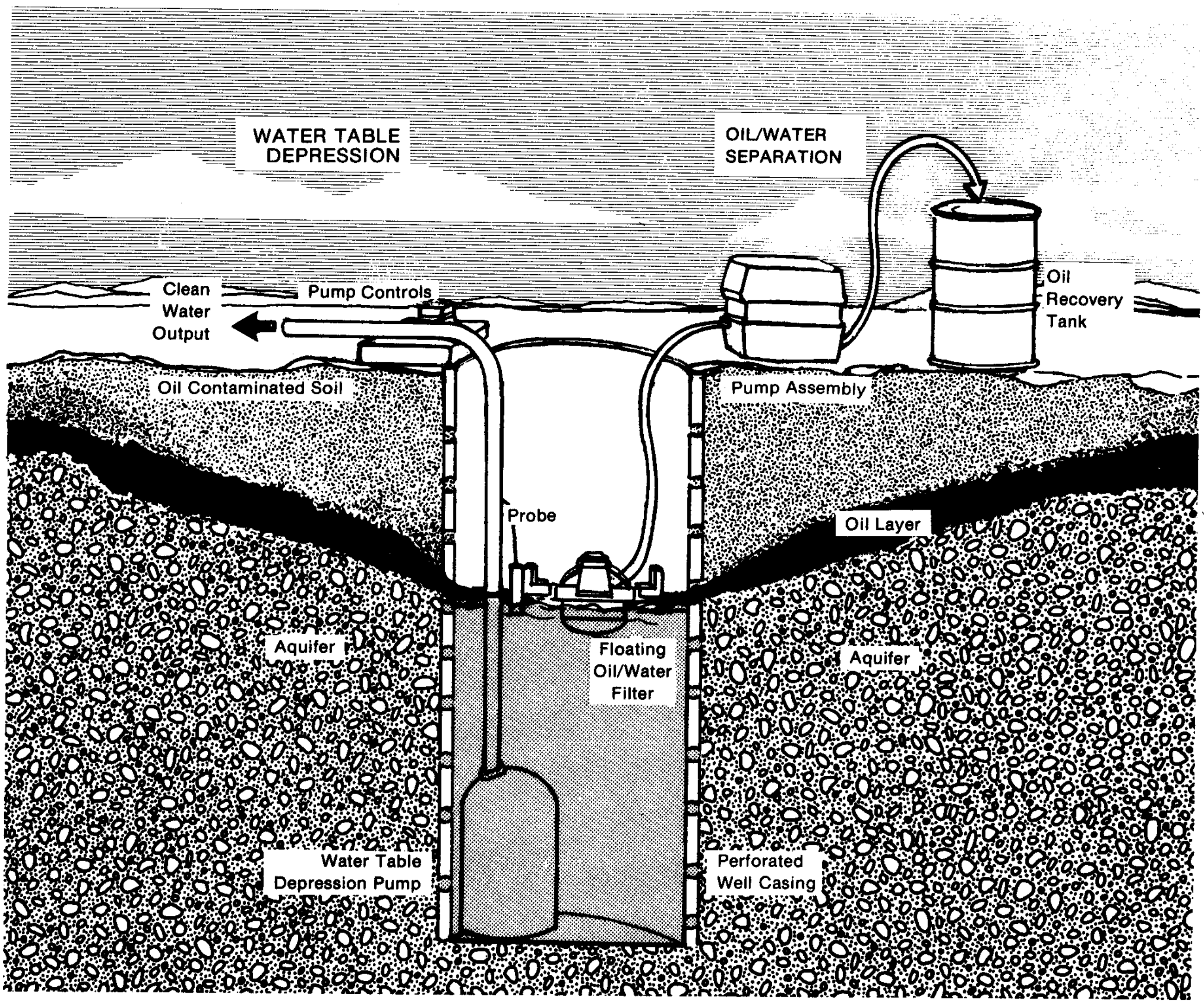


Figure 14-2 Pure Compound Recovery.
The water-table depression causes oil to build up in the vicinity of the well.
Source: Sanders, P.J. *Pollution Engineering* Sept. '85

Packed towers are cylindrical shells filled with packings designed to present the maximum surface area of the liquid (groundwater, in this case) to the air flow. The groundwater is distributed evenly at the tower top and percolates downward through the packing. Air is blown in at the tower base and flows upward, countercurrent to the falling water. The volatile organic compounds diffuse from the water to the air and are discharged to the atmosphere or to another treatment system. The tower height and diameter, and the water and air flow rates can be varied to achieve the desired removal efficiency, up to 99.999 percent for many contaminants.

The major disadvantage of air stripping is the discharge to the atmosphere of the stripped compounds. The volatile compounds are diluted by the air pumped through the tower and by mixing with the atmosphere. However, when the concentration of volatile organics in the atmosphere is unacceptable, an air pollution control device must be installed; vapor-phase carbon adsorption is the usual method of choice.

Treatment costs vary depending on the desired removal efficiency and the ease with which the organics can be removed from the groundwater. Costs can be expected to range from $.04 to $.30 per 1,000 gallons.

Tank aeration and diffused spray aeration are air stripping technologies suitable for removing volatile organic compounds from groundwater. These methods are applied where the high removal efficiency of packed tower aeration is not required. In tank aeration, air is bubbled through the water under treatment. Removal efficiency increases with the total surface area of the air bubbles. In diffused spray aeration, the creation of a very fine mist of the contaminated groundwater is the goal. Again, this provides a large surface area through which the transfer of the pollutant from water to air can occur. A disadvantage of this method is the potential for the spray to drift off the treatment site.

Steam stripping can be used to remove less volatile organics than is possible by air stripping. The process, which has high energy costs, is more expensive than air stripping. Steam stripping generates large volumes of waste water, frequently requiring treatment.

Activated carbon used to treat groundwater is often regenerated by steam stripping.

<u>Activated Carbon Adsorption</u> -- The use of activated carbon adsorption in the treatment of groundwater has the same strengths and liabilities as it does in the treatment of other waste streams (Chapter 6). Activated carbon can adsorb a wide range of organic compounds (although it is more effective in the removal of compounds of moderate molecular weight). This capability makes activated carbon adsorption well suited to groundwater treatment. This capability is also a weakness of the process; the carbon used to treat groundwater may be quickly saturated with compounds which do not need to be removed.

For effective and economical operation of an adsorption unit, the influent stream may require pretreatment. The choice of pretreatment technology will depend on the contaminants of the groundwater. Suspended solids may be removed by filtration and settling processes. Chemical precipitation/coagulation may remove heavy metal contaminants. Relatively high concentrations of organic molecules, especially of low molecular weight, may be removed with air stripping or biological treatment.

Aeration technologies complement carbon adsorption. Air stripping is best suited for the removal of volatile organics, whereas activated carbon will remove the remaining heavier organic compounds. These technologies are often used together to treat contaminated groundwater. Adsorption will also remove the small amounts of volatiles always left in the wastewater following air stripping.

Biological Treatment -- The application of biological treatment to groundwater treatment is restricted by the relatively low concentrations of organic matter usually found. Biological treatment processes must have an adequate and continuous nutrient supply. In practice, this means that some groundwater is too weak to sustain biological treatment. The minimum strength required for a biological treatment process is in the vicinity of 50 ppm biodegradable materials. A stronger waste stream can be combined with contaminated groundwater to make up the needed strength. For continuous biological reactors, such as activated sludge plants, the pumping and treatment operations must be operated around the clock to maintain the organisms.

Additionally, the long time required to begin biological treatment renders the method unsuitable for short-term cleanup projects. Bacteriological systems typically require two to six weeks following introduction of the waste to achieve steady, optimum operation. Feasibility studies to select the proper treatment process and bacterial culture should always be undertaken prior to the construction of a full-scale treatment system.

Biological treatments do have other advantages in addition to their low cost. Organic contaminants are destroyed rather than transferred to another medium. Although not all organic groundwater contaminants are biodegradable, many classes of organic compounds can be treated simultaneously.

A biological reactor, specifically for the treatment of contaminated groundwater, has been developed by Smith and Loveless, Inc. Their reactor combines the fixed film process (fixed film processes, such as trickling filters and rotating biological contractors, involve microorganisms grown on a solid surface, see Chapter 6) with sludge recycling. The process has the fixed film process's ability to provide high concentrations of bacteria and the treatment efficiency obtainable with an activated sludge reactor. A project underway in the Bay Area employs this process. Further refinements and the application of other biological unit processes to the treatment of groundwater are expected in the future.

Smaller groundwater flows have been treated in biological "bag" reactors. These are 500-gallon tanks containing a cloth bag permeable to water. In this continuous flow system, nutrients are added drop-wise, air is bubbled through the reactor contents, and bacteria are provided through the addition of municipal sewage sludge. Contaminated water flows into the neck of the bag and out through the fabric which is covered with bacterial culture.

The application of sequencing batch reactor technology to the treatment of contaminated groundwater is described in Chapter 6.

Oxidation -- Organic groundwater contaminants can be completely oxidized into carbon dioxide and water, or partially oxidized to increase the effectiveness of a downstream treatment. Partial oxidation of refractory organic compounds greatly increases their biodegradability. UV light, ozone (O3), and the hydroxyl radical (OH-, from hydrogen peroxide) are among the most powerful oxidants available.

Ozone, a molecular form of oxygen, is a powerful oxidizing agent. Because of the broad range of compounds that can be degraded, ozone oxidation is well suited to groundwater treatment applications. In waste treatment applications, ozone has been used to decompose cyanides, phenols, dyes, and a host of other organic compounds. Ozone, which is a gas and has a short lifetime, must be generated at the treatment site. The equipment used for ozone generation is expensive and ozone generation itself requires large amounts of energy.

Used in concert, UV irradiation and ozonation techniques completely oxidize many organic compounds; most notably, chlorinated hydrocarbons such as pesticide, and solvents. In one application, UV/ozonation has reducedtrichloroethylene from greater than 100 to less than 1 part per billion in about a minute. Ultrox International of Culver City, California, reports that their UV/ozonation system has successfully treated halogenated compounds, benzene derivatives, including PCBs, and other organic compounds.

Concerted UV/irradiation and treatment with hydrogen peroxide is also an effective oxidizing process.

Peroxidation Systems, Inc., of Tuscon, Arizona, has applied UV/irradiation and hydrogen peroxide oxidation technology to groundwater containing tetrahydrofuran, methylethyl ketone, toluene, and cycloehexanone. The costs to treat this groundwater, including energy and material, were $2.40 per 1,000 gallons. In a related bench scale test, the stream was treated by activated carbon adsorption. The spent carbon was regenerated on site using steam; the condensate from the regeneration process was treated with the UV/H_2O_2 technology.

C. TREATMENT FOR INORGANIC CONTAMINANTS

Groundwater generally contains only small concentrations of heavy metals and other inorganic contaminants; the bulk of these contaminants are removed through an adsorption process with the ground. However, some groundwater does have heavy metal contamination requiring removal. Precipitation/coagulation is a common and economical approach. Reverse osmosis has also been used to remove inorganic compounds from groundwater. As with organic contaminants, the applicability of the techniques for removal of inorganic chemical must be evaluated on the basis of the particular contaminants.

Treated groundwater is often reinjected into the ground. Reinjection solves the disposal problem for the treated water and prevents depletion of the aquifer. Furthermore, reinjection can help flush the soil and aquifer. The injection well is placed upstream of the contaminant source (upgradient with respect to the groundwater flow). The injected water carries the contaminant from its source to the extraction well. Treated water may also be recycled into groundwater by means of sprinklers, trenches, and ponds.

D. TREATMENT TECHNOLOGIES APPLIED IN CALIFORNIA

Some of the groundwater cleanup sites in California and the treatment technologies employed to effect decontamination of the groundwater are described below. At most sites in California, and elsewhere, a combination of air stripping and activated carbon filtration is the core of the treatment process train. These technologies are well understood, so much so that several computer programs are available to optimize the processes. Inexpensive, easily available packed towers are offered for rental costs of about $1,000 per day.

Concentrated industrial activities in the San Francisco Bay Area have resulted in many cases of contaminated groundwater. The problems in Silicon Valley from leaking solvent tanks are a well-known example. Air stripping and activated carbon adsorption are widely applied to these cleanups. At the Jones Chemical and the Pacific Gas and Electric plants, air stripping and activated carbon are used in concert to remove napthalene derivatives from groundwater. Carbon adsorption is used alone at Intel (Santa Clara), Synertek Technical Coating, and Avantek. Air stripping is used alone for the removal of volatile organic compounds at Intel Magnetic.

Air stripping packed tower aeration has been used for the decontamination of groundwater at Aerojet-General, near Sacramento. Several large towers treat a water flow of about four million gallons per day. The contaminating volatile organic compounds are predominantly tri- and tetra-chloroethylene, and Freon 113. Packed tower aeration removes 99.9 percent of the volatile organic compounds (VOCs); they are undetectable in the treated flow. The exhaust from the towers is filtered with activated carbon to recover solvent and to reduce air pollution. The solvent recovery takes place in two additional steps. First, the solvent is removed from the carbon by steam stripping; this also regenerates the carbon. Second, the collected steam is distilled to obtain almost pure solvent. Activated carbon treatment of the contaminated groundwater is under study as a possibly less expensive treatment method than tower aeration. The Aerojet installation is one of the largest tower aeration facilities in operation and has provided a wealth of operational data.

In coastal Northern California, wastes from the lumber milling and wood processing industries have caused significant groundwater contamination. At the Coast Wood and the Ecodyne/SHAH cleanup sites, reverse osmosis and ion exchange technologies are used in the removal of heavy metal ions. At the Ecodyne site, reverse osmosis is followed by ion exchange; granular activated carbon filtration is used as a final polishing step. At two other sites in this region, Hewlett-Packard and Fairchild manufacturing plants, packed tower aeration is used to remove trichloroethylene (TCE).

Pure compound recovery by the cone of depression technique with the use of an oil-water separator has been practiced in a cleanup at a Texaco installation in Fremont and at nearby locations. At this site, over 5,000 gallons of oil and gasoline have contaminated soil and groundwater.

At an abandoned bleach manufacturing plant in the San Francisco Bay Area, an estimated 3,000 pounds of mercury on the site has contaminated the local aquifer. The groundwater is treated with activated carbon adsorption and an ion exchange resin specific for mercury. Ninety-seven percent of the mercury is removed with the achievement of one to two ppm of mercury in the treated groundwater, which is discharged into San Francisco Bay.

In situ biodegradation has been practiced on some California sites for the treatment of both contaminated soils and groundwater. At KTI Chemical in Santa Clara, biodegradation is proposed for the treatment of groundwater contaminated by mineral spirits, a common mixture of olefins and parafins. The proposed system is a closed loop where groundwater is extracted, treated, and reinjected.

CHAPTER 15

TREATMENT OF CONTAMINATED SOIL AND IN SITU TREATMENT

A. INTRODUCTION

A general mechanism for the contamination of soil and groundwater is illustrated in Figure 14-1. The treatment technology chosen for a particular site will depend on the geologic and hydrologic characteristics of the site, and on whether the contamination encounters the aquifer or remains completely in the soil above the aquifer. The technology chosen may treat both groundwater and soil or separate technologies may be applied to these media. Groundwater treatment technologies, other than in situ approaches, are discussed in the preceding section of this report.

B. TREATMENT OF CONTAMINATED SOIL

The treatment of contaminated soils is emerging as one of the most difficult aspects of site mitigation. Although great progress is being made with the in situ treatments discussed below, large volumes of contaminated soil in California will probably require excavation. Contaminated soil excavated from hazardous waste sites can be treated by the same technologies as other solid hazardous wastes. Incineration is usually the best candidate for the treatment of hazardous waste. Many of the incinerators described in Chapter 9 are applicable to contaminated soil destruction. Fixed and multiple hearth incinerators, rotary kiln incinerators, and fluidized bed incinerators can all accept solid wastes.

Mobile incinerators are particularly well suited for site mitigation purposes. The volume of soil excavated from a contaminated site of moderate size may be greater than 10,000 or even 100,000 cubic yards, far more than can be reasonably transported. The EPA mobile incinerator was constructed expressly for site mitigation purposes. Shirco Infrared Systems reports that they have four mobile units under construction for site mitigation purposes. The Advanced Electric Reactor, which has a relatively small throughput but is highly efficient, is ideal for sites with severe contamination of difficult to degrade compounds.

Other treatment options for contaminated soil are extraction and stabilization. A wide variety of treatment methods cannot be applied to contaminants adhering to soil particles. It is difficult to contact the contaminants with chemical or biological reagents; nor is soil easily pumped into thermal oxidizing equipment such as a wet air oxidizer. Extraction of the contaminants facilitates the use of these treatment technologies.

Stabilization techniques applicable to contaminated soil are discussed in Chapter 12.

C. IN SITU TREATMENT TECHNOLOGIES

In situ (or in place) treatment systems degrade, remove, or detoxify hazardous waste in the zone of contamination. In situ treatment occurs primarily within the soil or aquifer differing from other on-site treatment techniques which are primarily aboveground processes. In situ methods reduce the need for expensive soil excavation and costly transportation to landfills or to off-site treatment facilities. In situ treatments are effective and economical detoxification methods that are the subject of intense research and development efforts.

There are five major categories of in situ treatment techniques. These are:

- Immobilization;
- Degradation;
- Soil Flushing;
- Attenuation; and
- Reduction of Volatilization.

The first three technologies are discussed below.

Immobilization

Immobilization techniques capture the contaminant in the soil, preventing contamination from spreading to groundwater, air, or surface water. Unfortunately, the contaminants remain in the soil, presenting the possibility of future exposure.

There are three major classes of immobilization techniques: adsorption (sorption), ion exchange, and precipitation.

Adsorption techniques cause chemical contaminants to bind to the soil particles. Adsorptive materials, such as activated carbon, may be added to the soil to enhance the soils inherent adsorptive properties. Adsorption methods can be applied to both inorganic and organic contaminants.

Ion exchange (Chapter 4) is an immobilization method similar to physical adsorption. Soil particles act as ion exchangers trading innocuous soil cations for toxic heavy metal cations. Common clay minerals are particularly excellent at binding such contaminants. The ion exchange activity of soils can be enhanced by mixing synthetic ion exchange resins with the soil. Such resins can be tailored to be highly selective for particular metals. Ion exchange techniques are applicable only to inorganic contaminants.

Precipitation is another immobilization technique. Soluble inorganic contaminants are chemically treated to form compounds of very low solubility. The insoluble products precipitate out and are retained by soil particles. This restricts the presence of toxic material to the original zone of contamination, preventing leaching into groundwater. Precipitating materials can be added directly to the soil or generated in place by chemical or biological methods. In situ precipitation of contaminants from groundwater is discussed in the degradation section below.

Degradation

Degradation techniques convert the hazardous materials contaminating the soil or groundwater into harmless or less harmful forms. Degradation techniques, particularly biodegradation, have more applicability to organic compounds, which because of their complex structures, are more easily degraded than inorganic compounds.

Biodegradation -- There are many approaches to in situ biodegradation. Among the most common are land farming, where contaminants are treated within two to three feet of the ground's surface; microbial inoculation, where microbes are added to an aquifer; and biologically active barriers, where flows of contaminated groundwater are directed to biologically active ponds.

In situ biodegradation is often the most economical method of site mitigation. The advantages of in situ biological treatment include:

- In situ biotreatment provides a permanent solution and future liabilities are minimized;
- The activity of the residual microbial population continues long after equipment and personnel have left the site;
- Minimal site disturbance is necessary, often allowing commercial activities to continue while treatment is underway; and
- Hauling and disposal costs are greatly reduced, if not eliminated.

Sufficient numbers of bacteria must be present to metabolize the contaminant within a reasonable time. For aerobic biodegradation, which is usually faster and more effective than anaerobic processes, plenty of oxygen must be made available to the bacteria. An effective means for contacting the bacteria with their food source (the contaminant) is necessary. Essential nutrients, including nitrates and phosphates, must be supplied. When suitable bacteria, enough oxygen and nutrients, and good contact are present, microbial growth is limited only by the food supply. Destruction of the pollutant can thus proceed at its fastest possible rate.

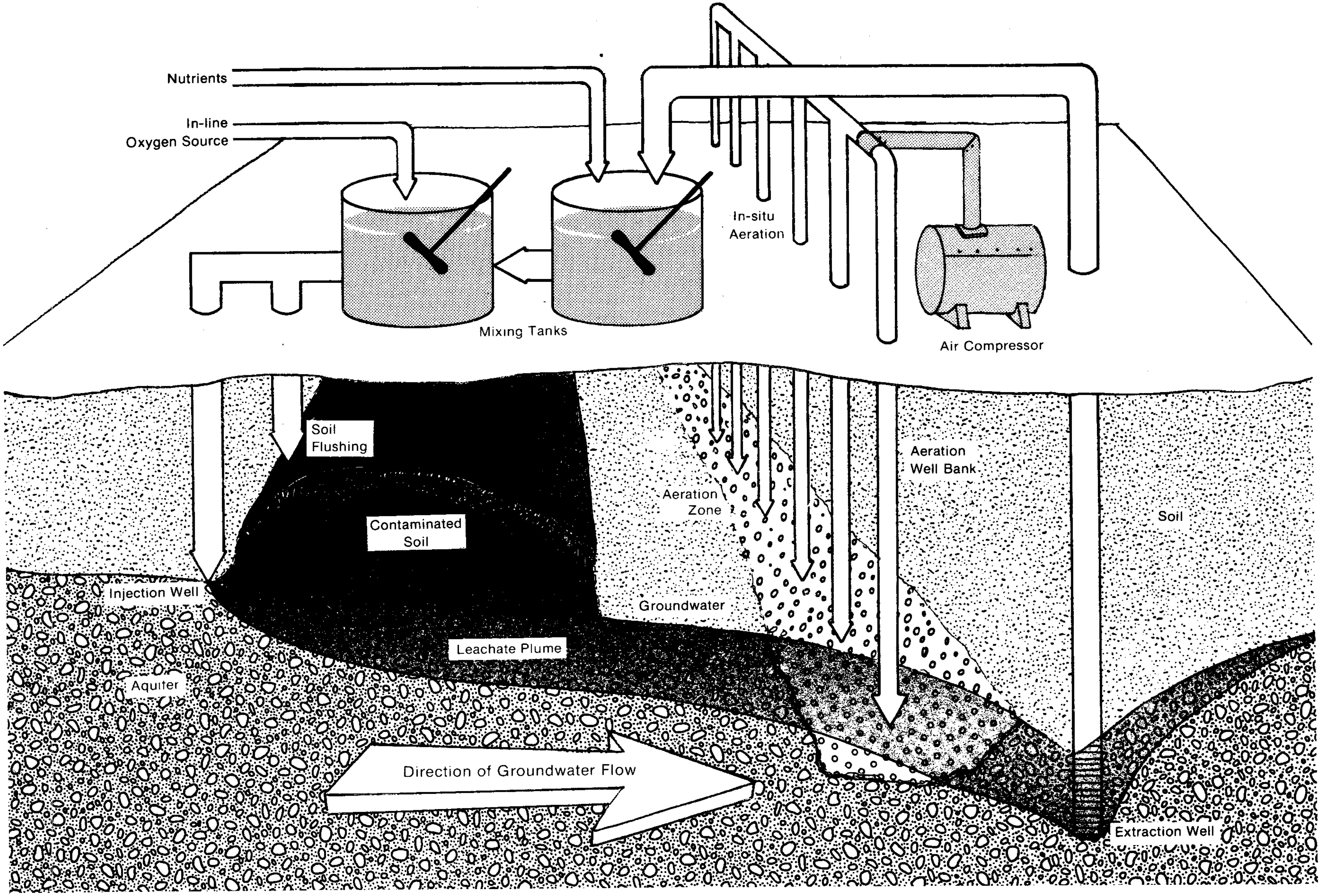


Figure 15-1 Microbial Inoculation or Bioreclamation.
This diagram illustrates groundwater cleanup and soil-flushing.
Source: EPA

Biodegradation can be enhanced through the use of a cosubstrate (or cometabolite) that provides an alternative bacterial food source to allow the development of an active, acclimated culture. An organic contaminant that is resistant to attack and cannot support microbial activity on its own, can thus be degraded at the same time the cosubstitute is metabolized. Depending on the situation, easily degraded compounds, such as glucose, can serve as a cosubstrate or a biodegradable analogue of the contaminant can be used in order to stimulate production of an enzyme capable of degrading both compounds.

Bacterial species indigenous to the soils at the contamination site, which are well adapted to the local conditions, are the organisms most commonly used for in situ biodegradation projects. Bacterial strains cultured in vitro to degrade a particular compound are also widely used. Microbes that have been genetically engineered to attack and degrade biologically recalcitrant hazardous waste may be considered for future decontamination projects.

Land farming, also known as soil aeration, involves soil tillage to a depth of two or three feet; biological and chemical processes take place in the tilled volume. Tillage aerates the soil, assisting in biodegradation and allowing volatile organic compounds to evaporate. Chemical and bioactive agents can be dispersed through this soil layer for the purpose of degradation or chemical neutralization.

Microbial inoculation is a widely used technique for treating easily biodegradable compounds in groundwater. Bacteria, nutrients, oxygen, or cosubstrates are added to the contaminated groundwater in aboveground tanks or bioreactors, and the mixture is reinjected into the ground. The degradation of the pollutants which begins in the aboveground facilities continues in the aquifer. Under ideal situations the bacteria remain active until the pollutant is almost completely removed. As in other biodegradation projects, bench-scale testing is usually necessary to develop the correct proportions of the components (nutrients, cosubstrate, microbes, etc.) in the inoculant.

Microbial inoculation is most often conducted in a recirculatory manner (see Figure 15-1). Groundwater is pumped from the ground into the tank; the effluent from the tank is reinjected into the ground upgradient of the contamination source. Recirculation facilitates the addition of nutrients and oxygen. As discussed in the section below on soil flushing, this process extracts the contaminant from the soil for treatment. Another adaptation to facilitate underground biodegradation is the drilling of wells to help aerate the aquifer (Figure 15-1). Aeration could also be accomplished by addition of dilute hydrogen peroxide.

Biologically, active barriers are impermeable walls set into the ground to direct groundwater flow to a pit in which is maintained a microbial culture capable of degrading the contaminant. The method is confined to treatment of groundwater found near the ground surface.

Many hazardous soil and groundwater contaminants, particularly petroleum derivatives, have been destroyed through the application of in situ biodegradation techniques. Ninety to ninety-five percent reductions of the total organic compounds found in hazardous waste leachates have been achieved through in situ biodegradation.

Chemical Degradation -- Chemical degradation can take several forms, including neutralization/ detoxification or detoxification and stabilization. For example, acrylonitrile contaminated soil has been treated by raising the soil pH to ten with lime and spraying the soil with sodium hypochlorite. The latter treatment oxidizes the acrylonitrile to less hazardous compounds. Phenol contaminated soils have been oxidized in situ through the application of hydrogen peroxide (H2O2). Pesticides have been removed from contaminated soil by plowing in soda ash and powdered activated carbon, with periodic reapplications to maintain the soil pH. Pesticide concentrations were reduced to 0.1 mg/l using this method.

Contaminated groundwater can also be treated by in situ chemical degradation. The contamination of an aquifer by arsenic has been remedied by injection of a dilute potassium permanganate solution. The trivalent arsenic was oxidized to pentavalent arsenic, which precipitates arsenic-iron-maganese compounds. Arsenic in the groundwater was thus reduced from 13.6 mg/l to 0.06 mg/l. Dioxin has been destroyed in situ through dechlorination using a mixture of alkali metal hydroxides, polyethylene glycols, and dimethyl sulfoxide.

Soil Flushing

Soil flushing is the extraction of the contaminant in a suitable solvent, usually water. The extracting solvent is injected into the ground; simultaneously, the contaminated groundwater or leachate is pumped to the surface. The injection well is positioned upgradient of the contamination zone so that the injected solvent will pass through the contamination. The process is often operated in a recirculatory manner in which the treated groundwater is used as the extracting solvent.

Soil flushing can greatly reduce the time required for treatment of contaminated water and soil. Reinjection of the cleaned water increases the flow of contaminated water to the treatment unit; and contaminant is rapidly desorbed from the soil as the water passes through it. Reliance solely upon natural undergroundwater movement is much less effective.

Special chemicals may be added to the treated water before it is reinjected into the soil. These chemicals include surfactants, added to dissolve oils and other petroleum products; acids or bases, added to detoxify the contaminants; or chelating agents such as EDTA or citric acid, added to dissolve metal ions.

Soil flushing removes the contaminants but usually does not destroy them. Other technologies must be used to detoxify the hazardous pollutants. Soil flushing is often used in conjunction with aboveground biological treatment and microbial inoculation.

D. EXAMPLES OF COMMERCIAL IN SITU BIODEGRADATION TREATMENT

The practice of in situ biotreatment can best be illustrated through the following short description of several approaches to the application of this technique.

Aquifer Remediation Systems (ARS), a division of FMC Corporation, employs a closed loop recirculating biodegradation approach to the treatment of contaminated ground and groundwater. ARS uses a dilute hydrogen peroxide solution to supply oxygen to the bacterial populations. This approach to aeration has been chosen by other contractors as well. The hydrogen peroxide solution is not toxic to the bacteria and helps to keep the casing pores of the reinjection well free of biological clogging. ARS uses the bacterial populations indigenous to the treatment site. A proprietary nutrient mix is added to the circulating contaminated groundwater in an aboveground mixing tank. ARS has treated mainly petroleum product spills.

Closed loop recirculatory biotreatment has also been applied to hazardous waste site cleanups by O. H. Materials, Inc. They have successfully treated acrylonitrite, gasoline, crude oil, ethylene glycol, butylcellosolve, and other wastes. Indigenous bacteria are cultivated in an aboveground activated sludge bioreactor through the addition of nutrients, oxygen, and acclimated bacteria. Treatment occurs both in the bioreactor and underground. The latter follows reinjection of the treated groundwater containing acclimated microbes. Packed tower aeration has been used upstream of the biotreatment to provide oxygenation and to remove volatile organic compounds. Five-fold cost savings over soil excavation have been realized.

E. EMERGING IN SITU TREATMENT TECHNOLOGIES

Photolysis -- UV light can photo chemically degrade many chemical compounds. Soil tillage facilitates photolysis because it exposes the contaminant to the UV source, sunlight, or a stronger source. Chemical pretreatment may contribute to a photolytic process. Pretreatment may include addition of organic solvents, proton-donating compounds (for example methanol), or surfactants. Tetrachlorodibenzo-p-dioxin (TCDD, see Chapter 11), ketones, and PCBs have been photodegraded by this means. Photolysis is especially well suited to dechlorination of compounds which are resistant to treatment through other means.

Colloidal Gas Aphrons -- This is an emerging technology for augmenting underground oxygen supplies. Solutions of millions of minute bubbles are injected into the groundwater. These tiny bubbles (about 25 micrometer) present an enormous surface area; treatment is most effective near a bubble's surface. Colloidal gas aphrons provide aeration for longer than conventional techniques. This technique may be used to improve aerobic conditions for subterranean aerobic biodegradation.

White Rot Fungus -- In laboratory tests, white rot fungus degraded persistent environmental pollutants such as the chlorinated hydrocarbons, DDT, lindane, and benzopyrene. Stephan Aust and his colleagues at Michigan State University are exploring this technology.

Radio Frequency In Situ Heating -- An expensive technology, radio heating, has been applied to the decontamination of dangerous, uncontrolled hazardous waste landfills. In this technique, the landfills were heated by means of strong radio waves to the point of decomposing, distilling, and vaporizing the hazardous constituents.

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APPENDICES

APPENDIX A:

CALIFORNIA OFF-SITE TREATMENT AND RECYCLING FACILITIES

Inclusion on this list does not constitute an endorsement by the Department of Health Services (DHS). The Department does not claim that this list is complete.

The status of a hazardous waste facility is subject to change. Generators are strongly urged to contact the local DHS regional office (page 167) before transferring waste to a facility they are not familiar with.

Facility Name Address Contact Name Telephone Number EPA Number	Treatment Methods	Wastes Accepted
Allied Chemical Corporation 525 Castro Street Richmond, CA 94801 H. F. Borghi (415) 232-7193 CAD 028981967	Sulfuric acid regeneration.	Waste sulfuric acid (80 percent minimum).
Appropriate Technologies, II 1700 Maxwell Road Chula Vista, CA 92011 Jim McKally (619) 421-1175 CAT 080010101	Neutralization, oil-water separation.	Acids, aqueous solution with metals, and oily water.
Baron-Blakeslee, Inc. 3596 California Street San Diego, CA 92101 David Thompson (619) 295-0041 CAT 000618652	Distillation.	Halogenated solvents.

Facility Name Address Contact Name Telephone Number EPA Number	Treatment Methods	Wastes Accepted
Baron-Blakeslee, Inc. 8333 Enterprise Drive Newark, CA 94560 Bill Jenkins (415) 794-6511 CAD 074644659	Distillation.	Halogenated solvents.
Bayday Chemical 2096-B Walsh Avenue Santa Clara, CA 95050 Thomas Taylor (408) 727-8634 CAT 080012263	Distillation.	Halogenated solvents.
Broco, Inc. 2824 North Locust Rialto, CA 92376 Jerry Brower (714) 350-4701 CAT 080022148	Detonation and open burning.	Explosive and pyrotechnic wastes. All materials approved on a per load basis.
California Oil Recyclers 977A Bransten Road San Carlos, CA 94070 Kirk Hayward (415) 791-1311 CAD 980695761	Refining.	Oils and petroleum wastes.
Casmalia Resources P. O. Box E Casmalia, CA 93429 Laboratory Office (805) 937-8449 CAD 020748125	Wet air oxidation.	Cyanides and pesticide rinse water.

Facility Name Address Contact Name Telephone Number EPA Number	Treatment Methods	Wastes Accepted
Chemical Waste Management P. O. Box 417 Kettleman Hills, CA 93239 Mark Langowski (209) 386-9711/(800) 222-2964 CAD 000646117	Cyanide oxidation, neutralization, and stabilization.	Cyanides, acids, caustics, and other aqueous wastes.
Chemwest Industries, Inc. 26970 Asti Road Cloverdale, CA Sales Office 50 California Street, Suite 2925 San Francisco, CA 94111 Mack Atkinson (415) 421-8745 CAD 990663296	Neutralization, precipitation tank.	Acids, pickling liquor.
Crosby and Overton, Inc. 1610 West 17th Street Long Beach, CA 90813 Bob Meyers (213) 432-5445 CAD 028409019	Oil-water separation.	Oily water wastes.
David H. Fell and Company, Inc. 4176 Pacific Way Commerce, CA 90023 Paul Richter (213) 623-1868 CAD 981384332	Precipitation and refining.	Acid and cyanide waste containing gold, silver, and selected precious metals.
Demenno/Kerdoon 2000 North Alameda Street Compton, CA 90222 Cathy Demenno (213) 537-7100 CAT 080013352	Refining.	Oils and petroleum wastes.

Facility Name Address Contact Name Telephone Number EPA Number	Treatment Methods	Wastes Accepted
Engelhard Industries West, Inc. 5510 East La Palma Avenue Anaheim, CA 92807 Philip Bates (714) 779-7231 CAT 000612150	Cyanide oxidation and electrostatic precipitation.	Cyanide solutions, plating solutions, and precious metals waste: Gold, silver, and palladium. Wastes Not Accepted: Photographic processing solutions and films.
General Portland Cement Systech Corp. 23505 Cranshaw Boulevard, Suite 201 Torrance, CA 90505 (Facility located in Lebec, CA) Mike Zimmer (213) 325-2800 CAT 080031628	Cement kiln incineration.	Organic incinerable wastes (maximum chlorine content five percent).
GNB Inc., Metals Division 2700 South Indiana Street Los Angeles, CA 90023 Ken Clark (213) 262-1101 CAD 097854541	Smelting and refining.	Lead-acid batteries. Minimum quantity truck load (approximately 9,000 pound) Battery case must be nonmetallic.
Gold Shield Solvents Division of Detrex Chemical Industries, Inc. 3027 Fruitland Avenue Los Angeles, CA 90058 Darrell W. Craft (213) 583-8736 CAD 020161642	Steam distillation.	Halogenated solvents.
Holchem/Service Chemical 1341 East Maywood Santa Ana, CA 92706 Elmer Dudash (714) 538-4556 CAT 00061233	Distillation.	Halogenated solvents.

Facility Name Address Contact Name Telephone Number EPA Number	Treatment Methods	Wastes Accepted
IT Corporation Martinez Treatment Plant Martinez, CA Sales Office 4575 Pacheco Boulevard Martinez, CA 94553 Mark Posson (415) 228-5100 (24 hours) CAD 000094771	Oxidation, reduction, neutralization, and precipitation.	Acids, caustics, cyanides, phenols, and nonhalogenated solvents.
Lubrication Company of America 4212 East Pacific Way Los Angeles, CA 90023 Grant Ivey (213) 264-1091 CAD 008247629	Distillation and precipitation.	Hydraulic oils, synthetics, soluble oil mixtures, crankcase drainings, contaminated diesel fuels and gasolines, cutting oils, and lube oils.
Mickey Corporation 206 Donahue Street Marin City, CA 94965 David Asano (415) 331-2195 CAD 981161367	Silver recovery.	X-ray and photographic fixer solutions.
Nelco Oil Refining Corporation 600 West 12th Street National City, CA, 92050 Steve Humphrey (619) 474-7511 CAD 008352890	Refining.	Waste or mixed oil and hydrocarbon solvents.

Facility Name Address Contact Name Telephone Number EPA Number	Treatment Methods	Wastes Accepted
Oil and Solvent Process Company 1704 West First Street Azusa, CA 91702 Bill Mitzel (818) 334-5117 CAD 008302903	Distillation.	Halogenated and nonhalogenated solvents and oily wastes.
Omega Recovery Services 12504 East Whittier Boulevard Whittier, CA 90602 Dennis R. O'Meara (213) 698-0911 CAD 042245001	Distillation, wiped film evaporation, alcohol extraction, and minor solidification.	Organic solvents, chlorinated solvents, fluorocarbons, and refrigerants.
Orange County Chemical Company 1230 East Saint Gertrude Place Santa Ana, CA 92707 Jim Gallade (714) 546-9901 CAD 029363876	Distillation.	Halogenated solvents. Chlorinated and fluorinated solvents.
Pacific Treatment Corporation (Cleaning Dynamics Corporation) 2190 Main Street San Diego, CA 92113 Mike H. Donley (619) 233-0863 CAD 095894556	Neutralization, oil-water separation, and solidification.	Hydrazine, sodium nitrate, hypochlorite, acids, caustics, freons, and waste oils.
Pease and Curren Reliable Recovery 15 Brasher Street Anaheim, CA 92807 Gerardo Robledo (714) 630-8880 CAT 000624999	Precipitation and refining.	Plating and jewelry waste; acids and cyanides containing gold, silver, platinum, palladium, and/or rhodium.

Facility Name Address Contact Name Telephone Number EPA Number	Treatment Methods	Wastes Accepted
Pepper Oil Company, Inc. 2300 Tidelands Avenue National City, CA 92050 Don Cobb (619) 477-9336 CAT 000613547	Oil-water separation.	Petroleum products.
Quicksilver Products, Inc. 200 Valley Drive, Suite 1 Brisbane, CA 94005 Ritchey Vaughn (415) 468-2000 CAD 044000438	Refinery and distillation.	Metallic mercury, flourescent tubes, mercury vapor lamps, mercury contaminated products, thermometers, switches, and sludges. Wastes Not Accepted: Biological or infectious mercury wastes.
Rafidain Refinery, Inc. 3060 Roswell Street Los Angeles, CA 90065 Krikor Mahrouk (213) 256-4522 CAD 981382831	Precipitation and smelting.	Jewlery industry waste.
Reclamar Corporation 131 North Marine Avenue Wilmington, CA 90744 Paul DeVries (213) 835-3103 CAD 980737548	Distillation.	Perchloroethylene.
Rho-Chem Corporation 425 Isis Avenue P. O. Box 6021 Inglewood, CA 90301 Dick Gustafson (213) 776-6233 CAD 008364432	Distillation.	Halogenated and nonhalogenated solvents. Customer Restrictions Services offered only to customers who buy virgin or reclaimed products from the firm.

Facility Name Address Contact Name Telephone Number EPA Number	Treatment Methods	Wastes Accepted
Romic Chemical Corporation 2081 Bay Road East Palo Alto, CA 94303 Peter Schneider (415) 324-1638 CAD 009452657	Distillation, stripping, and extraction processes.	Solvents (halogenated and nonhalogenated), commerical chemical products, paints and inks, water wastes containing lower concentrations of solvents.
RSR Quemetco, Inc. 720 South 7th Avenue City of Industry, CA 91746 Carl Fisher (800) 527-9452 CAD 066233966	Smelting and refining.	Scrap batteries. Minimum quantity: 7,500 pounds. Must be lead-acid type of the automotive, commercial, and/or steel-cased variety.
Solvent Services, Inc. 1021 Berryessa Road San Jose, CA 95133 Thomas Dinette (408) 286-6446 CAD 059494310	Oil-water seperation, neutralization, solidification/stabilization, and distillation.	Solvents (halogenated and nonhalogenated), acids, caustics, oily wastes.
Stauffer Chemical Company Basic Chemical Division Dominquez, CA Martinez, CA Sales Office 636 California Street San Francisco, CA 94108 Tim Guigino (415) 544-9000 Dominquez: CAT 000612202 Martinez: CAD 053049490	Sulfuric acid regeneration furnance.	Clean spent sulfuric acid.

Facility Name Address Contact Name Telephone Number EPA Number	Treatment Methods	Wastes Accepted
Triad Marine and Industrial Cleaning Corporation 1668 National Avenue San Diego, CA 92113 John Drumel/Larry Cairncross (619) 239-2024 CAD 098240062	Oil-water separation.	Oily water, diesel fuels.
Triple J Pacification 3650 East 26th Street Vernon, CA 90023 Martin Smith (213) 268-5056 CAT 080033681	Oil-water separation.	Oily-water wastes, sump wastes.

APPENDIX B: FINANCIAL ASSISTANCE FOR HAZARDOUS WASTE PROJECTS

Department of Health Services

The Department of Health Services sponsors the Hazardous Waste Reduction Grant Program. The purpose of the program, required by California law, is to provide funding for innovative projects involving hazardous waste reduction, recycling, or treatment. Grants are given to private individuals, companies, universities, governmental agencies, and private organizations. The Department selects proposals that offer the greatest opportunity to significantly reduce the generation of hazardous waste in California.

Grants are available in four stages:

- o Step I -- Feasibility Studies
- o Step II -- Project Design
- o Step III -- Construction, and
- o Step IV -- Evaluation

For more information contact:

John Low or Arvind Shaw
Alternative Technology and
Policy Development Section
Toxic Substances Control Division
Department of Health Services
714/744 P Street
Sacramento, CA 95814
(916) 324-1807

California Pollution Control Financing Authority

The California Pollution Control Financing Authority (CPCFA), created in 1972, provides financing for pollution control equipment. CPCFA offers loans with lower interest rates and longer payback times than are generally available from private sources. CPCFA raises money through the sale of tax-exempt bonds.

Since its inception, CPCFA has floated bonds with a total worth over $2 billion. Loans have been provided for projects ranging in cost from $75,000 to $200,000,000. Approximately one-third of the CPCFA bond issues sold since 1974 have been for air pollution control; one-quarter have been for water pollution control; and another quarter have been for combined air and water pollution control projects. The remainder (one-sixth) have been for solid waste and waste-to-energy projects.

CPCFA is developing several new programs which provide support for small businesses. Some of these programs are specifically designed to finance hazardous waste control programs. The structure of CPCFA's programs are subject to change pending changes in the state and federal tax codes.

For information on CPCFA's programs contact:

Mr. Douglas Chandler
Executive Secretary
California Pollution Control
Financing Authority
915 Capitol Mall, Room 110
Sacramento, CA 95814
(916) 445-9597

Small Business Administration

The Federal Small Business Administration (SBA) offers pollution control financing guarantees. Under this program the borrowing company obtains a loan from a private source, such as a bank, with the understanding that the loan is an obligation of the Federal Government. The SBA agrees to make timely payments to the lender in the event that the borrower defaults.

The guarantees are avilable only for projects which have as their primary purpose achieving compliance with environmental regulations. To be eligible for the guarantee the borrowing company must be an independently-owned, small business operated for profit; the company must have a minimum five-year operating history with profitable operation in any three of the past five years. The company must be ineligible for a comparable loan without the federal guarantee.

For information on SBAs pollution control financing guarantees contact:

Mr. Robert Tallon
Pollution Control Financing Staff
Small Business Administration
1441 L Street, N.W., Room 808
Washington, DC 20416
(202) 653-2548

Pooled Loan Marketing Corporation

The Pooled Loan Marketing Corporation (PLMC), a private corporation, offers a secondary market for loans bearing the SBA Pollution Control Financing Guarantee. PLMC both purchases existing loans and negotiates with companies and potential lenders to purchase loans once issued.

For information on PLMC's secondary loan purchases contact:

Mr. James H. McCall
General Manager
Pooled Loan Marketing Corporation
P.O. Box 946
Solana Beach, CA 92075
(800) 833-7565
(toll-free from California)
(800) 233-7565
(toll-free outside California)

PLMC pools small loans to create a larger package which is more easily marketed. Other private concerns, such as banks, and public concerns, such as CPCFA, may offer similar services.

Environmental Protection Agency

Like other federal agencies with large extra-mural research programs, EPA maintains a small business innovative research program. The program, which is restricted to small businesses, is designed to sponsor and promote highly innovative pollution control research. One topic area concerns solid and hazardous waste disposal and pollution control.

Grants are awarded in two phases. The first phase involves a six-month feasibility study and is eligible for up to $50,000. Applications for Phase I are accepted between November and January. Companies interested in receiving applications should send a request in October to:

Ms. Dana Lloyd
Contracts Specialist
Contract Management Division CMD-33
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Phase II is a development phase which is open only to companies that have successfully completed Phase I. Proposals are ranked by a peer review panel on the basis of the submitted proposal and the results of Phase I. Scientific feasibility is the primary criteria. Phase II projects may have a one-year or two-year duration and are eligible for up to $150,000.

Phase III is a entrepreneurial phase and does not involve EPA Small Business Innovative Research funding.

For information contact:

Mr. Walter Preston
SBIR-Program Manager
U.S. EPA RD-675
401 M. Street, S.W.
Washington, DC 20460
(202) 382-7445

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Note: This list is not exhaustive, other sources of financing for hazardous waste projects include private foundations, banks, and other government entities.
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APPENDIX C: CALIFORNIA AGENCIES INVOLVED IN HAZARDOUS WASTE MANAGEMENT

DEPARTMENT OF HEALTH SERVICES
Toxic Substances Control Division

HEADQUARTERS OFFICES

1219 K Street
714/744 P Street
Sacramento, CA 95814

Toxic Substances Control Division
(916) 322-1826

Alternative Technology and
Policy Development Section
(916) 324-1807

Hazardous Waste Management Section
(916) 322-2337

Office of Enforcement
(916) 324-2448

Office of Public Information and
Participation
(916) 324-1789

Site Cleanup and Emergency
Response Section
(916) 324-3773

REGIONAL OFFICES

Northern California Section (NCS)
4250 Power Inn Road
Sacramento, CA 95826
(916) 739-3145

Fresno Office (Fresno)
5545 East Shields Avenue
Fresno, CA 93727
(209) 445-5938

North Coast California Section (NCCS)
2151 Berkeley Way, Annex
Berkeley, CA 94704
(415) 540-2043

Southern California Section (SCS)
107 South Broadway, Room 7128
Los Angeles, CA 90012
(213) 620-2380

STATE WATER RESOURCES CONTROL BOARD
P.O. Box 100
Sacramento, CA 95801
(916) 445-9552 (Water Quality Division)

Regional Water Quality Control Boards

North Coast Region (1)
1000 Coddingtown Center
Santa Rosa, CA 95401
(707) 576-2220

San Francisco Bay Region (2)
1111 Jackson Street, Room 6040
Oakland, CA 94607
(415) 464-1255

Central Coast Region
1102-A Laurel Lane
San Luis Obispo, CA 93401
(805) 549-3147

Los Angeles Region (4)
107 South Broadway, Room 4027
Los Angeles, CA 90012
(213) 620-4460

Central Valley Region (5)
3201 S Street
Sacramento, CA 95816
(916) 445-0270

Fresno Branch Office
3374 East Shields Avenue, Room 18
Fresno, CA 93726
(209) 445-5116

Redding Branch Office
100 East Cypress Avenue
Redding, CA 96002
(916) 225-2045

Lahontan Region (6)
2092 Lake Tahoe Boulevard
P.O. Box 9428
South Lake Tahoe, CA 95731
(916) 544-3481

Victorville Branch Office
15371 Bonanza Road
Victorville, CA 92392
(619) 245-6583

Colorado River Basin Region (7)
73-271 Highway 111, Suite 21
Palm Desert, CA 92506
(619) 346-7491

Santa Ana Region (8)
6809 Indiana Avenue, Suite 200
Riverside, CA 92506
(714) 684-9330

San Diego Region (9)
6154 Mission Gorge Road, Suite 205
San Diego, CA 92120
(619) 265-5114

OTHER STATE AGENCIES

California Air Resources Board
1102 Q Street
P. O. Box 2815
Sacramento, CA 95812

Public Information
(916) 322-2990

Toxic Pollutants Branch
(916) 322-6023

California Waste Management Board
1020 9th Street, Suite 300
Sacramento, CA 95814

Office of Policy and Program Analysis
(916) 322-8742

Waste Management Division
(916) 322-6127

California Highway Patrol
2555 First Avenue
P.O. 898
Sacramento, CA 95804

Enforcement Services Division
Motor Carrier Section
(916) 445-6211

California Department of Food and Agriculture
1220 N Street
Sacramento, CA 95814

Public Information
(916) 445-9280

Pesticide Enforcement
(916) 322-5032

Department of Industrial Relations
Division of Occupational Health and Safety
525 Golden Gate Avenue
P.O. Box 603
San Francisco, CA 94101

Enforcement and Complaints
(415) 557-1946

Information or Consultation
(800) 652-1476

The CAL/OSHA Consultation Service:

Headquarters

San Francisco	(415) 557-2870 (800) 652-1476

Area Offices

Downey	(213) 861-9993
Emeryville	(415) 658-0900
Fresno	(209) 445-5072
Sacramento	(916) 920-6131
San Bernardino	(714) 383-4567
San Diego	(619) 280-5304

LOCAL ENVIRONMENTAL AGENCIES

ENVIRONMENTAL HEALTH DIRECTOR

LOCAL AIR POLLUTION CONTROL DISTRICT (APCD) OR AIR QUALITY MANAGEMENT DISTRICT (AQMD)

ALAMEDA COUNTY

Gerald H. Winn, Director
Division of Environmental Health
470 - 27th Street
Oakland, CA 94612
(415) 874-5116

Bay Area AQMD
939 Ellis Street
San Francisco, CA 94109
(415) 771-6000

ALPINE COUNTY

Gregory J. Hayes, M.D.
County Health Officer
P.O. Box 306
Markleeville, CA 96120
(916) 694-2146

Great Basin Unified APCD
157 Short Street, Suite 6
Bishop, CA 93514
(714) 872-8211

AMADOR COUNTY

James McClenahon, M.D.
County Health Officer
108 Court Street
Jackson, CA 95642
(209) 223-3230, Ext. 400

Amador County APCD
108 Court Street
Jackson, CA 95642
(209) 223-6394

BUTTE COUNTY

Lynn E. Vanhart, Director
Division of Environmental Health
7 County Center Drive
Oroville, CA 95965
(916) 534-4281

Butte County APCD
316 Nelson Avenue
P.O. Box 1229
Oroville, CA 95965
(916) 534-4383

CALAVERAS COUNTY

Harvey R. LaBounty, Director
Environmental Health
Government Center
891 Mountain Ranch Road
San Andreas, CA 95249
(209) 754-3849

Calaveras County APCD
Government Center
San Andreas, CA 95249
(209) 754-3849

COLUSA COUNTY

Janet E. Krug Director of Environmental Health 251 East Webster Street P.O. Box 610 Colusa, CA 95932 (916) 458-7717	Colusa County APCD P.O. Box 1029 Colusa, CA 95932 (916) 458-5891

CONTRA COSTA COUNTY

Daniel C. Bergman Assistant Director of Health Services Environmental Health 1111 Ward Street P.O. Box 871 Martinez, CA 94553 (415) 372-4416	Bay Area AQMD 939 Ellis Street San Francisco, CA 94109 (415) 771-6000

DEL NORTE COUNTY

(See Humboldt County)	(See Humboldt County)

EL DORADO COUNTY

Ronald D. Duncan Director of Environmental Health Community Development Department 360 Fair Lane Placerville, CA 95667 (916) 626-2411	El Dorado County APCD 360 Fair Lane Placerville, CA 95667 (916) 626-2407

FRESNO COUNTY

Louis A Dooley, Director Environmental Health Systems 1221 Fulton Mall P.O. Box 11867 Fresno, CA 93775 (209) 445-3391	Fresno County APCD 1221 Fulton Mall P.O. Box 11867 Fresno, CA 93775 (209) 445-3391

GLENN COUNTY

Joseph Duba, M.D. County Health Officer 240 North Villa Avenue Willows, CA 95988 (916) 934-5418	Glenn County APCD 720 North Colusa Street Willows, CA 95988 (916) 934-4651

HUMBOLDT-DEL NORTE COUNTIES

Jeffrey W. Arnold
Director of Environmental Health
529 I Street
Eureka, CA 95501
(707) 445-6215

North Coast Unified AQMD
5630 South Broadway
Eureka, CA 95501
(707) 443-3093

IMPERIAL COUNTY

Thomas L. Wolfe, Director
Division of Environmental
Health Services
939 Main Street
El Centro, CA 92243
(619) 339-4203

Imperial County APCD
150 South 9th Street
El Centro, CA 92243
(619) 339-4314

INYO COUNTY

David A. Oldenburg, Director
Environmental Health
218 East Market Street
P.O. Box Drawer H
Independence, CA 93526
(619) 878-2411

Great Basin Unified APCD
157 Short Street, Suite 6
Bishop, CA 93514
(714) 872-8211

KERN COUNTY

Vernon S. Reichard, Director
Environmental Health
1700 Flower Street
Bakersfield, CA 93305
(805) 861-3636

Kern County APCD
1601 H Street, Suite 250
Bakersfield, CA 93301
(805) 861-3682

KINGS COUNTY

Dennis M. Otani, Director
Division of Environmental Health
330 Campus Drive
Hanford, CA 93230
(209) 548-1411, Ext. 2625

Kings County APCD
330 Campus Drive
Hanford, CA 93230
(209) 584-1411

LAKE COUNTY

Russell A. Mull, Director
Environmental Health
922 Bevins Court
Lakeport, CA 95453
(707) 263-2241

Lake County APCD
225 North Forbes Street
Lakeport, CA 95453
(707) 263-2391

LASSEN COUNTY

Paul Holmes, M.D.
County Health Officer
555 Hospital Lane
Susanville, CA 96130
(916) 257-8311, Ext. 108

Lassen County APCD
175 Russell Avenue
Susanville, CA 96130
(916) 257-8311, Ext. 110

LOS ANGELES COUNTY

Al Hearne
Environmental Management Deputy
Department of Health Services
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APPENDIX D:

THE CALIFORNIA WASTE REDUCTION PROGRAM

A. REGULATORY INCENTIVES

Objectives:

The regulatory element of the waste reduction program provides a major driving force for moving industry towards alternatives to land disposal. In addition, it provides some of the tools which are necessary for the Department to effectively implement the technical assistance and information transfer components of the program. Given this, the Department has set the following objectives:

- To provide a clear message that hazardous waste management in California must move towards waste reduction and away from land disposal.
- To ensure utilization of available technology for hazardous waste treatment.
- To require that industry be aware of and consider waste reduction whenever possible.
- To expand the California land disposal restriction program to coincide with the federal program.

Activities:

Land Disposal Restrictions -- California has implemented a regulatory program to phase out land disposal of certain hazardous wastes. California's land disposal restrictions prohibit land disposal of liquid wastestreams which contain any of the following materials above the indicated level:

1. Free cyanides (1,000 ppm).
2. Toxic metal waste:
   - Arsenic (500 ppm)
   - Chromium (VI) (500 ppm)
   - Mercury (20 ppm)
   - Selenium (100 ppm)
   - Cadmium (100 ppm)
   - Lead (500 ppm)
   - Nickel (134 ppm)
   - Thallium (130)ppm
3. Polychlorinated biphenyls (PCBs) (50 ppm).
4. Acid waste (below pH 2.0).
5. Liquid wastes containing halogenated organics (1,000 ppm).

A land disposal ban for an additional category of waste, solid hazardous wastes containing halogenated organic compounds in total concentrations greater than 1,000 ppm, was originally scheduled to go into effect July 1, 1985. This restriction was postponed until July 8, 1987 due to the lack of available treatment capacity in the State.

The implementation of the Toxic Pits Cleanup Act (Katz, AB 3566, 1984) tightened the restriction program by eliminating the use of surface impoundments for treatment. This legislation prohibited the use of surface impoundments for the treatment of restricted waste unless the Department issues a variance. The effective date of this restriction was January 1, 1986.

Another ban implemented by the Environmental Protection Agency (EPA) prohibits the landfilling of bulk liquids, even if absorbents have been added.

In the near future, EPA will be expanding its land restriction program in accordance with the provisions of the Hazardous and Solid Waste Amendments Act of 1984, which reauthorized the Resource Conservation and Recovery Act (RCRA). The next wastes to be banned will be spent or discarded solvents, which are scheduled to be prohibited from land disposal effective November 8, 1986.

The Department is also undertaking an assessment of the effectiveness of the California land disposal restriction program. This is being done in conjunction with an EPA-funded research grant.

Reporting Requirements -- California regulations have been modified to be consistent with federal law. Hazardous waste generators must now submit a biennial report to the Department that covers the type and quantity of hazardous waste shipped off site. Operators of treatment, storage, and disposal facilities must submit similar reports on the wastes they handled. The Department has, in the forms provided to generators and operators, requested additional information on the constituents and concentrations of materials in the wastestreams. These reporting requirements will improve the Department's ability to assess potential for waste reduction, facility needs, and compliance with the land disposal restrictions.

Another reporting provision which came into effect with the passage of AB 685 of 1985 requires that generators describe, in their biennial reports, waste reduction efforts and changes in waste generation from the previous year. These reports will assist the Department in developing case studies on effective waste reduction projects.

A third new reporting requirement for generators concerns changes to the Uniform Hazardous Waste Manifest. Generators shipping waste off site must sign a certification which states:

> "I also certify that I have a program in place to reduce the volume and toxicity of waste generated to the degree determined to be economically practicable and I have selected the method of treatment, storage, or disposal currently available to me which minimizes the present and future threat to human health and the environment."

Other Requirements -- SB 509 (Carpenter, 1985) was signed into law as Chapter 1338 of the 1985 statutes. This new law will restrict hazardous wastes which have a heating value of more than 3,000 BTUs per pound to incineration or treatment as the only means of disposal. This restriction is scheduled to go into effect on January 1, 1988. Regulations restricting land disposal of hazardous waste containing volatile organics above a range of one to eight percent (to be specified) are to be developed by the Department on or before January 1, 1990.

B. TECHNICAL ASSISTANCE

Objectives:

The technical assistance component of the program is designed to address companies' or industries' specific needs. As such, the objectives include:

- To design and conduct a statewide program of outreach and assistance for medium to small industries and businesses which generate hazardous wastes.
- To identify cost-effective process changes, waste management practices, and technologies to reduce generation of hazardous wastes for selected industrial categories.
- To increase recovery, recycling, and reuse of hazardous waste both on site and off site.

Activities:

The Depatment is continuing to develop its multifaceted technical assistance program. The program element activities include: wastestream-specific studies, operation of the California Waste Exchange, waste reduction audits for small businesses, direct assistance by Department staff, and joint studies with industry associations. The Department also has a Technical Reference Center with an extensive collection of publications, periodicals, and reference books on waste reduction and alternative treatment technologies.

Wastestream Studies -- The first wastestream study is an assessment of solvent waste management alternatives. Solvents were targeted because this is the first major wastestream to be addressed by the federal land disposal restrictions. The contractor who is carrying out this project for the Department will perform the following:

1. Review and analyze current solvent waste management methods and future trends as they relate to in-plant solvent waste reduction projects.

2. Review and evaluate literature on the solvent waste reduction methods in use in other states, Canada, Japan, and Europe. Identify those which seem to be most effective.

3. Identify major solvent user industries in California.

4. Identify existing solvent waste reduction alternatives in California, including input solvent substitution, product reformulation, process modification, on-site recovery, recycling, and methods to improve solvent recyclability, including contaminant reduction and wastestream segregation. Include a discussion of good example cases.

5. Make recommendations for on-site reduction that would reduce the transportation, off-site storage, and off-site facility siting for solvent wastes.

6. Identify on-site or off-site solvent recycling alternatives.

7. Make recommendations for off-site solvent management alternatives to land disposal.

8. Make recommendations for in-plant or on-site changes that can increase the on-site or off-site recycling potential (recyclability) of the solvent waste that is generated.

9. Review of available small on-site stills suitable for small generator applications.

10. Make other technical recommendations for management of solvent wastes that would promote the objective of solvent waste reduction/land disposal phase-out.

The results of the study, a final report, will be distributed under the technology transfer component of the program in October 1986.

Some candidates under consideration for future wastestream studies are metal-bearing solutions, pentachlorophenol waste, and wastes originating from the electronics industry.

Waste Audits -- The Department is addressing some of the needs of small businesses through waste audits. Contractors have been selected to provide waste audits for firms in the following industrial categories:

- Paint formulators.
- Pesticide formulators.
- Automotive repairs.
- Circuit board manufacturers.
- Automotive paint shops.

The consultants audit three to five companies within each targeted industry category. The results will be provided free of cost to the companies which agree to participate. Based upon these audits and their expertise, the consultants will develop self-audit checklists, which the Department will distribute to other companies within the targeted industrial categories. Additional industries will be targeted by future waste audit studies.

California Waste Exchange

The Waste Exchange utilizes three major avenues to encourage recycling. A Directory of Industrial Recyclers is published annually to inform generators about companies presently available to recycle their wastes. A Newsletter/Catalog is published on a triannual basis. More details about these activities are provided in Chapter 2.

Some of the most positive results of the Waste Exchange are produced as a result of the periodic review of manifests. Under the provisions of Section 66796 of the California Administrative Code, the Department can require generators to report on why they are sending wastes to land disposal when other options exist. Often, the generators are unaware of the alternatives. This is something the Waste Exchange staff can readily correct.

Direct Staff Assistance

Staff assistance is usually provided through referrals, policy, and regulatory interpretations, and assistance in complying with the very complicated permitting process for treatment and recycling facilities. Some of the more significant projects in which staff have been involved with include:

- The General Portland Cement Kiln hazardous waste incinerator.
- The Sun-Ohio and Exceltech mobile PCB treatment units.
- The Zimpro wet-air oxidation unit located at the Casmalia disposal facility.

C. INFORMATION/TECHNOLOGY TRANSFER

Objectives:

All of the components of the waste reduction program are important. However, this is, perhaps, the most important. If industry is not aware of the regulatory requirements, the waste reduction opportunities, and the economic incentive, they will not actively seek alternatives to land disposal. The objectives of this program element are:

- To make industry more aware of economic, technical, and environmental advantages of waste reduction.
- To establish credibility with industry concerning the State wishes to assist them in moving away from the land disposal of hazardous waste.
- To disseminate the information and facts resulting from other components of the State's hazardous waste reduction program.

This element of the program is to be accomplished through seminars, fact sheets, reports, etc. The number of people and/or industries reached by this element of the program may be one of the most effective measures of success for the waste reduction program. Indeed, there is no way to accurately measure how many companies have reduced their waste generation as a direct result of the State's waste reduction program. Most often, a company's final decision to seek alternative technologies for managing waste will be driven by a variety of factors, such as rising costs, liability, and new-found awareness of innovative promising technologies. Thus, the number of people reached by the program becomes all important. Even if only a small percentage are convinced to seek alternatives, a significant shift away from land disposal could occur if a large enough percentage of the total waste-generating population is contacted.

Seminars -- The first seminar, fully funded and sponsored by the Department, will be on Solvent Waste Management Alternatives. These are being done in conjunction with a contractor. The seminars are scheduled for October and will be held in Los Angeles and the San Francisco Bay Area. Details of the exact location and agenda for the seminars are now being developed.

In addition, Department staff regularly makes presentations on alternative technologies at conferences, privately sponsored seminars, and university extension courses.

Fact Sheets -- In an effort to simplify the extremely complex regulations which exist on hazardous waste management, the Department has prepared fact sheets which summarize some of the more salient areas. Fact sheets presently completed or in preparation include the following:

- Land disposal and treatment options.
- The land disposal restrictions.
- Waste battery requirements.
- The new resource recovery regulations.

Newsletter/Catalog -- As mentioned in the previous section, the Department publishes a newsletter/catalog. This publication has two purposes: First, the "catalog" lists hazardous wastes available and hazardous wastes wanted so that industry can buy, sell, or exchange their wastes. Second, it informs interested persons about developments in the field of hazardous waste, such as new laws and regulations, new technologies for recycling hazardous wastes, etc. ("newsletter").

Biennial Report -- Under the provisions of the Health and Safety Code, Section 25171, the Department is required to prepare a comprehensive report on treatment/recycling technologies and waste reduction.

D. ECONOMIC INCENTIVES

Objectives:

The economic incentives component of the DHS program consists of both positive and negative elements that lure and push generators into reducing hazardous wastes. The objective of the positive incentives is to assist generators in overcoming specific financial barriers to waste reduction. The objective of the negative incentives is to make land disposal less attractive to industry.

Activities:

Study of Economic Incentives -- The Department has recently completed a comprehensive assessment of economic incentives. This project was carried out by a consultant who assessed the effectiveness of various alternative mechanisms, such as grants, loan guarantees, loans, interest subsidies, tax credits, and accelerated depreciation. The study looked at existing financial assistance programs in California and in other states. Also, the study looked at the specific needs of California industries and identified the barriers to waste reduction, both technical and economic.

Hazardous Waste Reduction Grant Program -- Under the provisions of AB 685 (Farr 1985), a waste reduction demonstration grant program has been established and is administered by the Department (see Appendix C).

<u>Fees/Taxes</u> -- The fees and taxes associated with the Hazardous Waste Control Account and the Hazardous Substances Account provide the major negative incentive. At present these fees are only applicable to wastes going to land disposal and are structured to provide reduced rates for treatment residues.