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Hazardous Waste Treatment Processes

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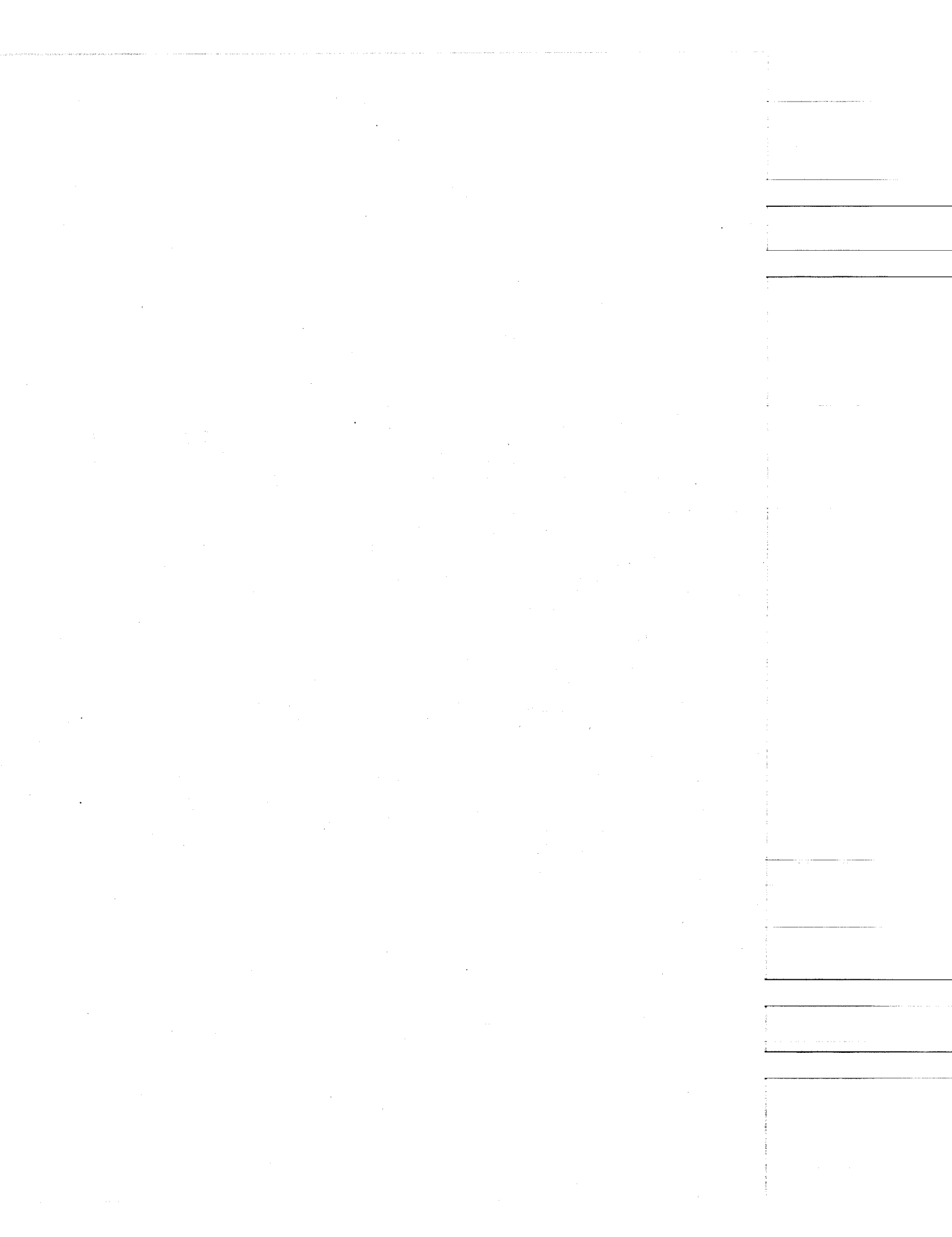
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Including Environmental
Audits and Waste Reduction



M A N U A L O F P R A C T I C E



Manuals of Practice for Water Pollution Control

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1989

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Hazardous Waste Treatment Processes

**Including Environmental Audits and Waste
Reduction**

Manual of Practice FD-18

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Preface

The purpose of this manual is to provide a description of the technical and regulatory approaches to hazardous waste treatment. It offers solutions to hazardous waste control problems and will be a useful tool to industrial environmental engineers and managers, practicing environmental engineers, and municipal agencies charged with the operation of a wastewater treatment facility or a solid waste landfill.

This manual should also be used by those responsible for hazardous waste management at private facilities or a public works department. It provides descriptions of the most widely applied technologies, including biological, physical, chemical, and thermal processes. This manual also includes guidelines for conducting environmental audits and approaches to waste reduction. It is intended for use and reference in planning, executing, and continuing a program of hazardous waste treatment.

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Chapter 1

Introduction

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***B**ACKGROUND*

Since World War II, the U.S. has experienced an industrial growth that has yielded the highest standard of living in the world. However, this way of life has created environmental concerns as to how to manage the increasing amounts of waste produced by industries and consumers. Recent estimates from the U.S. Environmental Protection Agency (EPA) indicate that this nation generates approximately 5.4×10^{12} kg (6 billion tons) of industrial, agricultural, commercial, and domestic waste each year. Of this figure, about 2.3×10^{11} kg (250 million tons) are considered hazardous waste. Over 90% of this waste is liquid.

A historical perspective shows that improper hazardous waste disposal has resulted in the contamination of the air, land, surface water, and groundwater, presenting potential risks to human health and the environment. A number of laws enacted by Congress have been directed toward a more effective hazardous waste management approach. In 1976, Congress enacted the Resource Conservation and Recovery Act (RCRA) authorizing EPA to regulate current and future waste management and disposal practices. The primary goals of RCRA are to

- Protect human health and the environment from the disposal of hazardous waste,

- Ensure that hazardous wastes are managed in an environmentally sound manner, and
- Reduce the amount of hazardous waste generated.

In 1984, Congress amended RCRA with passage of the Hazardous and Solid Waste Amendments (HSWA) to strengthen the approach to hazardous waste management developed in the earlier legislation. In particular, HSWA stated that the practice of land disposal was not safe and alternate treatment methods should be established.

The direct land disposal provisions in HSWA were in response to serious problems that were a consequence of Love Canal, N.Y., and Times Beach, Mo., which are examples of the philosophy of “out of sight out of mind” hazardous waste disposal practices. The passage of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and Superfund Amendments and Reauthorization Act (SARA) addressed the cleanup of inactive and abandoned hazardous waste sites.

Knowledge has been gained from the past. The policies that shape these laws present the framework for hazardous waste management for this country. These environmental mandates have three distinct focus areas:

- They address past practices through remediation. Past management of hazardous waste has created thousands of abandoned and inactive sites. EPA estimates that there are over 25 000 potentially dangerous sites throughout the nation. CERCLA and SARA provide the funding and policy framework for dealing with these problems. The WPCF Special Publication, “Hazardous Waste Site Remediation Management,”¹ provides guidance in this particular area.
- They control and require proper management of the waste currently generated. Increased regulatory authority such as RCRA; an expanded enforcement program; rising costs for handling, transporting, treatment, and disposal; concerns regarding future liabilities; and an adverse public image have demanded that effective and efficient controls of hazardous waste be employed. This Manual of Practice (MOP) will address this area in particular.
- They prevent creation of new hazardous waste problems through waste minimization. The promotion and enhancement of the reduction of the amount of waste generated through one or a combination of methods, such as source reduction and recycling, has recently become a more important factor in the proper management of hazardous waste. The HSWA set the national policy by declaring that, wherever feasible, the generation of hazardous waste is to be reduced or eliminated as expeditiously as possible. New legislative initiatives at the federal level and in many states will further promote the goals

of waste minimization. This MOP recognizes the importance of waste reduction and its relationship to treatment strategies.

The management of hazardous waste has become a critical issue to all sectors of society. In the engineering field, among government, in the company board rooms, at the plant, and throughout the public there is the recognition that answers to managing hazardous waste must be found. This challenge is complex, multidisciplinary, and multimedia. The demand for technically sound, implementable, and cost-effective approaches for treating hazardous waste is of immediate and growing concern. Types of waste that require proper management include solids, liquids, and vapors. They may be from manufacturing processes, wastewater stream spillage, discarded products, or construction materials.

There is general consensus that approaches to safe and efficient hazardous waste management are available. Extensive experience has been gained in treating industrial waste flows, giving us a reasonable foundation of scientific and technical understanding and knowledge. However, more needs to be learned about using these experiences to solve the complex problems faced today as an increasing number of mixed waste, solids, liquids, sludges, and soils require treatment.

In general, hazardous waste treatment is based on chemical structure. Compounds requiring treatment can be divided into two categories:

- Organic, which contain carbon as derived from or found in living things or man-made and capable of yielding electrons in oxidation reactions; and
- Inorganic, which do not contain carbon as an element and are incapable of yielding electrons in oxidation reactions.

Organic compounds as a class differ from inorganic compounds in several ways. They are combustible in air, usually have lower melting and boiling points, are less soluble in water, and are biodegradable. Reactions are molecular (that is, taking place one molecule at a time). As a result, equilibrium is very slow to develop. In addition, molecular weights can be very high, affecting properties such as solubility, volatility, and surface properties.

Organic compounds generally fall into categories based on their carbon linkage. For example, alkanes are carbon compounds linear in structure and saturated, and alkenes are unsaturated and aromatic (cyclic, benzene). Carbon compounds combined with sulfur, nitrogen, and oxygen represent another class that includes alcohols, ethers, ketones, esters, aldehydes, and amino compounds. Compounds that contain fluorine, chlorine, bromine, or iodine along with carbon and hydrogen atoms are another class of organic compounds called halogenated organic compounds.

The influence of these properties on the treatability of organic compounds can be subtle. Several factors should be kept in mind when attempting to deal with organic compounds.

- There are more than 300 000 identified organic compounds currently cataloged by the Chemical Abstract Service.
- About two-thirds have never been observed in air or water.
- Water-soluble compounds number in the tens of thousands.
- Most situations in the field involve mixtures (that is, more than one compound).

The complexity identifying and treating specific organic compounds can be overwhelming. For this reason, wastewater treatment practices incorporate nonspecific processes like carbon adsorption or biological treatment. These nonspecific processes generally follow a sequence of removal of classes of compounds from the easiest to the more difficult to remove. Depending on the mixtures of compounds present, the treatment objective of the wastewater treatment process is met incrementally with additional process units added to facilitate higher removals.

Inorganic compounds are distinguished from organic compounds by the fact that, in general, the inorganic compounds do not contain carbon. Except for cyanides, exceptions to this generalization are not significant in the context of treatment of hazardous substances in wastewater. For inorganic compounds, there are two general classes that encompass the broad variety of substances of interest in this context:

- Metals, or substances capable of giving up electrons in oxidation reduction reactions; and
- Nonmetals, or other substances that consist of oxygen, fluorine, chlorine, or sulfur.

Metals can be distinguished from nonmetals by two distinctive properties:

- Metals are substances that form salts with oxygen-bearing anions such as sulfate or nitrate.
- Metals form at least one oxide with a reasonably strong base to the limit of solubility.

This latter property can be used to further distinguish metals. Metal oxides or hydroxides are basic in character. They react with acids, especially with strong mineral acids such as hydrochloric, nitric, or sulfuric acid, to form salts. These product salts tend to be more soluble than the metal oxides or hydroxides themselves. Therefore, if a sample of a solid material exists in a

water solution, and this material dissolves in one of the mineral acids, the solid material is probably a metal oxide or hydroxide.

Nonmetals tend to form oxides that are acidic in character and they tend to react with bases but not acids. If a solid residue in a water solution dissolves when caustic soda (sodium hydroxide) is added, the substance could be a non-metal. Conversely, some insoluble hydroxides exhibit the property of being capable of being dissolved in both acids and bases. These compounds have the other characteristics of metals and are called amphoteric. Amphoteric metals include aluminum, cadmium, chromium, iron, and zinc, among others. The hydroxides of these amphoteric metals exhibit a minimum point of solubility that is pH dependent. This characteristic can be used to facilitate separation of the amphoteric metal hydroxide from other precipitated solids present.

Some metals are known as heavy metals. This characterization includes the amphoteric as well as other metals. Heavy metals are conveniently known by their chemical group and the relative position of the element with respect to sodium. Several heavy metals are very insoluble sulfides, a property that can be used in waste treatment to reduce the concentration of the heavy metal to very low levels.

OBJECTIVE

This Manual of Practice (MOP) is a presentation of current practice in the field of hazardous waste treatment. It offers technical solutions to hazardous waste control problems and should be a useful tool to industrial environmental engineers and managers, practicing environmental engineers, municipal agencies charged with the operation of wastewater treatment facilities or solid waste landfills, those responsible for hazardous waste management or part of a public works department, and citizens concerned about hazardous waste control problems in their community. This MOP includes discussions on a number of important topics including state-of-the-art approaches for managing hazardous waste; detailed descriptions of the most widely applied technologies (these technologies include biological, physical, chemical, and thermal processes); an overview of the application and use of hazardous waste treatment technologies, including the types and characteristics of waste handled by each technology; key design parameters that must be considered in the application of a technology; and regulatory requirements and their impact on the use of each technology. Table 1.1 provides a summary of the technologies covered by this MOP including the types of contaminants that each technology is capable of treating.

This MOP provides information on several important areas related to decisionmaking for hazardous waste management. Each technology chapter includes a discussion on waste characterization, treatability study require-

Table 1.1 Summary technologies.

Technology	Types of Contaminants
Biological	
Aerobic — Suspended, fixed film	Volatile organics, non volatile organics, phenol, phthalate esters, polycyclic aromatic hydrocarbons, PCBs, nitrogenous organic compounds, pesticides, solvents.
Anaerobic	Chlorinated solvents, phenolic compounds, polysulfide rubber waste-water, sulfonated benzene, nitrogen-substituted benzene.
Physical	
Clarification — coagulation, flocculation sedimentation, filtration (granular, membrane, ultrafiltration)	Aromatic hydrocarbon, polynuclear aromatics, phenolics, surfactants, chlorinated aromatics, solvents, chlorinated hydrocarbons.
Granular activated carbon (GAC)	
Air stripping	
Chemical	
Neutralization	Iron, organics, cyanide,
Oxidation	sulfides, phenol, benzene, metals.
Stabilization and solidification	
Precipitation	
Thermal	
Liquid and vapor incinerators	High organic waste, waste oils,
Catalytic vapor incinerators	halogenated solvents,
Fluidized bed	nonhalogenated solvents,
Rotary kiln	organic liquids, pesticides,
Multiple hearth	herbicides, PCBs.
Fixed hearth	
Wet oxidation	

ments, and the use of bench and pilot testing. Finally, the discussion considers safety aspects and new and innovative technologies.

This MOP also presents a comprehensive viewpoint on environmental auditing, waste reduction, and materials handling and storage as an integral part of managing hazardous waste. Environmental auditing involves identification of the points of hazardous waste generation and regulatory deficiencies in the operation. Once known, the points of waste generation can be changed or modified to improve the manufacturing and operational process to achieve better compliance with federal and state regulatory requirements. Waste reduction represents an economically beneficial response to growing regulatory requirements, higher disposal costs, and increased liability costs faced by both industry and government. Inventory controls, better housekeeping, process modifications, and materials substitution are several approaches

to waste reduction. Materials control is important in waste reduction. Whether they are raw materials for manufacturing, waste treatment chemicals, or wastes that are being stored, poor control results in higher costs. Changing the current operating practice for materials handling can produce short- and long-term benefits measured by less waste and a more stable and safe environment.

A key aspect to hazardous waste treatment is the proper selection of the treatment process train. This selection process is based on a number of site-specific factors:

- The chemical nature of the waste. Is it organic, inorganic, or mixed?
- The waste matrix. Is it solid, liquid, or gas?
- Hazardous versus nonhazardous stream.
- Treatment requirements, including
 - Ultimate disposal reuse,
 - Delisting considerations,
 - Zero discharge possibilities,
 - Discharge limitations (POTW or receiving stream),
 - On-site and off-site disposal, and
 - Permitting procedures.
- Unit process selection. Mixed waste streams have conflicting treatment objectives, result in equipment fouling, and can generate toxic byproducts.

As an illustration, Table 1.2 presents a conceptual treatment process for a liquid mixed waste stream. Four unit processes required to adequately treat the waste flow include phase separation, metals removal, organic treatment,

Table 1.2 Liquid treatment processes.

Phase separations first
Oil-free aqueous streams
Water free oil streams
Remove metals next
Will poison biological treatment
Will cause scaling in physical processes
Consider various treatment combinations for organics
Volatile with semivolatile
Biorefractory compounds, dioxins, pesticides
Chloride containing
Polishing treatment
Membrane
Thermal
Ion exchange

and finally polishing treatment as needed to meet stringent effluent limitations.

ORGANIZATION

This MOP has been structured so that each chapter provides information on a single topic and can be used independently. However, the MOP has both management and engineering details, so that problems identified through the application of the principles of the early chapters can be solved through the use of the treatment practices described in the later chapters.

The definition of hazardous waste treatment, the reasons for its importance, and who can make use of the information provided in this MOP are included in this introductory chapter. Methods for analyzing your operation to determine its regulatory deficiencies are described in Chapter 2. It presents the latest information on the various components and logical steps for a successful environmental audit, the elements of an environmental audit, and the regulatory policy associated with an environmental audit. Chapter 3 presents waste reduction techniques including a concise introduction to waste reduction concepts, insights into process evaluation, and a review of waste reduction technology such as inventory management, process modification, volume reduction, recovery, and reuse. Also presented are the components and approaches for implementing a waste reduction program. Chapter 4 presents operational techniques for hazardous materials and waste handling and storage. It includes such important topics as site location, structural considerations, compatibility, maintenance, management plans, and contingency planning.

The next four chapters describe treatment technologies under the broad headings of biological (Chapter 5), physical (Chapter 6), chemical (Chapter 7), and thermal (Chapter 8). Each of these chapters presents an in-depth discussion of the principals of each technology, waste process descriptions, basic design parameters, equipment descriptions, applicability, waste handling, treatability studies, specific regulatory requirements, and emerging technologies. Case studies are presented where useful to describe the technology and provide useful reference data.

Chapter 9 considers the integration of technologies into treatment trains to address complex and varied waste (that is, liquid, solid, sludges, organic, and inorganic waste). Waste character, design considerations, and options for ultimate disposal are covered in this chapter.

The definition of hazardous waste for purposes of this MOP will be the definition as defined in RCRA which states "garbage, refuse, or sludge or any other waste material." RCRA defines solid waste as a solid, semi-solid, liquid, or contained gas. RCRA also establishes that the definition meet certain criteria as they relate to quantity, concentration, characteristics, and an

increase in mortality, serious irreversible or incapacitating reversible illness, or potential hazard to human health and the environment.

EPA regulation establishes the process to determine whether a waste is hazardous and subject to hazardous waste regulations. This process includes

- Does the waste exhibit any of four characteristics (ignitability, corrosiveness, reactivity, or toxicity)?
- Is it a listed waste (source-specific based on specific industries such as petroleum refining and wood preserving)?
- Is it a generic waste such as a solvent or commercial chemical product (creosote, pesticides, and so on)?

Wastes included in this definition can be properly managed by the technologies as presented in this MOP. The regulatory requirements under RCRA and other statutes should be considered an important factor in decisionmaking. RCRA for example requires that generators manifest their waste. Treatment, storage, and disposal facilities that receive hazardous waste must receive an EPA permit that ensures compliance with established designs and operating criteria for safe operation. These requirements have substantial impact on the handling, treatment, storage, and disposal of wastes using the technologies covered by this MOP. RCRA regulations are codified in the Code of Federal Regulations (CFR), Parts 260-280. The code is updated annually and can be obtained from the U.S. Government Printing Office (Washington, D.C.). New and proposed regulations appear in the *Federal Register* (FR). A breakdown of 40 CFR 260-271 is provided in Table 1.3.

SARA deals with abandoned, inactive waste sites and establishes a program for private party or public funded cleanup. The federal National Contingency Plan (NCP) provides the framework for action such as the interaction between federal and state governments through the National and Regional Response team, policy such as how clean is clean, operating procedures, and enforcement requirements. The Clean Water Act (CWA), although generally viewed as a statute for water quality and wastewater treatment, includes certain provisions that are relevant to hazardous waste treatment. Industries discharging into waterways or publicly owned collection systems are being required to comply with toxic reductions. The Clean Air Act (CAA) established the National Emissions Standards for Hazardous Waste Pollutants (NESHAPS) to control the release of toxic substances that may adversely affect health. EPA has established NESHAPS for asbestos, beryllium, mercury, and vinyl chloride and has proposed standards for benzene and arsenic. Other CAA program areas include New Source Performance Standards (NSPS), Prevention of Significant Deterioration, Nonattainment Area Regulations, and Air Toxic Regulations. These regulatory requirements are discussed as they relate to hazardous waste treatment technologies. It is

Table 1.3 Outline for 40 CFR 260 – 271.

Part 260	General information, definitions, petitions.
Part 261	Hazardous waste identification system, criteria for listing and characteristics, lists of wastes and off-specification chemicals.
Part 262	Hazardous waste generator requirements, manifesting, pretransport, recordkeeping.
Part 263	Hazardous waste transporter requirements.
Part 264	Final standards for TSD facilities; contingency planning, preparedness, and prevention, manifesting, waste analysis, closure and postclosure care, groundwater monitoring, specific technical standards.
Part 265	Interim standards for TSD facilities that apply until a permit is issued.
Part 266	Standards for the management of specific hazardous waste and specific types of hazardous waste management facilities.
Part 267	Interim standards for new hazardous waste land disposal facilities.
Part 268	Land disposal restrictions.
Part 270	Hazardous waste permitting regulations for TSDs.
Part 271	Requirements for the authorization of state hazardous waste programs.
Part 280	Requirements for underground storage tanks.

suggested that the appropriate EPA or state agency be contacted when contemplating the selection of a specific hazardous waste treatment technology.

***R*EFERENCES**

1. "Hazardous Waste Site Remediation Management." Special Publication, Water Pollut. Control Fed., Alexandria, VA (1990).

Chapter 2

Environmental Audits — Internal Due Diligence

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12	Purpose	20	Pre-Audit Options for Information Gathering
13	Components of Successful Internal Due Diligence Audits	21	Conducting the Audit
15	EPA's Policy on Environmental Audits	32	Evaluation Phase
16	Types of Internal Due Diligence Audits	32	Audit Report and Follow-Up
17	Staffing Options for Audit Teams	33	Preserving the Confidentiality of Environmental Audits
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19	Planning	37	Suggested Readings

***I**NTRODUCTION*

There are several types of environmental audits being conducted throughout the U.S. today. Basically, audits are differentiated by their respective goals. Audits may also use somewhat differing approaches in order to accomplish these goals. One of the most prevalent types of audits is the transactional audit. These are performed during the acquisition, divestiture, or refinancing of an enterprise. These enterprises would typically include manufacturing facilities, laboratories, commercial facilities, and undeveloped land. Since environmental liabilities are transferred during a sale unless otherwise indemnified, transactional audits are commonly required by the lending institutions prior to finalizing the deal. This is also true for refinancing since environmen-

tal liabilities can be so costly that the survival of a facility could be jeopardized.

There are also regulatory or enforcement audits. These can be similar to the more routine inspections performed by regulatory personnel or can be part of a consent decree whereupon a facility is forced to have an audit performed by an independent group. This type of audit is requested to determine the general deficiencies that might exist at a site.

In recent years, audits have been performed with an emphasis on waste reduction or elimination. These audits often focus on the identification of waste sources and result in ideas for waste minimization and toxicity reduction through recycling, reclamation, material substitution, and so on. It is prudent to perform an Internal Due Diligence (IDD) audit prior to developing a waste reduction plan in order to include the complete facility and project the overall ramifications of the program. It can also be prudent to perform IDD audits subsequent to the implementation of a waste reduction program to assess its success and determine if other opportunities are available to affect further reductions.

The IDD audit is performed by company personnel or their outside contractors to evaluate the status of regulatory compliance and the ability of current standard operating procedures to meet the various needs of the facility in the areas of environmental, health, and safety concerns.

An IDD audit can be used to evaluate the efficiency of the current treatment technologies, or it can be used to help select various treatment options for a facility's hazardous waste. The efficiency of current waste treatment is assessed with respect to treatment performance (including maintenance and repair time), operational costs, and regulatory compliance. It is also critical to evaluate the hazardous waste treatment program in terms of capabilities versus anticipated changes (that is, residual limits, permitting, and so on).

As will be discussed later, the IDD audit can be comprehensive, addressing all aspects of a facility's environmental, health, and safety operations, or it can be focused. Focused audits target specific operations or concerns of the facility and are performed after an incident, a change in manufacturing processes, changes in the regulations, and so on. As indicated, different audits use different approaches. Much of the information provided about IDD audits, however, is applicable to all types of audits previously described.

PURPOSE

An IDD audit is a proactive, voluntary effort initiated by some level of management within a company. Its overall purpose is to identify any existing or potential problems so that remedies can be applied in a timely fashion.

The IDD audit is generally intended to accomplish one or more of the following tasks:

- Determine regulatory compliance status,
- Evaluate environmental management practices and facilities, and
- Identify risks and liabilities, including those attributable to past practices.

In some cases, compliance and consistency with corporate (and even facility) directives, policies, and procedures are also addressed.

The required corrective actions and recommended risk reduction measures resulting from audits can serve as the basis for long-term facility improvement plans and projected environmental control budgets.

Pertinent federal, state, and local environmental, health, and safety regulations are considered in comprehensive multimedia compliance audits. Practice and facility audits may evaluate the adequacy of

- Operating procedures;
- Maintenance programs;
- Staffing (type, number, and competence);
- Treatment, control, and monitoring devices; and
- Laboratory testing.

Risk and liability assessments are often extended to include items that are not required by law—for example, an evaluation of the potential for sudden or gradual hazardous chemical releases.

***C*OMPONENTS OF SUCCESSFUL IDD AUDITS**

Performance of an IDD audit needs the support of top management. This is especially true when an audit is performed for the first time at a facility. Management must communicate to all involved that this is a serious undertaking and that honest answers must be provided, even if the information is negative. This support must be felt through all subsequent levels of management at the given facility. Also there needs to be a commitment to follow up on the findings of the audit (from top management on down) or else it is a waste of time and funds. Commitment to follow up basically includes revising current practices and facilities to either affect regulatory compliance or providing better procedures by which given operations are performed. Additionally, management support is needed for the funds necessary to conduct an IDD audit. Significant expenditure of funds should be anticipated, especially if revisions are required.

Throughout the audit and the follow-up, individuals at the facility being audited must be prepared to spend additional time beyond that demanded by

their routine job tasks. Time is spent collecting the necessary information and duplicating materials for distribution to the audit team, as well as reviewing the standard operating procedures, regulatory requirements, and other associated data with the audit team both during the audit and in preparation of the report.

Another important component of a successful IDD audit is the creation of the audit team. The first aspect is selection of the team itself. One needs to find individuals whose expertise can assist the audit team leader in developing an accurate picture of the status of the facility. In addition, these individuals must have the time available to do their assigned task and a commitment to see that it is completed in a timely fashion. The impact on the daily duties of the individual, of course, varies from site to site. Each team member must not only be knowledgeable in his or her area of expertise, as previously mentioned, but must also be able to translate the requirements of the regulations and operating procedures to the real-world operations of the facility.

The team members must be impartial in their review of the status of the facility. Frequently, the most knowledgeable individual for a given area is the manager or supervisor of that area. If the audit team member is such an individual, negative or deficient areas within their own realm of responsibility must be accurately (impartially) reported. If this individual is too close to the situation to be objective, another audit team member or outside reviewer must be able to supply an accurate assessment. In any case, periodic audits by individuals completely independent of the audited facility are advisable.

A clear definition of the purpose of the audit should be provided to the audit team and those individuals who are required to respond to the demands of the team. Similarly, each member of the audit team must have a clear definition of his or her role in the conduct of the audit.

To expedite the audit, it is critical that the pertinent documents and personnel be readily available to the team. Availability means not only a presence in a file, but also that copies of all pertinent documents, such as laboratory results, permits, reports from internal or external consultants, relevant standard operating procedures, and training files are available for review and distribution. If these are not available, it is necessary that facility personnel know where any missing information can be obtained. As will be discussed later, guidance in this area of information retrieval and organization is often provided by a questionnaire. It is recommended that this questionnaire be given to facility personnel prior to the on-site phase of the audit, with sufficient lead time to answer the questions and prepare the documents files.

Throughout the audit, cross-checks need to be in place to ensure accuracy, consistency, and thoroughness. Cross-checks may be performed by asking the same question in different ways; asking the same question of facility personnel with different job functions; or reviewing and comparing records with common elements. Examples of such cross-checks include

- Reconciliation of waste disposal records (for example, manifests or certificates of destruction) with annual reports to regulatory agencies, and
- Comparison of hazardous material purchase records with waste disposal records.

The final phase of the IDD audit is the preparation and issuance of the audit report. This report should be concise and candid. It needs to address, in great detail, those areas of deficiency rather than those areas of good performance or compliance. Areas that are in compliance can, however, serve as a reference to help remediate deficient areas.

The audit report needs to be produced in a timely fashion so that the information in its contents remains accurate. It is also critical that the report be timely so that implementation of the recommendations can begin or additional study can be undertaken. Recommendations in the audit report might include

- No action,
- Revisions to the standard operating procedures,
- Issuance of standard operating procedures,
- Physical plant upgrades,
- Obtaining permits,
- Improved sampling and monitoring, and
- Additional study on the extent and impact of questionable areas that can not be readily determined from existing information (data, reports, and permits). Additional studies might, for example, be needed to determine ground water and soil contamination.

EPA'S POLICY ON ENVIRONMENTAL AUDITS

In July 1986, the U.S. Environmental Protection Agency (EPA) issued its final policy statement on environmental auditing (51 FR 25004). EPA's policy encourages the regulated community to develop, implement, and upgrade environmental auditing programs, because audits help ensure compliance with environmental regulations and lead to integrated management of environmental hazards. EPA believes that auditing should be a voluntary activity.

Copies of environmental audit reports will not be routinely requested by EPA, because such requests could serve to inhibit auditing activities. On a case-by-case basis, however, EPA may request all or portions of an audit report. Examples of these requests given in the policy statement are

- Audits conducted under consent decrees or other settlement agreements;
- Where a company places its management practices at issue by raising them as a defense; and
- Criminal investigations where state of mind or intent are of importance.

The regulated community is cautioned that certain audit findings may, by law, have to be reported to government agencies (for example, discovery of an unreported reportable quantity (RQ) release under the Comprehensive Environmental Response, Compensation, and Liability Act [CERCLA]), and also that audit reports cannot shield monitoring, compliance, or other information that would otherwise be reportable or accessible to EPA.

As a matter of general policy, EPA will not eliminate inspections or reduce enforcement responses in exchange for implementation of environmental auditing. On the other hand, effective audit programs should lead to an improved compliance status. To the extent that compliance performance is factored into assigning inspection priorities, facilities with a good history of compliance may be subject to fewer inspections. Furthermore, if a facility reports violations discovered during an audit which were not otherwise required to be reported, the EPA "may exercise its discretion to consider such actions as honest and genuine efforts to assure compliance" as relates to determining enforcement responses to violations. In certain cases, the EPA may stipulate environmental audits in consent decrees or other settlement negotiations where auditing could produce a remedy for identified problems and reduce the possibility of recurrences.

Federal facilities subject to the various environmental statutes and regulations are also encouraged to institute environmental auditing programs. EPA will provide technical assistance to other federal agencies in designing their audit programs. State and local regulatory agencies are encouraged to adopt EPA's auditing policies or similar policies.

***T*YPES OF INTERNAL DUE DILIGENCE AUDITS**

There are basically two types of IDD audits. One is comprehensive; the other is focused. The comprehensive audit addresses all aspects of environmental, health, and safety regulations and practices relevant to a given facility. This type of audit is performed to evaluate overall compliance with regulatory requirements and best management practices (BMPs). The duration of such an audit will vary according to the physical size of the plant, the complexity of the plant, and the number of members on the audit team. A comprehensive

audit may go on simultaneously in different areas of the facility if the auditing team is composed of independently functioning members. That is, one group might be addressing aspects relating to air discharges while another group is working with those individuals responsible for waste water treatment or hazardous waste management at the facility. Since it is frequently the case that only one individual has responsibility for environmental practices at a given facility, this approach may not be applicable.

It is not uncommon for a comprehensive audit to take between 1 and 5 days and be staffed by a team of up to 10 professionals. If it is a complex facility, it is helpful to convene a meeting at the end of each day to review what, if anything, significant has been found. If the audit involves simultaneous assessments of the various aspects of facility operations it is important that the team members interact while on site to help ensure the accuracy, thoroughness, and consistency of the audit being performed.

The focused audit is, as indicated by its name, more targeted and involves less time and fewer individuals on the audit team than the comprehensive IDD audit. Focused audits can be used after a facility incident, a change in process, a change in regulation, or as a follow-up to check areas that were targeted for revisions after a comprehensive audit. Because of their nature (that is, less manpower, time and cost), the focused audit can be performed more frequently and is often preferable to repeating a comprehensive audit. The results of the focused audit, however, must be included in the support documentation provided to audit teams performing future comprehensive audits.

STAFFING OPTIONS FOR AUDIT TEAMS

As has been discussed previously, a successful IDD audit team must be comprised of qualified, seasoned professionals capable of providing an impartial review of compliance and management practice situations. Company-internal personnel may form the audit team, as long as they can function independent of the entity being audited. Oftentimes, corporate staff conduct the audit, or the team is formed from a combination of corporate professionals and those stationed at other facilities in the organization.

Outside consultants and specialists may serve as audit team members as long as they are fully indoctrinated with regard to the audit's purpose and protocol. Consultants may be requested to conduct the audit in its entirety. External personnel, however, may not be well suited to evaluate compliance with company policies and procedures. If a sampling and testing program is to be implemented as a part of the audit (typically of a limited nature), cer-

Table 2.1 Reasons to use outside audit teams or team members.

-
- Facility too small to staff a team.
 - Facility personnel too busy to perform the audit.
 - Facility personnel lack expertise.
 - Management prefers an independent assessment.
 - More objective assessment.
 - Perceived anonymity of facility employees to independent auditors.
 - Multiple facilities can be compared for management consistency on corporate-wide issues.
-

tified laboratories and testing companies should be selected well in advance (see Table 2.1 for reasons to use an outside audit team).

Professionals from a variety of disciplines may be effective audit team members. Most commonly, audit professionals include the following disciplines:

- Environmental engineers,
- Environmental chemists,
- Chemical engineers,
- Civil engineers,
- Hydrogeologists,
- Industrial hygienists,
- Geotechnical engineers,
- Safety engineers,
- Atmospheric scientists,
- Health physicists,
- Nuclear engineers,
- Environmental attorneys, and
- Environmental control managers.

Frequently, the experience and expertise of the auditor is more important than the educational background. For example, an environmental engineer experienced only in industrial wastewater treatment would be an inappropriate auditor for the air pollution control topic. Hydrogeologists are essential for evaluating the adequacy of groundwater monitoring programs or corrective actions at land disposal facilities, but in most cases they are not trained to assess spill prevention control facilities and plans.

It is absolutely imperative that auditors possess a strong background in the federal, state, and local regulations they will be dealing with in the audit.

It is highly desirable for audit team members to have dual capabilities (a primary and secondary expertise). This allows for audit interaction and, generally, a more conclusive end product. Also, such an audit team can divide work assignments if unanticipated problems develop at the site.

AUDIT ELEMENTS

PLANNING. Since environmental IDD audits, especially comprehensive audits, represent a major commitment of time, personnel, and funding, planning is an essential element. Planning comes down to communication before, during, and after the audits. This communication is necessary for scheduling the site visit, determining the availability of facility personnel, and other aspects that will be discussed later. Communication must be complemented by organization. Usually, there is little time to waste. Examples of difficulties that could arise because an audit has been poorly organized is that people do not know where to go; data or reports are not available; and requirements for entry (such as physicals or personnel protective equipment) have not been met. Communication is also extremely important in delivering the message to facility personnel of what is needed and why.

Other aspects in the auditing planning phase include obtaining appropriate security clearances for team members touring the facility. Another concern is adequate working space for the audit team members. Areas must be set aside where team members can write notes, review notes, review documents, and, if necessary, have confidential discussions with various site personnel and other audit team members. This space should also have telephones and access to support personnel for rapid, on-site duplication of documents.

The logistics of an audit, especially in a large, complex plant, can be very involved. There must be planning relating to intrasite travel. Some facilities are millions of square yards under roof. The use of in-house travel can be essential for conducting an efficient audit in a large facility. These conveyances must be available, charged, and dedicated for the period of the audit. Another important aspect is having the proper safety equipment available should areas require hard hats, glasses, respirators, or special clothing. Team members need to have equipment that fits properly so that the possibility of accidental exposure is reduced. This includes fit testing for respirators. Audit team personnel must have appropriate medical monitoring. Additionally, if the audit is occurring on a Superfund site, certain training requirements must be met and documented prior to audit team entry.

Another aspect of planning for an audit is "contingency." Some contingencies are manageable than others. A prime example is weather. This includes weather that could delay the arrival of the audit team from off site, as well as weather that can impact the review of external areas of the facility. If sampling is involved during the audit, weather might preclude implementation of the sampling program (for example, surface water or ground is frozen).

Another contingency encountered by the audit team is an unanticipated manufacturing downtime at the time of the IDD audit. It is frequently critical to have the processes up and operating in a normal mode during an audit to assess ambient air sources and the resulting internal and external air quality,

wastewater discharges, sources of waste generation, and so on. Audits, therefore, should not be scheduled during operational downtime or during periods of nonroutine processing. (Note: Job shop facilities need to be evaluated on both an integrated and worst case basis.)

A final aspect in the planning phase are legal consideration. These are addressed in detail later in this chapter.

ETIQUETTE. During an IDD audit an adversarial relationship should not be generated. Etiquette, or more appropriately, the approach to facility personnel, should be friendly but serious. The auditor needs the assistance of facility personnel. An individual might have some trepidation about reporting deficiencies in his area. Also, it is possible that the audit may not be taken seriously. This is especially true when there have been no previous difficulties or need for an audit. Frequently individuals interviewed during an audit may be hostile or unable to understand exactly what is needed. Therefore, a question needs to be asked several times, in different ways, until the interviewee understands what is needed. Also, questions often need to be asked several times if the answer seems deficient or off target.

The approach should be in a friendly, nonaggressive manner. Audits are sometimes made more difficult in that inexperienced auditors may "attack" the various personnel as though they were on a witness stand. This is usually not the best way to obtain information, although in some instances it may be the only way. The auditor needs to go to a higher level of supervision or management if answers or information are not forthcoming.

Another area of "audit etiquette" relates to how and when outside (regulatory) agencies should be contacted to obtain information without prematurely raising flags that could cause unnecessary problems for the facility.

Auditors must understand the need for confidentiality before, during, and after the audit. It is not appropriate to share the audit results with others, including facility staff, without team leader and client approval.

As a courtesy, the auditors should, if at all possible, stick to the schedule so that the time set aside by the interviewees is not exceeded and the overall timetable for touring the facility is maintained. This, however, is frequently not possible. Facility personnel should be amenable to schedule changes when additional information is needed or delays are incurred. If possible, additional time should always be left at the end of each audit day so that timetables can be maintained and those interviews which run over can be completed.

PRE-AUDIT OPTIONS FOR INFORMATION GATHERING. The most common and useful mechanism for obtaining information about a site before the visit is a targeted questionnaire. A preprinted questionnaire with space available for answers, comments, and attachments should be forwarded

to the appropriate site personnel with a request to complete and forward by a certain date so the audit team can review them prior to going on site. This approach is frequently employed on IDD audits. It is not a viable option for other types of audits such as enforcement audits or audits implemented prior to acquisitions, refinancing, and so on, which are usually performed in a very short time. The questionnaires should be as simple as possible, but should address all aspects of the audit. Additionally, photographs, drawing, maps, and process flow diagrams should be provided to the audit team prior to going on site.

Requests to carry a camera on site and take pictures should be made as early as possible. Photographs and videos are quite useful not only for jogging the memories of the audit team members during report preparation but are also helpful for reviewing a given situation with people who have not been on site.

Receipt of documents requested is integral to developing a quality audit. These documents include permits, correspondence with regulatory agencies, analytical results, manifests, and copies of standard operating procedures relating to environmental, health, and safety programs at the facility. Also included in this information are copies of the last audit reports, both comprehensive and focused.

The time saving aspects of pre-audit information gathering can be exemplified by the review of manifests. The review of manifests indicates a facilities wastes were taken. It is frequently important to identify these sites in order to determine the status of the site regarding CERCLA or Superfund designations. Significant costs can be incurred if a facility is identified as a contributor to a site that is targeted by federal or state regulatory agencies for cleanup. This information, however, frequently takes a while to be received from the state and federal government. Requests often must be in writing. Any head start on this procedure would be beneficial in the timely completion of the audit report.

CONDUCTING THE AUDIT. Site Features And Operations. Early in the audit procedure, it is essential that the audit team develop a solid understanding of the nature of the facility being audited. This should include general location and layout information, an overview of environmental conditions, and a thorough description of site operations. Table 2.2 provides a summary of the types of data that have proven useful in an IDD audit. Without this profile, the team will not be able to conduct a thorough audit of the site.

Major Topic Areas. Practitioners are well aware of the ever-increasing number of environmental statutes and regulations. In Table 2.3, the principal environmental regulations are grouped according to major topic areas for comprehensive, multimedia environmental audits. The components of typical audit evaluations for these topics are described below. Undoubtedly, the first

Table 2.2 Site features and operations profile.

General information

- Location map
- Site topographic and property boundary map
- Site plan (buildings and environmental facilities)
- Fencing and security
- Buildings (area, type, and age)
- Surrounding land usage
- Closest residential area
- History of property ownership

Environmental conditions

- Proximity of floodplain and surface waters
- Vegetative cover
- Known threatened or endangered species

Environmental conditions

- Nearby surface impoundments (ponds, pits, and lagoons), landfills, dumps, and treatment sites)
- Subsurface drainage (number and locations of drains, routing, and discharge)
- Previous and on-going environmental investigations of nearby facilities
- Community relations
- Utility suppliers (electricity, water, gas, sewage, and refuse)
- Zoning and land use restrictions
- Air quality maintenance area (AQMA)
- Attainment and nonattainment status
- Previous audit reports and findings

Facility operations

- Previous owners, operators, and land use
 - Types and dates of major facility changes or additions
 - Process descriptions
 - Process flow diagrams
 - Applicable Standard Industrial Category (SIC) codes
 - Process changes over time
 - Major raw materials and method of delivery
 - History of fires, explosions, and major releases
 - Comprehensive chemical inventory
 - Material storage (drums, tanks, bins, and so on)
 - Employees (number, shifts, and unions)
 - Operations schedule (number of days per week, hours of operation, and so on)
 - Product or sales brochures
 - Expansion and modification plans
 - Environmental impairment liability (EIL) insurance
-

Table 2.3 Principal environmental regulations.

Topic	Key statutes and regulations
Air emissions	• Clean Air Act (CCA) • New Source Performance Standards (NSPS) • State Implementation Plan (SIP) • National Emission Standards for Hazardous Air Pollutants (NESHAPs) • State and local permitting and emissions regulations • Emergency episode plan requirements • Wastewater discharges • Clean Water Act (CWA) • Effluent limitations guidelines • National Pollutant Discharge Elimination System (NPDES) regulations • Pretreatment regulations • Local sewer use ordinance • State water quality standards • Toxic Substances Control Act (TSCA) regulations • Occupational Safety and Health Administration (OSHA) regulations
Water supply	• Safe Drinking Water Act (SWDA) • Drinking water standards and testing requirements • State withdrawal permits
Solid and hazardous waste	• Resource Conservation and Recovery Act (RCRA) • Hazardous waste regulations (federal and state) • State solid waste regulations • Hazardous Materials Transportation Act (HMTA)
Chemical and oil storage	• Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) • Hazardous substance release reporting requirements • Emergency Planning and Community Right-to-Know Act (EPCRA) • Oil spill prevention control and countermeasure (SPCC) plans • BMPs under the NPDES program • Underground storage tank (UST) regulations • OSHA regulations for storage • Local fire codes • State requirements

Table 2.3 Principal environmental regulations (continued).

Topic	Key statutes and regulations
PCBs	• TSCA • Usage, storage, and disposal regulations under TSCA • Hazardous waste land disposal restrictions
Pesticides	• Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) • FIFRA registration, certification, and disposal regulations
Injection wells	• Underground injection control (UIC) permit system • Hazardous waste land disposal restrictions
Health and safety	• OSHA regulations • OSHA permissible exposure limits (PELs) • Hazard Communication Standard (HCS) State requirements • RCRA hazardous waste management training
Radioactive substances	• NESHAPs • Uranium Mill Tailings Radiation Control Act • State regulations • Nuclear Regulatory Commission (NRC) regulations • Department of Energy (DOE) requirements

comprehensive audit at a facility will be the most time consuming. Subsequent audits can simply build on the historical data gathered during the first audit.

AIR EMISSIONS. The auditor should ask the facility to identify and locate all sources of air emissions. For each source, the contaminants present, gas flow volume, emission rates, and control devices should be defined. Emission permits should be reviewed to ensure that they have been secured where required; they have not expired, or renewals have been requested; and special conditions are being complied with. Permit applications should be evaluated to see if accurate emission and control data were supplied to the regulatory agency. Ideally, the auditor will inspect each source to verify data received and assess the efficacy of control devices. maintenance, inspection, and monitoring records should be evaluated to check for problems. Emission test

reports and monitoring instrument calibration data (for example, for continuous emission monitors [CEMs]) should be secured and reviewed.

Facility expansion and modification dates should be correlated to applications for new permits or permit modifications. Reports of regulatory agency inspections and notices of violations (NOVs) should be summarized to assess historical (and possibly ongoing) compliance patterns.

Records retention practices should be reviewed to see if the required records are available. It should be determined if NSPs, NESHAPs, or state air emission standards apply to any of the emissions, and if compliance with the standard is being achieved. The auditor should see if the facility has banked emission reduction credits which may be useful if expansions are desired in the future. State regulations should be reviewed to determine if an emergency episode plan is required at the facility. Also, the auditor should define air emission requirements under other programs, such as RCRA standards for hazardous waste management facilities. Finally, the auditor should determine if the facility is fully compliant with prevention of significant deterioration (PSD) and emission offset requirements for nonattainment areas.

WASTEWATER DISCHARGES. The results of recent in-plant wastewater surveys should be reviewed in summary form so that the auditor has an appreciation of the sources, volumes, and pollutants in the wastewater discharges. Discharges should be categorized as sanitary (sewage), process wastewater, cooling water (contact or noncontact), storm water, or combinations of these. Treatment or pretreatment facilities should be evaluated by obtaining and reviewing process flow diagrams and material balance data, process design criteria, unit sizing, engineering reports, plans and specifications, and operation and maintenance (O&M) manuals. A walk-through inspection should include discussions with operational supervisors. The physical condition of the treatment units, operational capability, competence of operators, operator licensing compliance, and so on should be assessed.

Outfalls or discharge points should be visually examined to check for obvious problems (for example, oily visible sheen, floatable solids, or highly colored or odorous discharges). Current versions of NPDES permits or indirect discharge permits should be obtained and evaluated with respect to compliance, especially for effluent limits. Pertinent categorical effluent guidelines should be identified.

The last 3 to 5 years of discharge monitoring reports (DMRs) should be reviewed to assess effluent performance. A copy of the local sewer ordinance should be obtained to verify compliance. The most recent permit applications should be checked to verify that accurate and complete data were provided. Sample collection, preservation, and analysis protocols should be evaluated with regard to appropriateness and permit conditions. The auditor should determine if certified laboratories are used for discharge analyses and if a laboratory audit program and quality assurance program are in effect.

Facility personnel should be asked if there are or were septic tanks at the site, the nature of the discharges, and if local permits and approvals were obtained. Expansion and modification dates should be correlated to new or modified permits and applications. Reports of regulatory agency inspections and NOV's should be summarized to assess historical compliance patterns and on-going problems. The adequacy of records retention practices should be confirmed.

WATER SUPPLY. The sources of water used should be determined. The auditor should determine if local water supply connection authorizations (and backflow preventors) or surface water or groundwater withdrawal permits have been obtained and are current. Evaluations of the adequacy of water treatment systems may be part of the audit scope. If the facility has its own drinking water supply, the auditor should check compliance with the SDWA standards and testing programs. Raw and finished water quality data should be summarized for review. The auditor should determine if there is reason to believe that present or future raw water quality will deteriorate. Nearby water usage points should be identified to determine if the facility being audited may affect the quality of off-site surface water intakes or groundwater wells. As with other topics, regulatory inspection, NOV's, and records retention practices should be included in the site assessment.

SOLID AND HAZARDOUS WASTES. The facility should be asked to provide a listing of the names, characteristics, generation rates, classifications, and disposition of all hazardous and nonhazardous wastes generated by or received at the site. The disposition should discuss on-site and off-site storage, treatment, disposal, recycling, recovery, reuse, and reclamation. Historical practices should be defined where they differ from the current situation.

The auditor must determine if the facility has done an adequate job of identifying and characterizing its wastes (for example, hazardous waste determination). The hazardous waste notification form should be reviewed for accuracy (that is, consistency with manifests and current waste production). The hazardous waste site classifications should be defined. These include

- Conditionally exempt small quantity generator,
- Small quantity generator,
- Transporter,
- Treatment facility,
- Storage facility, or
- Disposal facility.

The names, locations, and license and identification numbers of waste transporters should be obtained. The auditor must evaluate the adequacy of

waste transportation practices. For example, proper preparation of manifests, vehicle placards, loading and unloading procedures, and history of transportation spill incidents should be reviewed. For facilities that also own hazardous waste and material transport fleets, a focused audit of transportation procedures may be necessary (incident response, driver qualifications and training, and so on).

The audit team should evaluate the adequacy of written programs and actual practices for the hazardous waste facility standards, such as preparedness and prevention, contingency plans, inspections, training, storage practices, record-keeping, reports, and so on; The quarterly, annual, or biennial reports of hazardous waste activity submitted to regulatory agencies should be checked for accuracy. Facility expansion and modification dates should be correlated to applications for new permits or modifications to current permits. Reports of regulatory agency inspections and NOV's should be summarized to assess historical and on-going compliance patterns.

At permitted hazardous waste treatment, storage, and disposal (TSD) facilities, the auditors should obtain and review copies of the Part A and Part B permit applications and interim status or final operation permits. The audit team should assess adherence with the pertinent regulations and with the approved plans in the permit applications (for example, the waste analysis plan). For TSD facilities, it is suggested that the audit team use the checklists developed by the EPA's National Enforcement Investigations Center (NEIC). For hazardous waste units subject to groundwater monitoring, the EPA's RCRA Technical Enforcement Guidance Document (TEGD) on Groundwater Monitoring has a series of useful checklists.

Previous on-site disposal practices should be scrutinized extensively, including pits, ponds, lagoons, waste piles, landfills, storage areas, treatment units, burners, flares, incinerators, spill areas, and so on. The auditor should learn as much as possible about each past practice, such as size, waste characteristics and quantities, period of operation, and closure procedures. The auditors should determine the status of the RCRA Facility Investigation (RFI) Corrective Measures (CM) program for continuing releases from previous or existing solid waste management units (SWMUs).

The facility may have filed a CERCLA 103(g) form with EPA for notification of previous on-site disposal practices. If so, the auditor should determine if a preliminary assessment/site inspection (PA/SI) has been conducted and obtain a copy of the report. This information should be considered to determine if the facility has potential liability for CERCLA cleanup.

The recently promulgated prohibitions on land disposal of certain hazardous waste (also called the "land ban") have had a profound effect on generators and TSD facilities (40 CFR 268). The auditor should assess the validity of generator certifications and disposal facility adherence to the regulations.

Current and previous off-site waste disposal practices should be renewed to ensure compliance and define possible liabilities. The audit team should

define the names, locations, and overall compliance status of off-site management facilities. The facility should be asked to describe the mechanisms in place, if any, to minimize company liability (for example, disposal contracts or periodic audits). The appropriate facility personnel should be asked if they have shipped wastes to Superfund sites and if they are a potential responsible party (PRP) in any cleanup proceedings.

Waste oil handling practices and solid waste TSD practices should be evaluated for compliance during each audit. However, the regulations vary considerably from state to state and the auditor must check each site on a state-specific basis.

CHEMICAL AND OIL STORAGE. The audit team should begin their assessment of chemical storage practices with the chemical inventory and material storage information developed during the site features and operations profile. In addition to compliance with the various regulatory programs, the audit team should determine if there is a significant potential for either sudden or nonsudden releases of hazardous substances or oil to the environment. This can be accomplished by review of leak detection devices, spill containment provisions, spill contingency plans, and so on.

The facility chemical inventory should be reviewed to determine which of the materials are hazardous substances under the auspices of the CERCLA. Facility personnel should be questioned to determine whether they are aware of the RQ values for the hazardous substances and to determine if reporting procedures are well understood and followed. The release history of the facility should be examined to determine if improved management practices are necessary or if contingency plans should be modified.

The EPCRA was a part of the 1986 CERCLA amendments. The facility being audited may be subject to one or more of the emergency planning and reporting requirements contained in the EPCRA. The audit team should obtain copies of the facility's reports to responsible authorities for Sections 311, 312, and 313 of the EPCRA; these refer to material safety data sheets, emergency and hazardous chemical inventory forms, and toxic chemical release reporting, respectively. These should be evaluated for completeness and accuracy. The audit team should determine if the facility has or should prepare an emergency or contingency plan to deal with fires, explosions, or other hazardous substances incidents. Such a plan may transcend the hazardous waste contingency plan and oil spill prevention plan.

The oil shortage inventory and practices at the facility should be reviewed to determine if there is a requirement for the facility to have an oil SPCC plan. If such a plan is required, the auditors should determine its adequacy according to the regulations (40 CFR 112).

As part of its NPDES permit, the facility may have been required to prepare a BMP plan to minimize the possibility of releases of toxic or hazardous substances. If this is the case, the audit team should review the BMP plan

for compliance with permit conditions and the BMP guidance documents. The audit team should also determine if the facility is complying with the programs set forth in their own plan.

Underground storage tanks have been widely used for the storage of petroleum and hazardous substances. The facility should be asked to provide an inventory of these tanks along with information on the results of previous leak tests, installation details, and whether spill protection, cathodic protection, and leak protection are provided. The audit team should evaluate this information in the context of UST regulations promulgated under Subtitle I of the 1984 RCRA amendments and by state-specific regulations. Depending on the age of the tank system, the regulations provide for a phased compliance period for corrosion protection, leak detection, and spill and overfill control. There are also specific requirements for financial responsibility assurance. The regulations also contain requirements for UST system closure and corrective action in the event of a release. Appropriate facility personnel should be asked to describe closure plans and corrective action in the event of a release. Facility personnel should be asked to describe the program for compliance with these regulations and the audit team should determine its adequacy.

Certain hazardous substances are regulated under the OSHA regulations and local fire codes. These include flammable materials, among others. Facility personnel should be asked if they are aware of any building or fire code violations, and the audit team should obtain copies of recent fire insurance or fire marshal inspections. Certain states have promulgated regulations regarding the storage of hazardous substances. For example, New Jersey has enacted a Discharge Prevention Control and Countermeasure Plan requirement and a Discharge Cleanup and Removal Plan requirement for certain hazardous materials as well as a Toxic Catastrophe Prevention Act.

POLYCHLORINATED BIPHENYLS (PCBs). The use of storage, and disposal of PCB-containing materials is regulated under TSCA. Facility personnel should be asked to provide an inventory of PCB-containing items such as transformers, capacitors, lighting ballast, high-temperature hydraulic oils, and PCB wastes. Annual reports and inspection data should be correlated to manifests for off-site disposal. The hazardous waste land ban regulations contain certain restrictions for the disposal of PCB materials. If the facility has received a permit from the EPA for PCB waste management, it will be necessary for the audit team to fully evaluate compliance with these regulations in the same manner as for the hazardous waste management regulations.

ASBESTOS. The manufacturing, use, and disposal of asbestos and asbestos-containing materials is regulated under the NESHAPs, TSCA regulations, and OSHA regulations. The audit team should evaluate the facility for the presence of friable asbestos materials. It may be that a follow-up asbestos sur-

vey is in order if one has not already been completed. Asbestos containing insulation may be present around boilers, steam pipes, other heated vessels, and in ceiling insulation and floor tiles. The auditors must determine if manufacturing and demolition or renovation work are in compliance with these regulations.

PESTICIDES. Pesticide use in the U.S. is regulated under FIFRA, which contains certain requirements for the registration, certification, and disposal of pesticides. Some state-specific laws also apply. These regulations are most important to manufacturers and applicators of pesticides, and audits of these types of operations are usually considered to be product liability audits rather than environmental audits. Nonetheless, facilities should be questioned regarding their use of pesticides to ensure that proper application and disposal practices are used.

INJECTION WELLS. Underground injection control is regulated under a permit system as part of the SDWA regulations. Various classes have been established for different types of injection wells. The audit team should determine if injection wells are used at the facility and if operations are in compliance with the regulations. It should be noted that the land ban regulations have restricted the injection of various hazardous wastes.

HEALTH AND SAFETY. Audits of this topic may be conducted separately or as part of a facility environmental audit. Health and safety audits typically concentrate on compliance with the OSHA regulations, although building and fire code topics are often included. The auditors should determine if the company requires preemployment physicals, periodic medical monitoring, and so on. Especially important are the PELs for various chemicals and if the company has performed chemical exposure monitoring in the past. If PELs have been exceeded, the auditors should determine if the company has taken appropriate remedial action. The results of any noise monitoring facility should be obtained and reviewed to determine if the facility is required to have a hearing conservation program under OSHA regulations. Hearing conservation techniques and protective equipment should be described by facility personnel, as well as the results of any audiometric testing programs being conducted. The need for and adequacy of personnel protective equipment (PPE) should be assessed. All OSHA citations, building and fire code citations, and alleged unsafe working condition grievances during the last 3 to 5 years should be reviewed to check for patterns and trends. Record retention policies should be reviewed for adequacy and compliance. The auditors should determine if the facility has a written HCS program and if the program is adequate, including training of employees. Oftentimes, the adequacy of RCRA hazardous waste management training is assessed as a health and safety audit topic. Special attention should be given to training documenta-

tion records. It should be noted that many states have their own health and safety statutes that might be more stringent than the federal OSHA requirements.

RADIOACTIVE SUBSTANCES. The manufacture, use, and disposal of radioactive substances is regulated under a variety of programs by EPA, NRC, DOE, and the various states. Depending on the facility, it may be that health physicists or nuclear engineers are required to conduct this portion of the audit.

OTHER CONCERNS. If the audit team is to evaluate compliance with corporate and facility standard operating procedures and policies, it may be necessary to add a full-time auditor to the team for this particular topic. EPA has the authority to regulate certain types of noise sources under the Noise Control Act. Prior to the site visit, the audit team leader should determine if this particular concern needs to be addressed during the audit.

Audits of analytical and testing laboratories used by the facility are often conducted as a separate exercise from the overall environmental audit. Experienced analytical chemists should conduct these audits. At certain facilities, specialized topics may be added to the audit agenda, such as marine protection and coastal area regulations.

Lastly, it should be realized that there are certain topic areas that go beyond the focus of the traditional multimedia environmental audit of a facility. This would include review of premanufacture notifications under TSCA or pesticide registration under FIFRA. In many cases, the records and personnel that will be of importance to these topics will be at corporate offices rather than at site locations.

Methods To Obtain Necessary Information. The audit team can use a number of effective methods to obtain information and evaluate the facility. First hand, visual site inspections are extremely important. It is suggested that the auditors initially take a quick walk-through of the entire facility. This is followed by detailed inspection visits of the various units being audited. Site personnel interviews constitute one of the major methods of information gathering. auditors should be careful to document in their notes the date, time, name, and title of the person being interviewed. Historical photographs and maps are useful in understanding the evolution of a particular facility. Photographs taken during the audit site inspection are useful in refreshing the memory of the audit team as well as in presenting the results to management.

At a minimum, the types of files to be reviewed during the on-site audit include permits and permit applications, correspondence with regulatory agencies, internal and external reports, laboratory results, shipment manifests, and engineering and scientific investigatory reports. There are a variety of published checklists in the literature that the audit team might find

quite useful. In some cases, regulatory compliance information may be gathered by review of agency files; however, the auditors should be discrete in order to maintain the confidentiality of the audit. Obviously, it is extremely important that any additional regulatory interpretations that are required be obtained. The auditors should not hesitate to seek outside assistance in these matters when necessary.

EVALUATION PHASE. Prior to writing the audit report, all the information obtained during the site visit and the hard copies of the documentation need to be reviewed. The review may be performed by the audit team leader or as a joint effort with the various team members addressing their respective areas of expertise. The primary focus in evaluating the data is the determination of compliance or noncompliance of the facility with local, state, and federal regulations. Next is the determination of the effectiveness of the physical plant, policies, and practices of the facility in those areas relating to the environmental, health, and safety concerns. In addition to determining the effectiveness of the policies and practices, the auditor needs to address whether the employees are actually in compliance with these policies, especially if the effectiveness appears to be less than desired. Along with evaluating the environmental and health impacts, the auditor needs to determine if some of the impact in these areas reflects the physical condition of the facility and operating equipment, rather than the policies and practices themselves.

Once the auditor has determined the compliance or noncompliance with regulations, the efficacy level of the policies and practices, and the condition of the facility's equipment, he needs to evaluate the risks and potential liabilities associated with the existing situation. Frequently, the risks and associated liabilities can be reported on a percent probability basis. The costs for liability and remediation can then be estimated accordingly, if desired.

AUDIT REPORT AND FOLLOW-UP. The audit report should provide a concise summary of the results of the environmental audit. Facility description information is often summarized in appendices to the document or is presented in a very brief form in the document. The various sections of the audit report should be prepared by the auditors responsible for a given topic area. Once the draft report is complete, it is advisable that the team leader distribute copies to other members of the audit team to ensure consistency and to allow for a more refined product. Once the draft audit report is approved for release, it should first be distributed to facility personnel in order that they may correct any misconceptions. Most importantly, they need to understand what is required to correct deficiencies and provide schedules for these corrective actions. In most companies, the corrective action list and its implementation schedule is subject to approval by upper management.

The final report includes the corrected draft report along with the implementation schedule for required actions. The final audit report should be issued as soon as possible after completion of the field work, so that there is minimal loss of interest and momentum.

Finally, the company should provide for follow-up review to ensure that corrective actions are completed properly and on schedule. This follow-up step is absolutely essential to make the audit an effective management tool.

PRESERVING THE CONFIDENTIALITY OF ENVIRONMENTAL AUDITS

The environmental audit is a valuable tool for corporations to use in identifying and evaluating potential environmental problems. Maintaining the results of environmental audits as confidential within the corporation helps to encourage the free flow of information regarding past and present environmental practices, and thereby enhances the accuracy and effectiveness of the audit process.

Unfortunately, one must undertake an environmental audit recognizing that no environmental audit possesses an absolute guarantee of confidentiality. Many of the facts discovered during an audit (as distinguished from legal opinions and legal advice) are afforded little or no protection from ultimate disclosure in connection with government investigations and government and third-party litigation. Nevertheless, there are certain procedures that a corporation can institute that can heighten the possibility of keeping the environmental audit results and reports confidential and privileged.

The use of legal counsel to perform the audit may allow a corporation to take advantage of attorney-client privilege or the attorney work-product doctrine. When corporate management assumes primary authority for performing an audit, the corporation's ability to keep the information confidential and privileged from compelled disclosure, while still possible, is less likely.

Generally, communications made to an attorney by the client are protected by the attorney-client privilege. However, for the privilege to apply, the attorney must be used to provide legal advice. Thus, merely submitting factual information to an attorney will not preserve the confidentiality of the material submitted. The communication must be made with the attorney for the purpose of receiving advice or counsel. In determining whether or not counsel has been retained for the purpose of providing legal advice, courts focus on the authority given to the attorney in connection with the environmental audit and the attorney's responsibilities with respect to analyzing the data contained in the report. Counsel should be authorized to undertake a review of the corporation's compliance with and potential liabilities for violations of

environmental laws by investigating all environmental matters relating to a corporation's operations.

In order to ensure that legal counsel has the proper authority to implement an environmental audit, the board of directors of the corporation should authorize the performance of the audit by counsel through a corporate resolution. The resolution should set forth the corporation's objectives in having the environmental audit performed. In adopting such resolutions, the corporation cannot only assert its environmentally sensitive goals in performing the audit, it may also set the stage for a subsequent claim of confidentiality. The corporation can resolve to seek legal advice in connection with all findings developed during the course of the environmental audit and to request the recommendations of counsel. The board's resolutions are also the appropriate time to make known the board's desire that the audit and its results be kept confidential and privileged. The board of directors' resolutions also present a good opportunity to instruct management to comply with the audit program and provide the information requested by counsel. Of course, before undertaking any audit or setting forth such an objective, it is essential that the company decide to correct the deficiencies noted in the audit and comply with notification and reporting requirements. Otherwise, an audit serves only to underscore the willfulness of any violations.

The next requirement for establishing a claim of attorney-client privilege is that there be a communication between a client and an attorney. In the context of a corporation, the definition of client is not restricted solely to the most senior employees or board members. The clients may include any corporate employee whose communications to counsel are necessary in order for the attorney to render legal advice and who assists in the investigation which management has asked the counsel to undertake. Thus, the facility operation manager's communications to counsel are entitled to the same privilege as those of the director of the environmental office.

The privilege, however, only protects disclosures of communications. It does not protect disclosure of the underlying facts by those who communicated with the attorney. Therefore, the facts of the violations known to the company employees are discoverable from that employee; communication of those violations to the attorney and the attorney's advice may not be discoverable in the first instance.

Many corporations use their in-house environmental staff or environmental consultants to conduct the audit. If the audit is structured such that the in-house staff or consultants are conducting the audit to "assist" in providing legal advice, communications to these nonlawyers may also be treated as privileged. In-house staff and consultants may assist by conducting the fact-gathering portions of the audit, with the company's lawyers supplying the conclusion and advice regarding compliance. A third requirement for the attorney-client privilege to apply is that the communication to counsel be kept confidential by the company. If the audit report itself or the investiga-

tion notes are permitted to be circulated among a corporation to anyone other than those with a need to know, a court will be reluctant to consider the reports confidential. Thus, the disclosure to the attorney's in-house "assistant" and the attorney may be privileged as would the attorney's response back down the chain.

In contrast, the corporation's random or inadvertent disclosure of the attorney's advice with respect to the violations may not be privileged. Clearly, senior corporate management and those who need to implement corrective action are entitled to see the reports, and such disclosure should not put any privilege at risk.

Stamping documents as confidential and privileged and maintaining them as such within the confines of the corporation would greatly assist the corporation in later establishing a claim of confidentiality. Segregating the results of the audit into a nonconfidential report of fact that uses the non-privileged information and a confidential report that relies on both non-privileged and privileged information that has been kept confidential will also aid in showing that the requisite care has been taken in protecting the privilege.

Once it is determined that the materials are to be kept confidential and privileged, care must be taken to ensure that the privilege is not waived. By publicizing a confidential report for certain purposes, the corporation may lose its ability to keep it confidential for other purposes. For example, an audit report for one facility should not be volunteered to customers if the corporation later may want to refrain from disclosing an audit report in some litigation.

In addition to the protections afforded by the attorney-client privilege, the work-product doctrine may aid in providing protection to the audit. Simply stated, the work-product doctrine provides a qualified immunity from discovery of materials prepared by or for counsel in anticipation of litigation. The protection extends to investigations conducted by nonattorneys to assist counsel; however, the materials that contain the mental impressions, opinions, or legal theories of an attorney warrant the most protection. The work-product doctrine does not extend to facts or even the existence of the audit report. Opposing counsel can overcome the protection by showing "substantial need" for the materials and "undue hardship" in obtaining the equivalent from other sources.

In order to avail oneself of the work-product doctrine, the threshold requirement is that the audit is undertaken in anticipation of litigation. Litigation does not have to be imminent; a court will look to the specific situation surrounding a document to determine whether it was actually prepared in anticipation of litigation. The most important inquiry for a court is to determine the primary motivating purpose behind the creation of the document. Litigation that is reasonably predictable, or that is identifiable from specific claims that have already arisen will generally satisfy the anticipation of litigation.

tion test. Thus, if fear of or preparation for litigation does prompt the initiation of the audit, the board of directors' resolution and correspondence to counsel should generally document the reasons for the corporation's anticipation of litigation.

In summary, a corporation increases the likelihood that an environmental audit will be considered confidential and privileged by authorizing counsel to conduct the environmental audit for the purpose of giving legal advice and by ensuring that a corporation's employees are assisting counsel in providing legal advice in any auditing activities. Moreover, all communications to and from counsel should be made in confidence, stamped "confidential and privileged" and kept confidential.

Finally, EPA issued an Environmental Auditing Policy Statement on July 9, 1986. EPA asserts in that policy that

"EPA has broad statutory authority to request relevant information on the environmental compliance status of regulated entities. However, EPA believes routine agency requests for audit reports could inhibit auditing in the long run, decreasing both the quality and quantity of audits conducted. EPA will not routinely request environmental audit reports."

"EPA's authority to request an audit report or relevant portions thereof will be exercised on a case-by-case basis where the Agency determines it is needed to accomplish a statutory mission, or where the government deems it to be material to a criminal investigation."

Thus, except in extenuating circumstances such as a pattern of violations, it is unlikely that EPA will test the confidentiality of a corporate environmental audit. Alternatively, the mere existence of an auditing program will not insulate a corporation from liability if EPA discovers the existence of violations through monitoring, compliance reports, or other information or records required to be made available to EPA. An environmental audit is not a substitute for the corporation's legal responsibility to monitor, record, or report information discovered during the audit.

C ONCLUSIONS

The information resulting from a well-performed IDD audit can be a very powerful tool for ensuring compliance and minimizing liability. Audits can save many times their costs by preventing penalties and fines and by reducing time lost due to accidents or downtime for equipment. Audits used to identify (potential) problems can save money in legal and disposal costs. Audits can identify operations to streamline and improve practices to increase production. Audits can also be used to identify (and prevent) environmentally deleterious discharges and improve or maintain community relations.

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Chapter 3

Reduction Of Hazardous Waste

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An environmental audit or the results of reporting requirements such as those of Superfund Amendments and Reauthorization Act (SARA) Title III may encourage an organization to consider the advantages of operational changes leading to reduced hazardous waste generation. Regulatory burdens can be reduced, process economics can be improved, and long-term liability costs can be decreased. The increased public interest and concern about the quantity and risk of waste produced by industrial operations is likely to result in rewarding well-planned and measurable efforts to reduce waste with significant dividends in community relations and acceptance.

The principles of waste reduction apply not only to existing industrial operations but also to projected new facilities. With new facilities the economic impact can be particularly favorable because initial equipment

selection and return on investment determinations can be made based on optimized material use and minimized waste disposal costs. A similar waste minimization assessment during the design phase can also have significant favorable impact.

This chapter discusses examples of proven approaches to hazardous waste reduction in specific industries and generic approaches to waste minimization. The chapter concludes with a description of the process for identifying opportunities for waste reduction in existing facilities, as well as in proposed facilities and operations.

***I*NTRODUCTION TO HAZARDOUS WASTE REDUCTION**

Liquid, solid, or gaseous waste materials are generated during the manufacture of products. In addition to environmental problems, these wastes represent losses of valuable materials and energy from the production process requiring a significant investment in pollution control. Traditionally, pollution control focuses on “end-of-the-pipe” and “out-the-back-door” viewpoints. The control of pollution in this way requires manpower, energy, materials, and capital expenditures. Such an approach removes pollution from one source, such as wastewater treatment or air pollution abatement, and places it somewhere else, such as a landfill.

Added regulations, higher disposal expenses, and increased liability costs have caused industrial and governmental leaders to begin critical examinations of end-of-the-pipe pollution control measures. The value of waste reduction has become apparent to industries looking at broader environmental management objectives rather than concentrating solely on pollution control. Waste reduction is very often economically beneficial for an industry and also results in improved environmental quality.

Waste reduction should be a key component of any cost-effective, comprehensive waste management program. Reduction techniques do not have to be based on high technology or large capital expenditures. Many techniques require simple changes to the way materials are handled in the production process. The techniques used in a management program to minimize waste generation are discussed in detail in the following section. An approach for developing and implementing a multimedia waste reduction program using these techniques is presented later in this chapter.

***H*AZARDOUS WASTE REDUCTION TECHNIQUES**

Hazardous waste reduction techniques can be applied to any manufacturing process from something as simple as making a paper clip to as complex as assembling the space shuttle. Available techniques range from easy operational changes to state-of-the-art recovery equipment. The common factor in these techniques is that they reduce operational costs.

Waste reduction techniques can be broken down into four major categories as shown in Table 3.1. Because the classifications are broad there will be some overlap. In actual application, waste reduction techniques generally are used in combination to achieve the maximum effect at the lowest cost.

Table 3.1 Categories of waste reduction techniques.

Inventory management
Inventory control
Material control
Production process modification
Operation and maintenance procedures
Material change
Process equipment modification
Volume reduction
Source segregation
Concentration
Recovery
On-site recovery
Off-site recovery

INVENTORY MANAGEMENT. Proper control over raw materials, intermediate products, final products, and the associated waste streams is an important waste reduction technique.¹ In many cases waste is just out-of-date, off-spec, contaminated, or unnecessary raw materials. Wastes can also be spill residues or damaged final products. The cost of disposing of these materials not only includes the actual disposal costs but the cost of the lost raw materials or product. Methods for controlling inventory range from simple changes in ordering procedures to implementing just-in-time (JIT) manufacturing techniques. Many companies can reduce their waste generation by tightening up and expanding their current inventory control programs. This will significantly impact the three major sources of hazardous waste resulting from improper inventory control: excess, out-of-date, and no-longer-used raw materials.

Purchasing only the amount of raw materials needed for a production run or a set period of time is one of the keys to proper inventory control. Excess

Purchasing only the amount of raw materials needed for a production run or a set period of time is one of the keys to proper inventory control. Excess inventory often must be disposed of because it goes out-of-date. Better application of existing inventory management procedures should reduce this problem. This should be coupled with education programs for purchasing personnel on the problems and costs of disposing of excess materials. Additionally, the expiration dates should be evaluated, especially for stable compounds, to determine if they are too short.

Developing review procedures for all materials purchased is another step in establishing an inventory control program. Standard procedures should require that all materials be approved prior to purchase. In the approval process all production materials are evaluated to determine if they contain hazardous constituents, and if so, what alternative nonhazardous substitute materials are available. Development of the review procedures can be made either by one person with the necessary chemistry background or a committee made up of people with a variety of backgrounds. It may be possible to obtain needed information from the Material Safety Data Sheets (MSDSs) provided by the chemical supplier. Many companies from electronics to textiles have established successful material review programs.^{2,3}

The ultimate in inventory control procedures is JIT manufacturing, since this eliminates the existence of any inventory. This is done by directly moving raw materials from the receiving dock to the manufacturing area for immediate use. The final product is then shipped out without any intermediate storage. Just-in-time manufacturing is a complex program to implement and cannot be used by all facilities; however, it can reduce waste significantly. For example, using JIT techniques 3M Company reduced waste generation by 25 to 65% in their individual plants.¹

PRODUCTION PROCESS MODIFICATION. Improving the efficiency of a production process can significantly reduce waste generation. Some of the most cost-effective reduction techniques are included in this category; many are simple and relatively inexpensive changes to production procedures. Available techniques range from eliminating leaks from process equipment to new state-of-the-art production equipment. The waste reduction techniques in this category can be divided into improved operation and maintenance, material change, and equipment modification.

Operational Procedures. A wide range of methods are available to operate a production process at peak efficiency. These methods are neither new nor unknown and are usually inexpensive to institute, since little or no capital cost is necessary. For example, a producer of breaded foods instituted a number of operational changes such as dry cleanup, installing or modifying drip trays under process equipment, and developing better systems for collection and handling of waste material. This decreased water usage by about 30%,

wastewater by almost 80%, and allowed the company to sell 5 200 000 lb/yr (2 359 000 kg/a) of solids to recovery firms.⁴

Improved operation procedures are quite simply methods that make optimum use of the raw materials used in the production process. Some examples are shown in Table 3.2. The first step in instituting such a program is to review all current operational procedures and examine the production process for ways to improve its efficiency. A review should include all segments of the process, from the delivery area through the production process to final

Table 3.2 Examples of operational changes to reduce waste generation.

• Reduce raw material and product loss due to leaks, spills, drag-out, and off-spec process solution.	• mechanical wall wipers or squeegees; using pigs or compressed gas to clean pipes, and increasing drain time.
• Schedule production to reduce equipment cleaning. For example, formulate light to dark paint so the vats do not have to be cleaned out between batches.	• Segregate wastes to increase recoverability.
• Inspect parts before they are processed to reduce the number of rejects.	• Optimize operational parameters (such as temperature, pressure, reaction time, concentration, and chemicals) to reduce by product or waste generation.
• Consolidate types of equipment or chemicals to reduce quantity and variety of waste.	• Develop employee training procedures on waste reduction.
• Improve cleaning procedures to reduce generation of dilute mixed waste by using methods such as: dry cleanup techniques;	• Evaluate the need for each operational step and eliminate those that are unnecessary.
	• Collection of spilled or leaked material for reuse.

product storage. Procedures on how to conduct such a review are presented later in this chapter.

One important area commonly overlooked or not given proper attention is material handling procedures. Proper material handling will ensure that the raw material reaches the production process without loss of material through spills, leaks, or contamination. It also will ensure the material is efficiently handled during the production process.

Once proper operating procedures are established they must be fully documented and made part of the employee training program. A comprehensive training program is a key element of any effective waste reduction program. For example, through training, a dairy plant, a semiconductor manufacturer, and a furniture plant reduced waste by 14, 40, and 10%, respectively.⁵⁻⁷ For a program to be effective, all levels of personnel should be included, from the

line operator to the corporate executive officer. The goal of any program is to make the employee aware of waste generation, its impact on the company and the environment, and ways it can be reduced. Written materials should be prepared and used in conjunction with hands-on training. This should be an ongoing process with review updates and interaction between employees and supervisors on a regular basis.

Maintenance Programs. One company found that 25 to 50% of its waste load was due to poor maintenance.⁸ A strict maintenance program that stresses corrective and preventive maintenance can thus reduce waste generation caused by equipment failure. Such a program will help identify potential sources of release and correct the problem before any material is lost. A good maintenance program is important because the benefits of any waste reduction program can be wiped out by just one process leak or equipment malfunction.

A maintenance program can include cost tracking and preventive maintenance scheduling and monitoring. To be effective, a maintenance program should be developed and followed for each operational step in the production process, with special attention to potential problem points. A strict schedule and accurate records of all maintenance activities should be maintained. Computer-based maintenance scheduling and tracking programs are available from a variety of vendors. A comprehensive program should also include predictive maintenance. This approach provides the means to schedule repairs or replacement of equipment based on the actual condition of the machinery. A number of nondestructive testing technologies are available for making the needed evaluations for this approach.

Material Change. Hazardous materials used in either a product formulation or in a production process may be replaced with a less-hazardous or non-hazardous material. Reformulating a product to contain less-hazardous material will reduce both the amount of hazardous waste generated during the product's formulation and end use. Using a less hazardous material in a production process will generally reduce the amount of hazardous waste produced. This can, in turn, reduce the cost of capital equipment needed to meet environmental regulatory limits. Some examples of material change to reduce waste generation are given in Table 3.3.

Product reformulation is one of the more difficult waste reduction techniques, yet it can be very effective. Examples of product reformulation include eliminating pigments containing heavy metals from ink, dye, and paint formulations; replacing phenolic biocides with other less toxic compounds in metal-working fluids, and developing new paint, ink, and adhesive formulations based on water rather than organic solvents.

Table 3.3 Examples of waste reduction through material change.

Industry	Technique
Household appliances	Eliminated cleaning step by selecting a lubricant compatible with the next process step.
Textile	Reduce phosphorus in wastewater by reducing the use of phosphate-containing chemicals.
Aerospace	Replace cyanide cadmium plating bath with a non-cyanide bath.
Ink manufacture	Remove cadmium from product.
Textile	Use UV light instead of biocides in cooling towers).

Hazardous chemicals used in the production process can also be replaced with less- or nonhazardous materials. Changes can range from using purer raw materials to replacing solvents with water-based products. This is a very widely used waste reduction technique and is applicable to many industries. Many of these changes involve switching from a solvent to a water-based process solution. For example a diesel engine remanufacturing facility switched from cleaning solvents and oil-based, metal-working fluids to water-based products. This change reduced their coolant and cleaning costs by about 40%. Additionally, the company was able to eliminate one cleaning step and machine filters lasted twice as long, thus reducing material and labor costs.⁹

One important area that is sometimes overlooked in making a material change is its impact on the total waste stream. Switching from a solvent-based to a water-based product can increase wastewater volumes and concentrations. This can adversely affect the current wastewater treatment system, cause effluent limits to be exceeded, and possibly increase wastewater treatment sludge production. Therefore, before any change is made, its impact on all discharges must be evaluated.

Process Equipment Modifications. Waste generation may be reduced by installing more efficient process equipment or modifying existing equipment to take advantage of better production techniques. New or updated equipment can use process materials more efficiently, producing less waste. Additionally, higher-efficiency systems may reduce the number of rejected or off-specification products, thereby reducing the amount of material that has to be disposed of or reworked. Some examples of process modifications are given in Table 3.4.

Modifying existing process equipment can be a very cost-effective method to reduce waste generation. In many cases, relatively simple and inex-

Table 3.4 Examples of production modifications for waste reduction.

Process step	Technique
Parts cleaning	• Enclose all solvent cleaning units. • Use refrigerated freeboard on vapor degreaser units. • Improve parts draining before and after cleaning. • Use mechanical cleaning devices. • Use plastic bead blasting.
Surface finishing	• Prolong process bath life by removing contaminants. • Redesign part racks to reduce drag-out. • Reuse rinse water. • Install spray or fog nozzle rinse systems. • Properly design and operate all rinse tanks. • Install drag-out recovery tanks. • Install rinse water flow control valves. • Install drip racks and drainboards.
Surface coating	• Use airless air-assisted spray guns. • Use electrostatic spray-coating systems. • Control coating viscosity with heat units. • Use high solids coatings. • Use powder coating systems.
Equipment cleaning	• Use high-pressure rinse systems. • Use mechanical wipers. • Use counter-current rinse sequence. • Reuse spent rinse water. • Use "pigs" to clean lines. • Use compressed gas to blow out lines.
Spills/leaks	• Use bellow-sealed valves. • Install spill basins or dikes. • Use seal-less pumps. • Maximize use of welded pipe joints. • Install splash guards and drip boards. • Install overflow control devices.

pensive changes in the way the materials are handled within the process can ensure that they are not wasted or lost. This can be as easy as redesigning parts racks to reduce drag-out in electroplating operations, installing better seals on process equipment to eliminate leakage, or installing drip pans under equipment to collect leaking process material for reuse. One chemical company reduced the waste from a sump in a production area from 70 000 to 3000 lb/yr (31 750 to 1360 kg/a) by installing a sight glass, using better pump seals, and purchasing a broom.¹⁰

Installing new, more efficient equipment and, in some cases, modifying current equipment will require capital investment in equipment, facility modifications, and employee training. The extent of the investment will vary over a large range depending on the type of equipment used. These investments, however, can have a rapid payback. For example, a power tool manufacturer replaced a spray solvent paint system with a water-based electrostatic immersion painting unit. This new equipment paid for itself in just over 1 year by reducing raw material costs by \$600 000/yr, reducing waste disposal costs by 97%, and greatly increasing productivity.¹¹

VOLUME REDUCTION

Volume reduction includes techniques to separate toxic, hazardous, or recoverable wastes from the total waste stream. These techniques are usually used to increase recoverability; reduce the volume and thus disposal costs; or

Table 3.5 Examples of waste reduction through volume reduction.

Industry	Technique
X-ray film	Segregate polyester film scrap from other production waste and recycle.
Printed circuit boards	Use filter press to dewater sludge to 60% solids and send sludge to metal recovery.
Pesticide formulation	Use separate bag houses, as each process line and recycle collected dust into product.
Paint formulation	Segregate and reuse tank cleaning solvents in paint formulations.
Furniture	Segregate and reuse solvents used to flush spray coating lines and pumps as coating thinner.

increase management options. The available techniques used range from simple segregation of wastes at the source to complex concentration technologies, as shown in Table 3.5. These techniques can be divided into two general areas: source segregation and waste concentration. Only those methods that are actual waste reduction techniques will be discussed in this section.

SOURCE SEGREGATION. Segregation of wastes is, in many cases, a simple and economical technique for waste reduction. For example, by segregating wastes at the source of generation and handling the hazardous

and nonhazardous wastes separately, waste volume and thus management costs will be reduced. Additionally, the uncontaminated or undiluted wastes may be reusable in the production process or sent off-site for recovery.

This technique is applicable to a wide variety of waste streams and industries, and usually involves simple changes in operational procedures. For example, in metal finishing facilities, wastes containing different types of metals can be treated separately so that the metals in the sludge can be recovered. Keeping spent solvents or waste oils segregated from other solid or liquid waste may allow them to be recycled. Wastewater containing toxic material should be kept separate from uncontaminated process water, reducing the volume of water that must be treated.

A commonly used waste segregation technique is to collect and store wash water or solvents used to clean process equipment (such as tanks, pipes, pumps, or printing presses) for reuse in the production process. This technique is used by paint, ink, and chemical manufacturers as well as by printers and metal fabricators. For example, a printing firm segregates and collects toluene used for press and roller cleanup operations. By segregating the used toluene by color and type of ink contaminant, it can be reused later for thinning the same type and color of ink. The firm now recovers 100% of the waste toluene, totally eliminating a hazardous waste stream.¹¹

CONCENTRATION. Various techniques are available to reduce the volume of a waste through physical treatment. Such techniques usually remove a portion of a waste, such as water. Available concentration methods include gravity and vacuum filtration, evaporation, ultrafiltration, reverse osmosis, freeze vaporization, filter press, heat drying, and compaction. Many of these are actually recovery techniques and will be discussed further in the next section.

Unless the material can be recycled, just concentrating a waste so more can be fit into a drum is not waste reduction. In some cases concentration of a waste stream may also increase the likelihood that the material can be reused or recycled. For example, filter presses or sludge driers can increase the concentration of metals in electroplating wastewater treatment sludge to such a level that they become a valuable raw material for metal smelters. A printed circuit board manufacturer dewateres its sludge using a filter press to 60% solids. The company receives \$7200/yr from the sale of the dewatered sludge for copper reclamation.¹¹

***R*ECOVERY**

Recovering wastes can provide a very cost-effective waste management alternative. This technique can help eliminate waste disposal costs, reduce raw material costs, and possibly provide income from sale of the waste. Recovery

Table 3.6 Examples of waste reduction through recovery and reuse.

Industry	Technique
Mirror manufacturer	Recover spent xylene using a batch-distillation system.
Printed circuit boards	An electrolytic recovery system used to recover copper and tin/lead from process wastewater.
Power tools	Recover alkaline degreasing baths using an ultrafiltration system.
Hosiery	Reconstitute and reuse spent dye baths.
Pickles	Transfer waste brine pickle solution to a textile plant as a replacement for virgin acetic acid.
Chemical manufacture	Spent electrolyte from one division used as raw material by another.

of wastes is a widely used practice in many manufacturing processes and can be done on-site or at an off-site facility, as shown in Table 3.6.

The effective use of recovery depends on the segregation of the recoverable waste from other process wastes or extraneous material. This ensures that the waste is uncontaminated and the concentration of recoverable material is maximized. Some companies have assigned the responsibility for the handling, collection, and scheduling of recovery of waste material to one individual.^{4, 12} This helps ensure that the maximum value of the waste can be recovered.

ON-SITE RECOVERY. In most cases the best place to recover process wastes is within the production facility. Wastes that are simply contaminated versions of the process raw materials are good candidates for in-plant recycling. Waste can be recovered most efficiently at the point of generation. The possibility of contamination with other waste materials is reduced, as is the risk involved with handling and transporting waste materials.

Some waste streams can be reused directly back into the original production process as raw material. This is usually accomplished when the waste material is lightly contaminated or is excess raw material. Examples include cleaning waste from printers, coaters, and chemical or product manufacturers; electroplating drag-out solutions; process solutions from filter changes; and dust collector residue from pesticide manufacturers. Lightly contaminated waste can sometimes be reused in operations not requiring high-purity materials. For example, spent high-purity solvents generated

during the production of microelectronics can be reused in less critical metal degreasing operations, or a caustic waste material can be reused to treat an acid waste stream.

Some waste may have to undergo purification before it can be reused. A number of physical and chemical techniques can be used to reclaim a waste material. These range from simple filtration to state-of-the-art techniques such as freeze crystallization. The method of choice will depend on the physical and chemical characteristics of the waste stream, recovery economics, and operational requirements. Most on-site recovery systems will generate some type of residue (that is, the contaminants removed from the recovered material). This residue can either be processed for further recovery or it should be disposed of properly. The economic evaluations of any recovery technique must include the management of these residues.

OFF-SITE RECOVERY. Wastes may be recovered at an off-site facility when the equipment is not available on-site, when not enough waste is generated to make an in-plant system cost effective, or when the recovered material cannot be reused in the production process. Off-site recovery usually entails recovering a valuable portion of the waste through chemical or physical processes. Some materials that are commonly reprocessed off-site are oils, solvents, electroplating sludges and process baths, lead-acid batteries, scrap metal, food processing waste, plastic scrap, and cardboard. The cost of off-site recycling will depend on the purity of the waste and the market for the waste or recovered material.

In some situations a waste may be transferred to another company for use as a raw material in its manufacturing process. This exchange can be economically advantageous to both firms as it will reduce the waste disposal costs of the generator and reduce the raw material costs of the user. For example, an X-ray film manufacturer produces a saleable product from waste film stock. The company installed equipment that flakes and bales waste polyester-coated film stock. This is then sold as raw material to another firm. Over 20 million lb (9 million kg) of film stock is exchanged each year, representing a \$200 000 annual savings in collection, transport, and processing costs, and an annual profit of \$150 000 from the sale of the materials.¹¹

The upgrade of a waste into a product requires a strong commitment from the generator to find markets, both inside and outside the company, for the waste material. In some cases the production process or the waste may have to undergo some modification to make a more saleable product. Regional waste exchanges have been set up by a number of states to help companies find markets by acting as information clearinghouses of wastes available and wanted. The service usually offered is a listing of wastes available from generators and wanted by users in a catalog or computer database form.

IMPLEMENTING A HAZARDOUS WASTE REDUCTION PROGRAM

Incentives for implementing a waste reduction program include, as previously indicated, new regulations, increased waste disposal costs, the potential for long-term liability, or simply a desire to operate a business in a more efficient way. The potential approaches to waste reduction already described demonstrate the diversity of techniques used to initiate a program.

The most effective programs are the result of planning developed from knowledge of the operation in question and by setting priorities for waste reduction based on the goals and results expected from the program. For example, a different approach may be taken initially if a primary goal is to adjust to new regulatory concerns than if the major goal is to reduce disposal costs. Whatever the goal, the planning requires the gathering of information about the processes and operations underway at the facility.

A factual and accurate understanding of the location and practices where wastes are generated is essential before steps leading to waste reduction can be taken. A process for information gathering and option identification must be developed. While there may be several approaches to carrying out the process, the EPA has prepared a "Waste Minimization Opportunity Assessment Manual" which outlines a process for gathering information, setting priorities, and selecting the most promising options for waste reduction.

CORPORATE COMMITMENT. Where waste reduction has been most successful, an important contributor has been a steadfast corporate commitment to the program. Success is derived from agreement throughout the organization that waste reduction is an important objective and that the necessary time and effort will be taken to identify opportunities and to initiate changes. Personal involvement from top management, as well as from the person working on the manufacturing line, is important in making the process work well. Depending on the size and complexity of the organization, a formal corporate policy committing the company and its employees to waste reduction may be an effective way to initiate the program.

PROGRAM ORGANIZATION. In a typical organization, waste is created throughout all parts of the operation. Because a waste reduction program will impact personnel and operating groups throughout the company, it is important to have representatives from all the potentially affected groups involved in the information gathering, assessment, and implementation aspects of the waste reduction program. Often a waste reduction task force is an effective type of organization to initiate a reduction program. Any such task force should include representatives from all portions of the company that may be affected. Some examples of such groups are production, main-

tenance, engineering, quality assurance, research, marketing, purchasing, and legal. The exact composition of the task force will depend on the size, formality, and complexity of the particular plant or line operation initiating the program. In a very small operation, the task force may include the entire work force. In establishing the task force a key to success is ensuring all groups are represented and that the members of the task force are enthusiastic.

To ensure that the task force develops and maintains momentum and has a point of contact with company management there should be an acknowledged leader. In some cases, the leader may be the person who felt most compelled to investigate the potential for waste reduction at the facility and worked to achieve recognition by employees and management of the incentives and needs. In other cases, the leader may be designated by management. The leader must provide motivation, secure continued management support, overcome inertia and suspicion, and serve as a source of new ideas and suggested approaches.

The waste reduction task force should have clearly understood responsibility and authority for organizing and carrying out the waste reduction program within the organization. A systematic approach for discharging this responsibility may include the steps outlined in the following sections.

CORPORATE COMMITMENT OR POLICY STATEMENT. The task force should strive to obtain a written policy statement or corporate commitment supporting the waste reduction program. This ensures management interest and allocation of resources to accomplish waste reduction. Moreover, it sends a message to all employees that waste reduction efforts are important and cooperation with the task force is "acceptable" behavior.

ESTABLISHMENT OF PROGRAM GOALS. The task force should establish some overall waste reduction program goals. Such goals are important. They serve to characterize the company expectations for the waste reduction program. Different organizations may set different types of goals based on varying needs and experiences. Whatever they are, it is important that they be measurable goals. The goals may be defined in terms of disposal costs avoided, other manufacturing costs saved, increased use of raw materials, reduction in the quantities of waste materials leaving the site, or perhaps net reduction in "risk" because of the operation of the plant. Obviously, some of these goals are easier to measure than others. Also, they should be indexed in some way to plant output to ensure that waste reduction is occurring while maintaining production rather than achieving minimal waste generation by slowing production. Some organizations may establish percentage reduction goals, others may establish absolute quantity reduction goals, or zero emission goals. The goals may be changed when more is learned about the waste generating activities at the facility. It is important to have an

initial set of goals, however, because they serve as the context for assessing, evaluating, and setting priorities for waste reduction options.

IDENTIFICATION OF WASTE GENERATING SITES AND

PROCESSES. The task force should develop a plan and procedures for understanding waste generation at the facility. Comprehensive waste reduction will require an understanding of all locations and processes within the manufacturing site that produce waste. All waste should be defined. Waste includes fugitive emissions to the air, aqueous waste streams, and nonhazardous solid wastes. The task force should organize a systematic investigation of the operations to develop a database defining the types and quantities of waste streams in the facility and carefully linking the waste streams with the particular processes or operations that produce them. Further subcharacterization according to whether the waste streams are hazardous or nonhazardous and the reasons for this description are also important.

Equally important is an understanding of the types and quantities of the raw materials entering each process. The task force should be particularly interested in balancing the quantities of material entering and exiting the process because large discrepancies in this material balance indicate fugitive or “invisible” losses that should be addressed. The task force should also gather information regarding the existing process controls, waste segregation, and housekeeping practices that may affect the quantity and composition of the waste streams.

Once information about the nature, quantity, and sources of the waste streams has been assembled, the task force should agree on which streams have first priority for further assessment. Ideally, in a small facility, all waste streams should be considered for waste reduction possibilities. In a larger installation, limitations of personnel, time, or budget may require a sequential approach with those waste streams having the greatest potential impact on waste reduction being considered first. The priorities should be established on the basis of the goals established for the program. Some factors that should be considered in setting priorities include compliance with regulations, waste treatment and disposal costs, quantity of waste currently generated, and hazardous properties of the waste stream.

DETAILED SITE INSPECTION. The task force should designate an assessment team with the responsibility to conduct a detailed site inspection. While the waste reduction task force has a responsibility for the entire facility, the designated assessment team should have intimate knowledge of the prioritized processes or operations. The assessment team may be a subset of the task force augmented with other experienced employees or even outside consulting experts. In smaller organizations, the assessment team may be the same as the task force. The assignment of the assessment team should be to conduct a “walk-around,” “inside-out” survey of the entire specific opera-

tion. The survey should follow the process from the entrance of raw materials to the exit of products and wastes. The team should identify potential sources of waste including any waste treatment operations and possible fugitive emissions. The survey may produce some tentative ideas about waste generation causes. These preliminary conclusions may require additional information, comparison with industry standards, or additional site visits in order to be confirmed.

Once the probable causes of waste generation in the process have been identified, the assessment team should turn to identifying potential options for waste reduction. The options can be developed internally or outside sources such as trade associations, equipment vendors, environmental agencies, or consultants can be contacted for information about possible options. While specific waste reduction options exist for specific processes, generally they will fall within the basic categories described earlier in this chapter. Many options are possible and the assessment team should consider use of a "brainstorming" process that encourages group creativity in listing options.

The final aspect of this portion of the assessment team's activity should be to screen the options identified and select some for further consideration. Because a detailed study of feasibility should be the next step, selection at this stage should be on the basis of elimination of options that are impractical or show obvious marginal or inferior waste reduction potential. The informal evaluation and selection may be performed by the entire assessment team or a smaller group. Ideally, it should be done using some weighted, quantitative method.

FORMAL FEASIBILITY ANALYSIS. The task force should be responsible for conducting a formal feasibility analysis. Any such analysis requires gathering additional specific information about the identified options. Normally two types of evaluative questions arise—technical (Can it be done?) and economic (How much will it cost? What will be the return on investment?). Specifically, the technical questions may involve consideration of safety, product quality, compatibility of changes with present practices, availability of necessary equipment, and new environmental complications. The economic questions may involve consideration of factors such as capital costs, operating costs, payback periods, and predictable profit. Typically, profitability is improved with successful waste reduction options and frequently the payback period can be relatively short.

The total feasibility study may require expertise that is not found on the assessment team or on the task force. The commitment by management should include provision for this necessary expertise in order to complete this phase of the program.

STARTING TO USE THE FAVORED OPTIONS. The task force has a major obligation to insist that steps be taken to incorporate the favored

options into the routine practices and processes of the facility. By this point in the program, waste reduction options capable of furthering the company goals in a technically and economically feasible manner have been identified. Because the program involves a broad spectrum of company personnel and stresses the importance of waste reduction, implementation of low-cost options should be met with wide and easy acceptance. Options requiring substantial capital or increased operating costs may have to compete with other projects with similar financial needs. The task force leader has an important role to play at this stage in reminding management of the commitment by the company to waste reduction, the need for funding, and the favorable economic impacts to be expected from the investment. When the funding is obtained, actual acceptance of the option should again be relatively easy due to the preparatory aspects of the work of the task force.

MEASUREMENT OF EFFECTIVENESS AND CONTINUING ASSESSMENT. The task force has a final and continuing responsibility to measure the effectiveness of the implemented waste reduction options. An accurate determination of the effects of waste reduction activities is important to provide a sense of reward to those involved in the program, to monitor the progress of waste reduction, to justify and demonstrate the financial impacts of the investments made, and to serve as new assessment data for continued waste reduction activities. While all of these are important reasons for measuring the success of waste reduction initiatives, the last illustrates a final important point. A waste reduction program should not be a one-time, isolated activity. Ideally, it should become a philosophy, a corporate and personal way of life that continually seeks new options and opportunities to further reduce the generation of waste and to accrue the resulting benefits.

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Chapter 4

Hazardous Material and Waste Handling and Storage

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INTRODUCTION

There are specific handling standards for raw materials storage and for the treatment, storage, and disposal of hazardous waste. Regulations require that ignitable, reactive, and incompatible materials be handled in a manner that will not generate extreme heat, pressure, fire, violent reactions, or produce uncontrolled toxic mists, fumes, dusts, or gases that will pose a risk of fire or explosion or threaten human health or the environment. Therefore, raw material storage must be well planned, and those industries that generate waste must manage their materials in a manner that will not violate established regulations. When considering chemical storage, the containment and ancillary equipment must be able to withstand the forces acting on it and

must be noncorrosive for the specific application. Some general considerations include the site location, nearby structures and storage areas, existing plant operations, location of existing utilities, total container volume, type of material stored, and type of containers.

*C*OMPATIBILITY

One of the most important considerations is the compatibility of the material to be stored in a tank or any container. Table 4.1 lists some incompatible chemical compounds or mixtures. This list should be used as a guideline and should be used on a site-specific basis. The tank or container material's resistance to certain parameters can be used as a guide to predict compatibility with a given substance.

Table 4.1 Incompatible chemical compounds or mixtures.

Tank or container lining material	Incompatibility
Steel	Mineral acids, nitric, hydrochloric, dilute sulfuric acids. Aluminum alkalis, potassium hydroxide, sodium hydroxide, mineral acids.
Magnesium	Mineral acids.
Lead	Acetic acid, nitric acid.
Copper	Nitric acid, ammonia.
Zinc	Hydrochloric acid, nitric acid.
Tin	Organic acids, alkalis.
Titanium	Sulfuric acid, hydrochloric acid.
Fiberglass-reinforced plastics	Sulfuric acid 95%, nitric acid 50%, hydrofluoric acid 40%, aromatic solvents, ketone solvents, chlorinated solvents.
Alkyds	Strong mineral acids, strong alkalis, alcohol, ketones, esters, aromatic hydrocarbons.
Vinyls (PVC)	Ketones, esters, aromatic hydrocarbons.
Chlorinated rubbers	Organic solvents.
Epoxy (amines, polyamide, or esters)	Oxidizing acids (nitric acid), ketones.

Table 4.1 Incompatible chemical compounds or mixtures (continued).

Tank or container lining material	Incompatibility
Coal tar epoxy	Strong organic solvents.
Polyesters	Oxidizing acids, strong alkalis, mineral acids, ketones, aromatic hydrocarbons.
Silicones	Strong mineral acids, strong alkalis, alcohols, ketones, aromatic hydrocarbons.

For example, acids with a pH of 0 to 2 are highly corrosive acids, and alkalies with a pH of 12.5 to 14 are highly corrosive bases. These liquids under some environmental conditions, such as temperature, tank agitation, and tank construction material, uniformly dissolve a significant percentage of the thickness of metal walls. Corrosive substances rapidly attack carbon steel tanks, but most plastics have excellent resistance to acids and bases. When chloride or fluoride solutions are stored in a metal tank, the compounds will generally remove metal atoms from the tank to form soluble salts. This form of tank wall deterioration may not be uniform over tank walls, instead the attack may be concentrated in areas of stress (that is, joints, welds, corners, and bends) and result in leaks in these places long before the overall strength of a tank is noticeably reduced. Oxidation of some types of nonmetallic tank and liner materials causes softening, dissolution, or decomposition by solvents.

Corrosion protection may be required against galvanic corrosion, stray current corrosion, and soil corrosiveness. Metal corrosion is accelerated when the metal contacts oxygen and moisture in the ground, thereby causing the metal to break down. There are a number of corrosion protection methods, some of which are listed below:

- Cathodic protection. These systems reverse the current through sacrificial anodes or impressed DC current.
- Fiberglass-reinforced plastic (FRP). This is a noncorrosive construction material.
- Steel clad with noncorrosive material. This involves coating a steel tank with a nonconductive coating, for example, coal tar epoxy (15 mils) and FRP (125 mils). Care must be exercised to touch up any blemishes or scratches in the coating systems prior to burial.

Some states require specific corrosion protection for specific containers.

Product and waste storage in above-ground tanks or drums should be stored in groups by chemical class. Examples of potentially incompatible wastes are provided in 40 CFR Part 265, Appendix V. This list is not

intended to be exhaustive and serves only as an example of potential incompatibilities. Table 4.2 provides a partial list of incompatible wastes.

Table 4.2 Potentially incompatible wastes.

Group 1-A	Group 1-B
Acetylene sludge	Acid sludge
Alkaline caustic liquids	Acid and water
Alkaline cleaner	Battery acid
Alkaline corrosive liquids	Chemical cleaners
Alkaline corrosive battery fluid	Electrolyte, acid
Caustic wastewater	Etching acid liquid or solvent
Lime sludge and other corrosive alkalis	Pickling liquor and other corrosive acids
Lime wastewater	Spent acid
Lime and water	Spent mixed acid
Spent caustic	Spent sulfuric acid

Potential consequences: heat generation or violent reactions.

Group 2-A	Group 2-B
Aluminum	Any waste in Group 1-A or 1-B.
Beryllium	
Calcium	
Lithium	
Magnesium	
Potassium	
Sodium	
Zinc powder	

The number of tanks and the types of materials to be stored are factors to consider when designing above-ground storage containment areas. Local, state, and federal regulations should be consulted for each site-specific application.

Any product or waste storage in 55-gal Department of Transportation (DOT)-approved containers should be managed as carefully as tanks. This includes worker safety and inventory tracking.

***S*ORAGE AREAS**

Raw materials may be stored at several locations throughout a manufacturing facility. These materials are typically stored in a receiving area, a warehouse or tank farm, and small quantities on the production floor. Specific details for hazardous waste storage is discussed later in this chapter.

There are two distinctive types of waste storage areas: central storage areas and satellite accumulation areas. A central storage area is an area of a

generator's facility where more than one drum of hazardous waste is stored at a time, and which is not in the area where the hazardous waste is generated. For example, a company might accumulate three or four drums of waste paint thinner in a flammables storage room before they are picked up by the waste hauler at the end of each quarter. Another generator might have a paved, fenced, roofed, and bermed area outside where 40 drums of various types of hazardous waste accumulate before they are picked up at the end of each month. Both of these areas would be called central storage areas.

Satellite accumulation areas are locations where one drum is kept to collect the waste as it is being generated. An example of this would be in a research laboratory of a manufacturing facility where a 55-gal drum is used to collect waste chromic acid that was used to clean glassware. Another example would be a drum kept in the painting area to collect solvent from cleaning paint guns.

When the satellite accumulation drum is full, it must be marked with the date it became full and moved to a central storage area within 3 days. The drum must then be shipped off-site within 90 days of the date it became full (unless the generator is a small quantity generator) and the waste must be stored in compliance with all applicable regulations for a central storage area.

The reason for the distinction between these two types of storage areas is in 40 CFR 262.34 (c) (1) which allows generators of hazardous waste to accumulate up to 55 gal of hazardous waste at or near the point of generation (that is, in satellite accumulation areas) without complying with the applicable time limit (90 or 180 days), as long as the specific requirements for satellite accumulation are being met. This differs from the old system (prior to December 1984) which specified that the 90-day time limit for on-site storage by generators started when the first drop of waste was put in the drum.

All drums containing hazardous waste are to be inspected as required by State and EPA policy. Drums are inspected for correct labeling and integrity of the container (that is, leaks, signs of corrosion, deterioration, pitting, bulging, and secure closure of all bungs and top rings). Adequate space should be available between each drum to allow for a thorough inspection of each drum. During these inspections each drum is visually observed and inspected.

Prior to shipping (within 90 days of the accumulation start date) each drum is inspected to make sure that all hazardous wastes are packaged, labeled, and marked in compliance with DOT regulations 49 CFR Parts 172, 173, 178, and 179. The results of each inspection are entered in the required inspection log.

CONTAINER STORAGE

Tanks containing hazardous waste must be managed in accordance with EPA regulations. These regulations require that tanks be inspected daily to ensure

that discharge control equipment and monitoring equipment are operating properly, and to check and record the level of waste in the tank. The regulations also require weekly inspections of tank construction materials for corrosion and deterioration, and weekly inspections of the area surrounding the tank for signs of leakage and erosion. The results of the daily and weekly inspections are recorded in a separate inspection log.

Many of the requirements for hazardous waste storage and handling are also the best management practice for raw materials and chemical products. The goal is to separate incompatible materials and to be able to respond to a spill so there is no adverse environmental impact.

Many of the requirements for hazardous waste storage and handling are also the best management practices for raw materials and chemical products. The goal is to separate incompatible materials and to be able to respond to a spill while avoiding any adverse environmental impact.

On July 14, 1986, the EPA promulgated new regulations for the management of hazardous waste in underground tanks. These regulations went into effect January 12, 1987. These regulations can be found in 40 CFR 260.10 and 264.190. A major provision of these new regulations is that secondary containment will eventually be required for all tanks including underground tanks. Secondary containment systems are designed to temporarily contain leaks or spills, preventing them from contaminating the surrounding environment. A secondary leak detection system is necessary and should be located in the bottom of the containment below the tank. Some of the more common forms of secondary containment are double-walled tanks, vaults, and underground lining systems.

Existing tanks that are not currently equipped with secondary containment must be retrofitted in accordance with the following schedule:

- Tanks used to store F020, F021, F022, F026, or F027 wastes by January 12, 1989;
- Existing tanks of known and documented age by January 12, 1989, or when the tank system reaches 15 years of age, whichever is later; and
- Existing tanks of unknown or undocumented age by January 12, 1995, unless the facility where the tank is located is older than 7 years, in which case the time limits of known-age tanks apply.

The regulations also require that the integrity of existing tanks that do not have secondary containment be assessed every year by a qualified registered professional engineer and be certified to be nonleaking. Detailed design standards for new tanks are included in the new regulations.

Tanks and containers used by generators to store or accumulate hazardous waste no matter where they are located, must be clearly marked and labeled throughout the period of accumulation with the words "Hazardous Waste", DOT shipping name for the waste, and the date on which each period of

accumulation began in the tank or container. Marks and labels should be placed on the sides of each tank or container and must be clearly visible for inspection.

In addition, if the generator is taking advantage of the satellite accumulation regulation, full drums should also be marked with the date the drum became full along with the accumulation start date. Before drums are shipped off-site, they must be marked and labeled in accordance with all applicable DOT regulations. Many generators label containers with preprinted labels that are designed to meet DOT's marking requirements. These preprinted labels should be reviewed carefully to determine if they meet EPA and DOT labeling requirements.

EPA prescribes special regulatory standards for managing hazardous waste in containers and tanks. Each kind of vessel has separate standards. Containers that are portable have standards that address the risks coming from their portability. Tanks, which are higher-capacity stationary installations, have standards that apply to those characteristics.

All containers used to store hazardous waste, raw materials, or product chemicals must be in good condition, nonleaking, and compatible with the materials stored in them. The contents of leaking containers must be transferred immediately to a nonleaking container. Those containers that are used to ship waste off-site as well as to store it on-site must also meet DOT packaging regulations. DOT packaging regulations are also a good guideline to use when determining what type of drum to use to store waste on-site. Another guideline is that waste material can generally (though not always) be stored in the drum that the product from which the waste was generated came in. This may not hold true if the waste material is very different from the product.

There are specific requirements for the management of containers of hazardous waste. These include

- Containers of hazardous waste must be kept closed at all times except when waste is actually being added to or removed from the container.
- Containers of hazardous waste must not be handled or stored in a manner that would cause them to rupture or leak. (For example, containers that are stacked must be separated with pallets).
- Containers of hazardous waste must be labeled at all times and the labels must be legible and visible.

Containers must be stored on an impervious surface that is bermed to prevent leakage in case of a spill. Storage areas should meet the requirements of 40 CFR 264.175, unless the area is inside a building and it can be demonstrated that a spill cannot escape to the environment and can be easily cleaned up. 40 CFR 264.175 requirements outline what is needed in a container storage area.

All generators who store hazardous waste in containers must inspect the containers and the area surrounding the containers at least once per week. The inspector should look at the condition of the containers and look for signs of leaks, spills, and deterioration. It is also important to ensure that labels are in place and correct, and that all hazardous waste management requirements are being met. The inspections must include containers in central storage areas and all satellite accumulation containers.

All inspections must be documented by recording the results in an inspection log. The inspection log should include spaces for the name or initials of the inspector, the date of the inspection, the inspector's observations, and a notation to indicate that any observed problems have been corrected.

***R*EGULATIONS**

CONTINGENCY PLANS. Any industry that handles hazardous materials (raw materials or stored waste) must have a contingency plan and a hazard communication program. These are required for the protection of human health and the environment.

A contingency plan is a written plan detailing the measures to be taken to minimize harm to public health, safety, and welfare, and the environment. Specific equipment may be required under these regulations. Copies of the contingency plan must be sent to the local police and fire departments, emergency response contractors (if needed), the local hospital, and local, state, and federal regulatory agencies for their review and approval of the emergency response arrangements.

The primary purpose of a written contingency plan is to clearly describe the actions to be taken by facility personnel and the equipment to be used in response to potential or actual fires, explosions, or any other unplanned releases of hazardous waste or hazardous waste constituents to the air, soil, surface water, or ground water. All employees are subject to testing on proper behavior during an emergency. The specifics of the plan for hazardous wastes are detailed in 49 CFR 265.52.

Generators are required to send copies of their contingency plan to the following agencies or authorities:

- Local fire departments,
- Local police departments,
- Local hospitals,
- State and local emergency response teams, and
- State and federal regulatory authorities.

It is very important that the contingency plan be clear and detailed so it can be understood by someone who is not familiar with the plant. A general

description of the facility (type of business or manufacturing operations) and a site plan are usually included for this purpose. It is particularly important for firefighters to know what kinds of wastes are stored at the plant, the hazards that may result due to a fire such as toxic gases released in a fire and explosion dangers, and where the wastes are stored. All of this information should be included in the plan. The plan should be kept up to date, and it should be amended whenever

- The facility license is revised,
- The plan fails in an emergency,
- The list of emergency coordinators changes,
- The list of emergency equipment changes, or
- There is any change in maintenance or operation at the facility.

Updated copies should be sent to the agencies mentioned earlier. A suggested outline for the generator contingency plan can be found at the end of this chapter.

To make the required arrangements with the police department, fire department, hospital, and state emergency response agency, the generator should send a letter explaining why the contingency plan is being sent and what agreements are being requested. A self-addressed response letter should be included in the package so the emergency response can sign it and mail it back. In addition, it is suggested that all contingency plans be sent by certified mail with return receipt requested for proof that the plans were received by the agencies, even if you don't receive a response.

Prior to any individual handling waste, employers are required to provide certain information and training to their employees. The methods of providing this information and training must be described in the required written hazard communication program. The information has to be provided to employees when they are initially assigned to a position or when a new hazard is introduced to their work area.

HAZARD COMMUNICATION STANDARD. The hazard communication standard (29 CFR 1910.1200) was promulgated by the U.S. Department of Labor's Occupational Safety and Health Administration (OSHA). This standard became effective November 25, 1985, for manufacturers and distributors of hazardous chemicals, and on May 25, 1986, for employers who use hazardous chemicals in the workplace if those employers are included in Groups 20 to 39 of the Standard Industrial Classification (SIC). On August 24, 1987, the hazard communication standard was amended to include all employers with employees who may be exposed to hazardous chemicals in the workplace. This change became effective September 23, 1987, for all chemical manufacturers, importers, and distributors insofar as they must

include Material Safety Data Sheets (MSDSs) with their next shipment of hazardous chemicals.

The hazard communication standard requires a comprehensive program of dissemination of information about hazardous chemicals by manufacturers, distributors, and employers. Information is transmitted by labeling of containers, MSDSs, and formal training of employees.

Employers must develop a written hazard communication program to describe how they will comply with labeling, MSDS, and employee training requirements. The most important part of any training session is to teach personnel the correct emergency response procedures, as described in the contingency plan. This training must include an explanation of the hazards of the wastes at the plant, the use of emergency equipment, and all other aspects of the contingency plan.

Training can either be conducted by qualified personnel from within the plant or by outside consulting firms. The regulations do not specify what is required of a person to be "qualified" to teach personnel about hazardous waste management. Generally, the qualifications of trainers are documented by attaching certifications of training from seminars or hazardous waste--related courses that the trainer has attended. Obviously, any person or firm selected to conduct training should be extremely knowledgeable in state and EPA hazardous waste regulations and their application. Many companies prefer to have a consulting firm conduct the initial training in a classroom setting to ensure that all important areas are discussed.

SARA. In addition to the new OSHA standards, on October 17, 1986, Congress enacted the Superfund Amendments and Reauthorization Act (SARA) of 1986. This legislation governed many areas including Title III, the Emergency Planning and Community Right-to-Know Act of 1986, which impacts on many companies in several ways including

- Requiring companies to report to state and local officials whether or not certain chemicals are used on-site;
- Requiring companies to notify state and local officials of emergency situations that arise;
- Allowing community access to information regarding chemicals used at plants; and
- Requiring companies to submit emissions inventories to state, federal, and local officials.

All of these amendments are aimed at making the community more aware and industries more responsible for the handling of their waste.

PACKAGING, LABELING, MARKING, and PLACARDING. EPA and each state have hazardous waste regulations that refer directly to DOT haz-

ardous materials regulations for proper packaging, labeling, marking, and placarding requirements. EPA and the DOT have worked together in promulgating certain segments of the hazardous waste regulations so that both agencies' regulations are be uniform and consistent. Table 4.3 gives examples of EPA hazardous waste regulations that directly reference DOT shipping requirements. There are three categories of items regulated by the DOT: hazardous wastes, hazardous materials, and hazardous substance, each with a specific and different definition.

Table 4.3 EPA regulations that reference DOT shipping requirements.

	EPA regulations	DOT regulatory reference
Packaging	40 CFR 262.30	49 CFR Parts 173, 178, and 179
Labeling	40 CFR 262.31	49 CFR Part 172
Marking	40 CFR 262.32	49 CFR Part 172
Placarding	40 CFR 262.33	49 CFR Part 172, Subpart F

Hazardous wastes are items that are listed or classified as such by EPA. These may be found in 40 CFR Part 261, Subparts C and D. For the purpose of DOT regulations, the term hazardous waste does not include state-regulated hazardous waste which would not be considered hazardous under the EPA system.

A hazardous material is any material listed in DOT Hazardous Materials Table in 49 CFR 172.101. These materials have been determined by the DOT to be capable of posing an unreasonable risk to health, safety, and property when being transported. They include both used and unused materials.

Finally, hazardous substances are substances designated by the Clean Water Act that, when in sufficient quantity, pose a significant danger if spilled to a waterway. These materials were identified by an "E" in Column 1 of the Hazardous Materials Table, but this was amended in the November 21, 1986, *Federal Register*. Currently, hazardous substances are items listed in an appendix to the Hazardous Materials Table. Wastes generated at a plant may meet any one or all of these hazardous definitions. Once the appropriate designation has been located, the facility must comply with the specified requirements.

It is important to distinguish between EPA and DOT regulations. Resource Conservation and Recovery Act (RCRA), which is administered by EPA, regulates hazardous waste. The Hazardous Materials Transportation Act (HMTA), administered by the DOT, regulates hazardous materials. It is important to note that the universe of hazardous materials includes the subset of hazardous wastes. Although the EPA regulations governing packaging, labeling, marking, and placarding directly refer to the DOT regulations, all their definitions are not the same. Some examples are shown in Table 4.4.

The Hazardous Materials Table found in 49 CFR 172.101 is the heart of DOT regulations. It is an alphabetical listing of proper shipping names and

related information that is extremely important. It is, therefore, very important to learn how to use this table and to become familiar with the information it contains.

Table 4.4 DOT and EPA definitions.

DOT		EPA
Shipper	is equivalent to	Generator
Carrier	is equivalent to	Transporter
Destination	is equivalent to	Designated facility
Shipping paper	is equivalent to	Manifest

Perhaps the single most important step to take in complying with 49 CFR is to select the correct "proper shipping name." If this name is not properly selected, much of the remaining information required will be incorrect because it is based on the shipping name. Part 172.101 (c) describes the necessary procedures in selecting a shipping name.

Certain guidelines are recommended when determining the proper DOT shipping name. First, the shipping name must be obtained directly from the Hazardous Materials Table. The table is an alphabetical listing of all proper shipping names, each of which has an associated hazard class and UN/NA number. The shipping name selected is used on all manifests, marking, and so on. It is very important to choose the correct name, because most other shipping information is based on the shipping name. Second, the EPA waste code or unlisted characteristic of the waste must be looked up in the appendix to 49 CFR 172.101. Finally, the reportable quantity (RQ) in the third column of the appendix must be compared with the quantity being shipped in each container. If the quantity being shipped in one container exceeds the RQ, the letters "RQ" and the EPA waste code or characteristic must be added to the shipping name that is used on the manifests and markings to indicate that the material is a hazardous substance.

DOT maintains its own set of labeling requirements. DOT labels are color-coded diamond-shaped stickers that attach to the shipping container. The purpose of the labels is to identify the principal hazard or hazards of the material in order to alert anyone who handles the waste of the potential hazards associated with the material. Labeling requirements are delineated in 49 CFR Part 172, Subpart E. The 49 CFR 172.400 requirements sets forth general labeling requirements and indicates specific instances where labels are not required.

Another responsibility of the shipper is to provide the required placards to the transporter (49 CR Part 172.500). A placard is a color-coded diamond-shaped sign placed on the outside of a transport vehicle; one on each end and one on each side. Placards warn of the potential hazards of the material being transported.

As when selecting a proper shipping name, there is a stepwise procedure that must be followed in determining the correct vehicle placards. These requirements are found in 49 CFR 172, Subpart F.

BEST MANAGEMENT

Many industries have various people involved in the use and management of hazardous materials. It is important to maintain a single uniform plan for the entire facility. Conducting self-audits assures best management and provides a concise overview of what is going on at the facility. Internal Due Diligence Facility Audits are described in Chapter 2. Audits specific to hazardous material handling and waste classification are presented below.

The first step in conducting a self-audit inspection of a plant is to determine which areas and operations in the plant generate hazardous wastes. To do this, each operation in the plant and all the wastes generated must be reviewed and listed, respectively. The wastes that are obviously nonhazardous, such as paper, wood, scrap metal, and other ordinary trash must be eliminated. However, be careful not to eliminate potentially hazardous wastes such as paint booth filters, spill clean-up residue, and other industrial wastes.

Then the list of potentially hazardous wastes is reviewed to determine whether they are hazardous or not. Material safety data sheets and other information from the product suppliers may be helpful if they name the chemical components and physical characteristics (flash point, pH, and so on) of the product.

This type of information may indicate that the product contains a listed waste or exhibits one of the characteristics of a hazardous waste. If this is the case, it can be assumed that the waste will also be hazardous. This is not always true. A hazardous product does not always yield a hazardous waste, just as a nonhazardous product may result in a hazardous waste. At this point it may be necessary to collect samples for laboratory analysis to complete the hazardous waste determination.

After completing the hazardous waste determination, an inspection that covers the major requirements for large- and small-quantity generators should be conducted. Those large-quantity generators who store waste for longer than 90 days are subject to a more stringent and extensive list of requirements than those large-quantity generators who store waste for less than 90 days. The checklist used in an audit should be specific to the site being audited.

Proper handling of industry waste makes the overall management process considerably easier. Self-audits should be conducted routinely to ensure that the plant is maintaining compliance with the regulations. The potential for violations is dramatically reduced and the costs of operation are also mini-

mized when better management and handling practices of hazardous wastes are followed.

S**UGGESTED READINGS**

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Chapter 5

Biological Treatment of Hazardous Wastes

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*I*NTRODUCTION

GENERAL. Aitken and Irvine,¹ in their introductory remarks to their chapter on biological treatment of hazardous wastes, stated

“... most, if not all, ‘toxic’ organic chemicals can be degraded biologically. There is, however, a tremendous difference between what a microbe can do under controlled laboratory conditions, and what it does do in the environment or in the waste treatment system.”

Biological treatment technologies have been successfully used for treatment of industrial and municipal wastes containing hazardous constituents.

There are many examples of the successful utilization of conventional and emerging technologies on the bench- and pilot-scale level, and the number of full-scale plants using these technologies increases each year. The advantages of biological treatment over other methods are that when complete or nearly complete biodegradation occurs, the waste stream can become non-hazardous. Successful biological treatment can completely remove contaminants by the action of microbes breaking down the wastes into nonhazardous byproducts. The cost is often less expensive than many other alternatives. When complete biodegradation is not possible, concentration of the hazardous components can be accomplished in the sludge, which can be more economical than some other concentration alternatives such as ion exchange and activated carbon.

This chapter is divided into four parts. The first part outlines the metabolism of biological treatment of hazardous wastes, followed by parts on aerobic suspended growth, aerobic fixed growth, and anaerobic treatment technologies. When biological treatment is to be evaluated, the choice of aerobic or anaerobic, and suspended or fixed-film cultures must be determined. Aerobic processes, in general, are the methods of choice when the BOD of the waste to be biologically treated is below 10 000 mg/L and removals below 100 mg/L are desired. When the BOD is above 5000 to 10 000 mg/L, anaerobic reactors can often achieve better results, but the final BOD will typically be between 100 and 1000 mg/L. Processing wastes in stages from anaerobic to aerobic may be advantageous when a high-strength waste must be treated to achieve a low-strength effluent concentration.

The choice between fixed-film and suspended growth reactor modes is based on several factors. One of the chief disadvantages of fixed-film reactors is the difficulty in accessing and controlling the amount of biomass present. For example, the biomass in suspended growth reactors may be estimated and the sludge wasted to control mixed liquor concentrations. However, operational attention is generally greater for suspended growth systems. This may not be true for a highly variable strength wastewater such as a leachate. Aerobic suspended growth cultures also have the disadvantage of requiring more energy to operate because of the need for blowers or mechanical mixers. Fixed-film systems do often utilize effluent recycle pumps to moderate loading, however.

An important fundamental difference in fixed-film and suspended growth reactors is the biological community. Although these systems have many common microorganisms, fixed-film reactors tend to also have biological populations that contain organisms from higher trophic levels, such as mollusks, insect larvae, arthropods, and other grazing organisms. In a fixed-film reactor the organisms common to suspended growth reactors may appear in a stalked or attached morphology. The community in a fixed-film reactor also consists of a succession of communities at different depths. Grazing organisms and algae may be apparent near the surface, aerobic biological forms are

present in the upper layers of the biological film, and facultative and anaerobic organisms are typically in the deeper portions of the biological film. Suspended growth cultures tend to be more uniform and aquatic in nature and generally lack grazing organisms except at the reactor tank walls.

In selecting aerobic or anaerobic, or fixed-film versus suspended growth processes, the typical approach is to research the literature and use a technology that has proven successful on a similar waste. With hazardous wastes, bench and pilot testing is often necessary. Side-by-side evaluations on a bench scale of anaerobic, aerobic, fixed-film, and suspended growth combinations may be needed to screen for ineffective methods and for preliminary identification of the appropriate technology. Once this is accomplished, further bench-scale or pilot studies are warranted to identify optimum operational modes and waste loading criteria.

Few generalizations can be made when discussing biodegradation of toxic and hazardous materials by conventional biological treatment. The removal capabilities of any given system are strongly influenced by its physical configuration, regardless of the inherent biodegradability of the compounds of interest. However, the fate of any compound in a biological treatment system will depend on its inherent biodegradability.² Recalcitrant compounds will not be removed by biological mechanisms regardless of the engineering efforts applied. Biodegradable compounds may or may not be removed, depending on the reaction environment. The primary goal in the engineering of biological treatment systems for the removal of toxic and hazardous chemicals is to allow maximum expression of inherent biodegradation potential. The biodegradability depends on the environmental conditions the compound encounters. Other than the type of compounds targeted for biodegradation, factors influencing their removal include the concentration of the compounds, synergistic chemical reactions, nutrient availability, and conditions in the aeration basins, such as the solids retention time (SRT), oxygen level and transfer, and operational mode.²

Because approximately 90% of hazardous wastes are in the aqueous form, this chapter will concentrate on treatment of liquid hazardous wastes. Successful treatment of hazardous wastes in solids, soils, and slurries is covered briefly at the end of the aerobic suspended growth section of this chapter. For information on *in situ* treatment refer to the WPCF Special Publication, "Hazardous Waste Site Remediation Management."³

The discussions that follow are an attempt to consolidate the research and designs conducted on aerobic biological treatment of hazardous wastes. Review of these results can help determine the mechanisms that remove the contaminants, predictions for removal efficiencies, whether the constituents in their waste stream are amenable to biological treatment, and some successful design and operational strategies.

BIOLOGICAL METABOLISM. Knowledge of the mechanisms by which microorganisms utilize food sources for growth and cell maintenance is fundamental to the understanding of biodegradation. These mechanisms are collectively referred to as "metabolism."

All cells must have sources of carbon and energy to live and grow. In waste treatment, engineers take advantage of this fact by providing an environment where the waste serves as the carbon or energy source. In this way, the growth of a biomass culture is dependent on the utilization of the same constituents in the medium targeted for removal. In domestic aerobic wastewater treatment this process results in the conversion of organic compounds to carbon dioxide, water, and new cell mass. The use of biological treatment for the destruction of hazardous wastes is based on the same principles. However, a more complicated set of parameters needs to be analyzed. This section will offer a brief overview of the fundamentals of metabolism before discussing the specialized application to hazardous waste treatment.

Metabolic Processes. Energy conservation in biological systems requires the transfer of electrons between donor and acceptor molecules. The primary energy source is the electron donor. The electron acceptor provides the means of microbial classification. It also provides for chemical transformations.

If electrons are accepted by a molecule present in the extracellular medium, the metabolism is termed a respiration. If the electron acceptor is molecular oxygen, the respiration is termed aerobic. If it is some other inorganic compound such as nitrate or sulfate, the respiration is termed anaerobic or anoxic. Microorganisms that respire oxidize the energy source by transferring electrons to the acceptor. If the energy source is an organic compound, oxidation goes to carbon dioxide and water and all available electrons are removed. The transformation is mineralization. Often, in the degradation of complex organic compounds (such as some hazardous wastes), the oxidation is only partial, resulting in organic compounds remaining in the medium. This concept is important because the products of incomplete biodegradation can be just as, or more, toxic as the original compound. Therefore, any analysis concerning the biodegradation of a toxic organic compound must consider byproduct formation.

In some cases, no external electron acceptor is present in the growth medium. This environment would not allow growth of organisms by respiration. In these cases, only those organisms capable of transferring the electrons to an acceptor present inside the cell would grow. This type of metabolism is termed fermentation. Fermentation does not result in a net oxidation of organic carbon present in the growth medium because all electrons are transferred to other organic molecules. It can, however, transform a specific organic compound by this electron transfer. Indeed, some research

has found organic priority pollutants that are transformed only by fermentative pathways.

Metabolic Classification. An understanding of the meanings of microbial classification is required for the determination of the types of transformations that a specific organism or culture can catalyze. Because much hazardous waste engineering involves the use of treatability studies or novel processes, a background in this area is needed.

Microorganisms are classified by the type of metabolism they employ for growth. These classifications are based on the carbon source and the energy source. All cells need an external source of carbon for biosynthesis because carbon typically comprises about 50% of the total dry mass of cells. Only two such sources exist in nature, organic compounds and carbon dioxide. Microorganisms that can utilize carbon dioxide as their primary source of carbon are known as autotrophs. Many microbes, however, do not possess the specialized apparatus necessary for the utilization of carbon dioxide as a principal carbon source. They must rely on organic compounds for this purpose. These organisms are known as heterotrophs. Because many hazardous wastes are organic in nature, the heterotrophs are the most important group for biodegradation of hazardous wastes.

Cells may obtain energy either from organic or inorganic compounds assimilated from the extracellular environment or from harnessing energy present in visible light through a specialized cellular apparatus. Few microorganisms can use both energy sources. Those that utilize chemical compounds (organic or inorganic) for their primary energy source are known as chemotrophs, while those that extract energy from visible light are called phototrophs. A widely used classification scheme employs these terms to divide microorganisms into four metabolic groups:

- Chemoheterotrophs are those organisms that utilize organic compounds as an energy source and must rely on organic compounds as the primary carbon source. This group includes all fungi (yeasts and molds), protozoa, and many bacteria. They are the primary organisms responsible for organic compound degradation.
- Chemoautotrophs are those organisms that utilize inorganic compounds as an energy source and can utilize carbon dioxide as their primary carbon source. Only certain highly specialized bacteria, including the nitrifying bacteria, are chemoautotrophic.
- Photoautotrophs are those organisms that utilize light as an energy source and can utilize carbon dioxide as their primary carbon source. Most of the algae and the cyanobacteria (blue-green bacteria) belong to this group.
- Photoheterotrophs are those organisms that utilize light as a principal energy source and must rely on organic compounds as their primary

carbon source. Only a few algae and cyanobacteria are classified in this small group which is dominated by anaerobic, photosynthetic bacteria.

Co-metabolism. As stated in the Metabolic Processes section, all organisms require sources of carbon and energy for growth. If a particular carbon source also happens to be a compound that is undesirable, exploitation of microbial metabolism will serve a useful purpose. In some cases, however, an organic compound cannot by itself serve as a carbon and energy source. This may be due to a lack of adequate available chemical energy (electrons), a lack of requisite systems to allow uptake by biochemical pathways, or a lack of sufficient quantities of compound to allow proliferation of an active culture. It has been observed, however, that microorganisms can transform substances present in the growth medium while actively growing on a different substance. This process is referred to as co-metabolism, defined as "the concomitant oxidation of a nongrowth substrate during the growth on a utilizable carbon and energy source."⁴

The concept of co-metabolism is especially important in the evaluation of treatment technologies because the absence of biodegradation of a specific organic compound may not preclude it from treatment with a cosubstrate. The evaluation of biodegradation in the presence and absence of cosubstrates should be evaluated before biological treatment is abandoned as a feasible alternative.

Biochemical Principles of the Anaerobic Processes. The molecules resulting from hydrolysis are used as carbon and energy sources by the bacteria that carry out fermentations. The oxidation end products of these fermentation processes are primarily short-chain volatile acids such as acetic, propionic, butyric, valeric, and caproic. Their production is referred to as acidogenesis and the responsible organisms are called acid-producing bacteria. The reduced end products of the fermentation depend on the nature of the culture and the environmental conditions in the reactor. Some of the acid-producing bacteria possess a specialized enzyme system that allows them to oxidize reduced coenzymes without passing the electrons to an organic acceptor, thereby releasing hydrogen gas (H_2) to the medium. The collective activity of these hydrogen-producing bacteria is called hydrogenesis.

The distinction between acid- and hydrogen-producing bacteria is not clear. Because hydrogen-producing bacteria usually produce acids, but acid-producing bacteria do not all produce hydrogen, it is probably best to think of the hydrogen-producing bacteria as a subset of the acid-producing group. The combined groups of acid- and hydrogen-producing bacteria are generally referred to as nonmethanogenic bacteria and their integrated metabolism results primarily in formic acid, acetic acid, CO_2 , and H_2 . If no hydrogen is formed, the nonmethanogenic phase results in insignificant reductions in

COD because all electrons released in the oxidation of organic compounds are passed to organic acceptors that remain in the medium. Consequently, the energy level of the entire system is lowered only by losses due to microbial inefficiency. When hydrogen is formed, however, it represents a gaseous product that escapes from the medium, causing a reduction in the energy content, and thus the COD, of the liquid.⁵

The products of the nonmethanogenic phase (that is, formic acid, CO₂, and H₂) are utilized by methanogenic bacteria to produce methane gas. Almost all of the energy removed from the liquid is recovered in the methane.

The complications involved in the process kinetics during the catabolic activities of the consortium of anaerobic bacteria amplify when considering hazardous wastes treatment. However, researchers consider that methanogenesis is probably the rate limiting step because of the following reasons:

- Production of methane, essentially insoluble in water, drives the overall reaction to completion.
- During hydrolysis and acidogenesis, only a molecular rearrangement occurs. During methanogenesis stabilization occurs.
- Methane bacteria are slower and more sensitive to the environment than their counterparts. Therefore an upset to methanogens will cause upset of the entire treatment system.

Figure 5.1 shows the multi-step anaerobic reactions.

WASTE CHARACTERIZATION, TREATABILITY STUDIES, AND MODELING

GENERAL. The definition of a hazardous waste is any waste that is hazardous corrosive, toxic, flammable, or reactive, or is a listed waste. The first step in assessing if a waste can be treated by biological treatment (or other methods) is to characterize the constituents of the waste.

WASTE CHARACTERIZATION. An evaluation of processes that contribute to the waste stream can identify constituents. When the source is a leachate or a waste stream of unknown composition, laboratory analyses should be conducted to determine the type of contaminants and their concentrations. After assessing the character of the waste stream, the feasibility of biological treatment can be initially assessed on paper. Typically, heavy metal concentrations should be below 5 to 10 mg/L. This varies with the

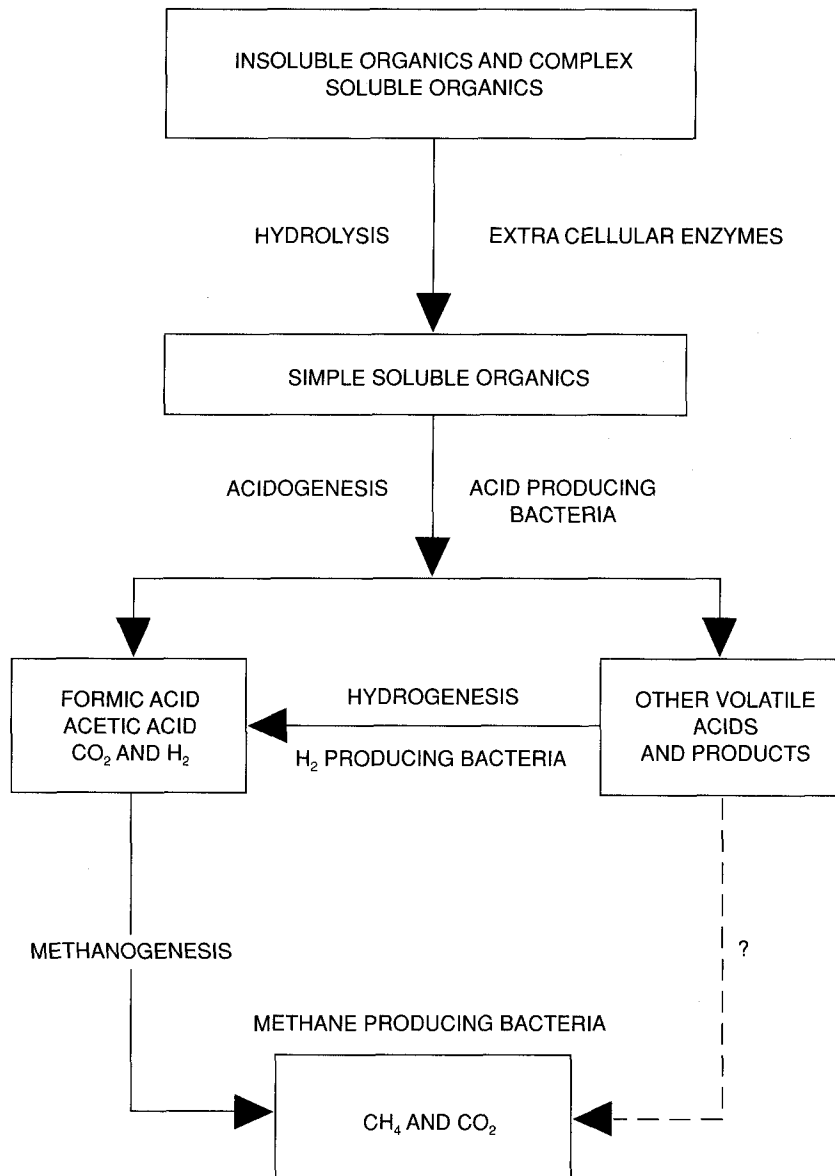


Figure 5.1 The multi-step anaerobic reactions.

metal and, as discussed subsequently, acclimated biomasses have tolerated much higher levels.

TREATABILITY STUDIES. After an evaluation, initial laboratory screening using dilutions in a BOD₅ test, specific dissolved oxygen (DO) uptake rates, Microtox, adenosine triphosphate, or respirometry can give a gross in-

dication of the feasibility of continuing with biological treatment. The potential use of emerging technologies requires similar tactics.

If the results of waste characterization are favorable, the next phase is to set up bench-scale (0.5- to 5-L) reactors and test various loadings and operational configurations. Tests should be ideally carried out over three to four sludge ages to ensure stabilization of the system. These bench-scale tests are followed by larger-scale pilot studies. The larger reactors are run to more closely define operational requirements and refine design parameters. If all of the above prove successful, full-scale design implementation can proceed with a much higher degree of confidence than if these steps are abbreviated or deleted. A later section of this chapter presents considerations for scale-up to full-scale treatment.

Regulatory Considerations. Prior to treating hazardous wastes, permitting by the regulatory authority (state or federal) is required. Analyses of samples may be conducted by a laboratory to characterize the wastes without a permit if the sole purpose of testing is to determine the wastes' characteristics.⁶ Some states may require certification of the laboratory for acceptance of the results.

According to federal regulations (not adopted uniformly by all states), a permit is required prior to undertaking pilot- or bench-scale investigations to evaluate treatment alternatives (treatability studies). These federal regulations (40 CFR 261.4(e))⁶ make it possible for the people who generate or collect samples for treatability studies to be exempt from 40 CFR, Parts 261-263 and the notification requirements of Part 3010 of RCRA. Certain other conditions that must be met for treatability studies include limitations on the quantity of waste treated and transported; packaging, labeling, and shipping requirements; and reporting and recordkeeping specifications. The EPA Regional Administrator or the State Director (if in an authorized state) may grant requests for variations.

Samples undergoing treatability studies and the laboratory or testing facility conducting such treatability studies (to the extent such facilities are not otherwise subject to RCRA requirements) are not subject to any requirement of 40 CFR Part 124, Parts 262-266, 268, and 270, or to the notification requirements of Section 3010 of RCRA provided specific conditions are met. A mobile treatment unit (MTU) may also qualify as a testing facility. Conditions to be met include notification of the appropriate state or EPA officials; procurement of an EPA identification number; limitation on the mass of hazardous waste treated, received, or stored per day; and requirements that specific time limits for completion are not exceeded, no open burning or direct land application occurs, records are kept and properly maintained, a report is submitted to the state or EPA, and residues are properly disposed.

Seeding, acclimation, and Bioaugmentation of Bioreactors. SEEDING.

This section discusses the alternatives for development of a viable culture for start-up of an activated sludge plant.⁷ The following sources were considered for seed cultures:

- Mixed liquor from another activated sludge plant,
- Naturally occurring microbes in the wastewater to be treated (self-seeding),
- Soil, and
- Enriched freeze-dried cultures.

The use of mixed liquor from another activated sludge plant is a popular method for developing an acclimated seed. Major problems are normally associated with the different species of microorganisms developed for particular wastewaters. A specific type of substrate will result in the development of a specific microbial population. To minimize acclimation problems, mixed liquor should be obtained from an activated sludge plant that is treating a wastewater with similar characteristics to the wastewater that will be treated. A municipal sludge required 4 to 8 weeks to develop a stable mixed liquor concentration of 3000 to 4000 mg/L suspended solids for a petrochemical wastewater.⁷

Another typical method for an activated sludge start-up is to develop an acclimated culture from naturally occurring microorganisms in the wastewater. The self-seeding approach was used to develop mixed liquor cultures during start-up of activated sludge plants at several refineries worldwide. At one refinery, 1 month was required to reach a MLSS concentration of 2000 mg/L, while at two others, about 2 months were required to develop a high concentration of microorganisms.⁷

Soil seeding reportedly is an economical method for activated sludge start-up that can be substantially faster than the previous methods discussed. In addition to supplying a source of bacteria, the soil particles can result in nucleation for development of microbial flocs.⁷

A recent addition to the above techniques is the use of freeze-dried cultures of mutant bacteria acclimated to specific waste components. The advantages claimed are that the addition of this active microbial mass results in a rapid growth rate and a short period necessary to develop a viable mixed liquor population. This method would be especially attractive when a mixed liquor treating a similar wastewater is not available in the geographic area and a short start-up period is required.⁷

During a recent seminar on treatment of hazardous wastes, Aitken and Irvine¹ presented the following information on the sources of seed cultures:

"The most appropriate source of inoculum for a biological treatability study is any local environment to which the waste has been introduced, if microorganisms are also likely to be present. Such sources can include contaminated soil or materials from waste storage impoundments, biological sludges from systems treating similar wastes, or sludges from municipal treatment plants receiving a substantial input of industrial wastes. Primary treatment sludges can be a source of aerobic, anaerobic, or facultative organisms. Secondary treatment sludges may be good sources of aerobic inocula. Primary and secondary anaerobic digestion sludges often are used to start up anaerobic systems. Other sources of anaerobic inocula include manure, or fluids obtained directly from the rumen of animals such as sheep or cattle. It is well worth the effort to collect inocula from a variety of sources. Sources can be tested individually in shake flasks or serum bottles, or can be combined to increase the probability of success."

ACCLIMATION. The need for patience during treatability testing stems from the long acclimation periods often required before a mixed culture "takes off" and responds aggressively to a particular waste. A major factor affecting the length of the acclimation period is the selection of an appropriate seed culture. If the required genetic information is not present in the seed culture (or in the waste), it is not likely to develop from spontaneous mutation under normal laboratory conditions. As a result, compounds that are initially toxic or nonbiodegradable will remain so, independent of the acclimation period length. When the desired genetic information is present in the start-up culture or in the waste, an acclimation period will be productive if the organisms with the appropriate genes can compete. Alternatively, the necessary genes can be transferred to other more competitive organisms, provided the proper operating strategies are implemented.¹

Standard microbiological enrichment techniques involve the introduction of a relatively small inoculum to a relatively large volume of solution containing the material to be treated. Alternately, engineers generally begin with the addition of a relatively small volume of waste to a massive population of organisms in the reactor to be evaluated. Since the toxicity or inhibitory properties of the waste constituents are often a function of their concentration, the enrichment techniques must take such effects into account. Enrichment techniques are more likely to develop competitive cultures in a short period of time if concentration effects are overcome. In the engineering approach, the diversity of the genetic pool is likely to be greater, which can increase the probability that some members of the "audience" will be satisfied. However, it may take several weeks after the desired treatment activity begins before nonessential or unwanted members of the culture are reduced to insignificant numbers.¹

For wastes with a significant amount of potential growth substrates, the initial success of the enrichment techniques is judged by noticeable increases

in the microbial population, either observed visually or measured as optical absorbency or turbidity. The activity of larger populations in a reactor can be judged by measuring changes in parameters such as COD, total organic carbon (TOC), or gas production. Activity of aerobic cultures can also be evaluated using respirometric techniques. Respirometry is particularly useful in determining the activity of the culture towards specific waste constituents. For acclimation periods aimed at the conversion of low concentrations of xenobiotics, direct measurement of the xenobiotic or readily analyzed byproduct is necessary.¹

The use of two or more reactors operated in parallel allows evaluation of a number of variables, both during acclimation and after continuous operation is established. One of the important variables to evaluate during the acclimation period is the waste feed pattern or loading rate. Many biological treatment evaluations begin with a period of batch treatment, even if the treatment process to be evaluated is continuous. It should be noted here that sustained batch feeding techniques in laboratory systems intended to evaluate continuous processes may be subject to unreliable scale-up. Intuition might suggest that slow initial feeding is most appropriate, since removal kinetics are of secondary importance to population establishment during acclimation. However, a more rigorous feeding strategy may be appropriate in some instances. Initial feeding patterns often allow for accumulation in reactor volume. This can help in maintaining all potentially vital components of the culture, provided they don't allow for the accumulation of an unwanted inhibitor. Eventually volume displacement equivalent to the feed volume is necessary.¹

Abundant data collection is very important during the acclimation period. Feeding should be reduced substantially or terminated if indicators such as gas production, oxygen consumption rates, or TOC removal drop off suddenly. The pH of the culture (or effluent) should be monitored carefully because large pH changes are quite possible as a result of biological activity, and are a frequent cause of upsets. Process control strategies such as sludge wasting should be varied slowly, until the desired operating conditions are reached. Among the advantages of operating multiple reactors is that more creative or risky operating techniques can be evaluated. Failure of a reactor can provide as much information as success if the reason for failure is understood.¹

BIOAUGMENTATION. In an operating bioreactor used for waste treatment, an indigenous bacterial population arises which is unique from the standpoint of species diversity. This population is the result of physiological and genetic adaptation to the waste characteristics and process operation parameters. In bioreactors treating a variable mixture of toxic or inhibitory wastes, bacterial diversity is reduced by the increased selective pressure on the population due to the presence of selected waste components. Reducing the types of bacteria present can diminish the genetic pool of the reactor population, and decrease the ability of the population to respond to changes in the environment or

waste composition. Because of the diminished capacity for adaptation, biological hazardous waste treatment processes are often plagued by upsets and are unable to degrade new compounds entering the waste stream. Bioaugmentation is the process of adding nonindigenous bacterial supplements to a bioreactor for the purpose of artificially increasing the bacterial diversity and activity of the population by adding bacteria with enzymatic systems that allow degradation of previously biodegradable organics or by adding bacteria that have higher metabolic rates. Many bacterial supplements are available commercially to augment existing populations of biological hazardous waste treatment processes. To date, no clear consensus has been reached on the relative merits of bioaugmentation.⁸

A compilation of findings from published papers on bioaugmentation are presented in Table 5.1. The location of the testing, the waste type, and whether or not treatment performance was enhanced by bioaugmentation are given. Based on the information presented in Table 5.1, enhanced biological treatment performance has been attributed to bioaugmentation for those studies conducted under field conditions, while those studies conducted in the laboratory have been generally negative.

Table 5.1 **Compilation of current supplementation reports.**

Test setting	Waste type	Bioaugmentation effective	
		Yes	No
Field	Pharmaceutical	X	
Field	Petrochemical	X	
Field	Refinery	X	
Field	Refinery	X	
Field	Municipal	X	
Field	Dairy	X	
Laboratory	Dairy		X
Laboratory	Hazardous		X
Laboratory	Synthetic		X
Laboratory	Chlorinated organics		X

It is also important to note that even when bacterial supplements were acclimated to test conditions they did not perform better than the indigenous population. This result raises further questions about the utility of commercial supplements when compared to an indigenous population.

In summary, published results from recent research dealing with the effectiveness of bacterial supplementation have been inconclusive. However, on the basis of a literature review, a number of criteria that may affect the potential success of bioaugmentation were identified. These criteria were the viability of the bacterial supplements should remain high when added to the indigenous reactor population; once supplements are added they should initiate biodegradation of the target compound rapidly, or degrade compounds

not degraded by the indigenous population; and added supplements should have the necessary characteristics to maintain their population in the reactor.⁸

Inhibition and Shock Loading. Important factors determined during bench-, pilot-, and full-scale testing are the concentrations of hazardous components that can be tolerated by the biological treatment system and the responses that can be expected. The specific dissolved oxygen uptake rate (SDOUR) and adenosine triphosphate (ATP) can be used as indicators of microbial activity.⁹

A change in a system such as substrate leaking, reactor appearance, or biomass characteristics are occurrences that operators need to watch for to identify when an inhibitory situation is occurring. For example, the work of Rozich and Gaudy¹⁰ showed that for both inhibitory and noninhibitory substrate quantitative shock loads, the effluent COD increases following a shock, although little or none of the original substrate may appear in the effluent. The primary effect of the shock is, in both cases, an apparent increase in production and release of metabolic products. The products released by the cells in the phenol system are almost certainly less toxic than phenol.¹⁰

Rozich and Gaudy¹⁰ noted that the similarity in the reactions to severe shock loads in systems treating inhibitory and noninhibitory wastes was the difference in the duration of the predicted and observed transients. In both types of systems, the transient, as judged by fluctuations in COD and solids, continues for much longer than predicted by kinetic equations. This prolonged instability is attributed to ecological shifts in the biomass that result from the change in operational conditions. Research has not yet led to a prediction of the occurrence of the changes in predominance characteristic of the delayed or ecological response that ultimately correlated the complete system failure occurring in the phenol system reported. For a nontoxic substrate, this secondary response, while leading to severe COD leakage, did not lead to wash out of the system. The biomass was able to recover, but when phenol was the carbon source, no recovery ensued. The analysis of the model, using experimentally determined biokinetic constants, gave some insight as to why recovery may not be possible, even if changes in predominance do not occur and cause wash out. If the specific growth rate exceeds μ^* (peak or critical growth rate) with substrate diluting into the system, the biomass can no longer respond to the increased S_i by an increase in μ and the resultant system failure cannot be avoided. In the phenol system described, when COD in the reactor increased drastically several days after the original shock essentially all of the COD was due to phenol; the cells were no longer taking up phenol and utilizing it for either replication or conversion to metabolic products. Likely, once phenol began to accumulate in the reactor, because μ^* and S^* had been exceeded, the toxic effects of phenol caused cell lysis, exacerbating the decrease in solids level due to decreased growth rate.

From a practical engineering point of view, Rozich and Gaudy¹⁰ concluded that successful treatment calls for design of low, rather than high, specific growth rates and for providing the operator with the means to keep the specific growth rate low, regardless of the changing influent conditions.

Considerations for Treatability Studies for Anaerobic Processes. Waste characterization requirements for anaerobic treatment studies are similar to aerobic treatment. However, special attention should be given to the pH conditions of the waste and if the waste is contaminated with toxic organics or heavy metals. See the section on Treatment Methods, Anaerobic Processes, for more details.

The equipment required for determining the design parameters for anaerobic degradation of hazardous wastewaters consists of various types of reactors that may be batch or continuously fed systems. The reactors can be completely mixed or plug flow. The experimental systems must have the capability to contain the off-gases from the system. A typical completely mixed, continuously fed reactor is presented in Figure 5.2. An operational start-up procedure follows:

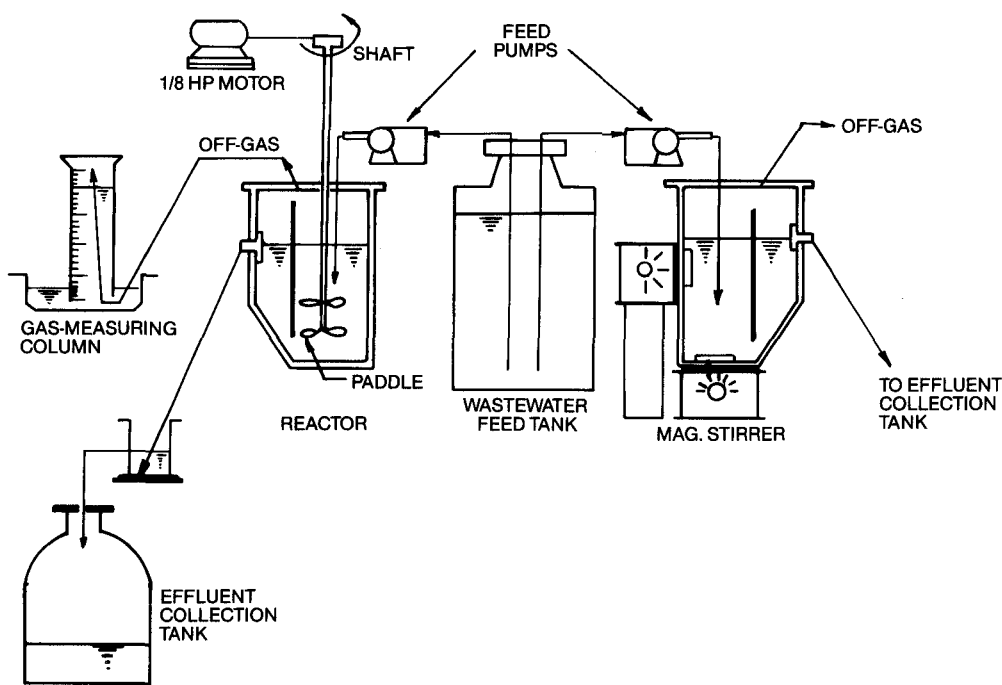


Figure 5.2 Schematic of the complete mix anaerobic systems.

1. Set up the apparatus, as shown in Figure 5.2.
2. Obtain an actively digesting seed from a municipal plant and immediately place it in the reactor. If possible, maintain the contents at 35°C during start-up and acclimation.

3. If a significant quantity of air is trapped in the digester, purge with an inert gas, preferably helium.
4. Adjust the suspended solids concentration to a level of approximately 6000 to 10 000 mg/L.
5. Begin feeding a starter substrate to the reactor contents at a preestablished rate. This starter substrate should be readily degradable by the anaerobic culture present.
6. Adjust the flow of the gas recirculation pump to completely mix the contents of the reactor. Alternatively, use a mechanical mixer or magnetic stirrer.
7. Check the entire system for gas leaks by putting small quantities of water or mineral oil around the joints and observing for bubbles.
8. After gas production is noticed and appears to be consistent (approximately 5 to 6 cu ft of gas/lb of COD removed (0.35 mL of gas/mg COD removed) at STP conditions), begin to introduce the hazardous liquid wastewater diluted by the starter substrate. It is recommended that the initial feed contain only a 10% dilution (by COD, not volume) of the wastewater. Cautiously, increase the dilution factor to 100% hazardous wastewater over a period of 5 to 20 days, depending on such factors as the relative degradability of the waste and the presence of inhibitors. During this acclimation period, it is desirable to maintain the organic loading to the system at less than 1.0 mg BOD/mg VSS d. Another control parameter during acclimation is to feed the waste at a rate of less than 200 lb of BOD/1000 cu ft/day ($3.2 \text{ kg/m}^3 \text{ d}$) of reactor volume.
9. Withdraw samples periodically for analysis of BOD or COD removals, pH, VSS level, and volatile acids:alkalinity ratio. During start-up and acclimation, the volatile acids:alkalinity ratio should be carefully observed and controlled to ensure that it stays above 0.4.¹¹ This ratio is often the first indicator of an anaerobic reactor being upset due to the overproduction of organic acids. Alkalinity should be added to maintain the pH within the range of 6.6 to 7.6.
10. After stabilized conditions are obtained, the systems can be operated at the desired test conditions and samples should be withdrawn daily for analysis of BOD, COD, VSS, and pH. In addition, the gas production should be measured and recorded daily.

MODELING. Steady-State Assumptions. Marshall *et al.*¹² observed the limitations of assuming steady-state conditions and applied the assumption in the use of empirical models. This skepticism is an appropriate means of introducing this section on modeling.

According to Marshall *et al.*,¹² a major assumption in the development of design relationships is that the biological system is in steady state. The inability to reach steady state has also been observed by others, in spite of using constant wastewater flows and compositions. Marshall *et al.*¹² stated that full-

scale biological treatment systems rarely operate in a steady-state fashion and most laboratory activated sludge reactors never reach a true steady state. If steady-state conditions exist, then the average effluent TOC and MLVSS concentrations will be representative of the operating conditions over the entire data collection period. On days when the reactors produced an effluent TOC equal to the average effluent TOC in these studies, the corresponding MLVSS in the reactor were not the same as the average MLVSS over the data period. Without steady state, the average values lose their significance because they may not be representative of actual operating conditions, and difficulties in applying design models may be expected.¹²

Modeling Equations — Monod and Haldane. Philbrook and Grady¹³ evaluated biodegradation kinetics for priority pollutants. They presented modeling equations describing the biokinetics and techniques for measuring kinetic parameters once a “competent” biomass was established. Their work is representative of the many discussions of modeling and should be referenced for a more detailed discussion.¹³

The most commonly employed rate equation for the noninhibitory case is by Monod:

$$\mu = \frac{\mu_m S}{K_s + S}$$

Where

- μ = specific growth rate, time⁻¹;
- μ_m = maximum specific growth rate, time⁻¹;
- S = substrate concentration, ML⁻³; and
- K_s = saturation constant, ML⁻³.

Engineers commonly use the specific substrate removal rate (Q) rather than :

$$Q = \frac{Q_m S}{K_s + S}$$

or

$$Q = \mu/Y_g$$

Where

- Y_g = true growth yield, million cells formed⁻¹.

The saturation constant represents the substrate concentration at which and Q are one-half of their maximal values.

A widely accepted expression capable of fitting the data for an inhibitory substrate is the Haldane equation:

$$\mu = \frac{\mu_m S}{K_s + S + S^2/K_i}$$

or

$$Q = \frac{Q_m S}{K_s + S + S^2/K_i}$$

Where

K_i = inhibition constant, ML^{-3} .

When K_i is very large, the Haldane equation reduces to the Monod equation.

Determining Kinetic Parameters. Although many methods have been developed for measuring the kinetic parameters μ_m , Q_m , K_s , and K_i Philbrook and Grady¹³ grouped them into five categories, three employing batch procedures and two relying on continuous culture.

A commonly used method has its origin in the work of Monod and has been used on a number of compounds, both noninhibitory and inhibitory. In this method, batch reactors containing the pollutant of interest at different concentrations are inoculated with small quantities of biomass capable of performing the desired biodegradation. The increase in biomass concentration in each reactor is measured as a function of time and analyzed to obtain μ . The values are then correlated with the initial substrate concentration to obtain μ_m and K_s of the Monod equation or μ_m , K_s , and K_i of the Haldane equation.

Another batch technique focuses on substrate removal rather than growth, and thus provides data for determining Q_m , K_s , and K_i . As commonly used in engineering studies the batch reactors are inoculated with large quantities of biomass and substrate removal is measured as a function of time. If a specific test is available for the target pollutant it need not be provided as the sole substrate and thus some data may be obtained on the effects of other waste constituents, although care must be used when doing this or the data may be misinterpreted. The data on substrate concentration as a function of time must be differentiated for conversion into data on Q as a function of substrate concentration. It is then analyzed to evaluate the parameters.

Both of the above techniques have been widely applied to wastewater treatment problems using general measures of waste strength such as 5-day biochemical oxygen demand (BOD₅) and chemical oxygen demand (COD), but they lead to several problems when they are applied to compounds like the priority pollutants. The first, and most serious, is associated with the fact

that the K_s values for many individual organic compounds are quite low; often less than 100 g/L. To employ a simple measure of cell concentration in the growth technique, such as absorbance measurement, then it is impossible to detect any growth at the substrate concentration range over which will be affected. In that case, the only way to measure is with viable cell counts, which greatly increases both the effort and the error associated with the procedure. In the substrate removal experiment, the combination of a high cell concentration with a low K_s value results in a linear substrate removal curve which can lead to the erroneous conclusion that removal of the pollutant is zero-order. It must be recognized that completely mixed bioreactors will be operating at very low pollutant concentrations where zero-order kinetics are not valid, and accurate prediction of the effluent concentration requires accurate assessment of K_s .

Infinite Dilution Technique and Modifications. To reduce the time required to evaluate kinetic parameters and to alleviate the problems associated with shifts in the composition of the microbial community, Williamson and McCarty¹⁴ developed a pseudo-steady-state procedure which they called the infinite dilution technique. The test was predicated on the self-regulating nature of microbial metabolism. If a microbial culture was placed into a batch reactor and an organic substrate was added continually at a rate less than the maximum rate at which the organisms can use it, they will match their rate of utilization with the rate of addition by regulating the substrate concentration surrounding them to a value consistent with that rate. If the volume of feed added was negligibly small with respect to the reactor volume and if the mass of cells formed was small with respect to the mass carrying out the removal, then a pseudo-steady-state would be achieved during which the substrate concentration in the reactor was constant and consistent with the rate of substrate utilization. Such a reactor has been termed a "fed-batch" reactor. Measurement of the pseudo-steady-state concentrations in several reactors receiving feed at different rates provides data on Q versus S that can be analyzed to estimate Q_m and K_s .¹³

The procedure has several distinct advantages over the traditional procedure. First, it is fast. If a culture is available, its kinetics can be evaluated in as little as 1 day. This means that during pilot-scale testing, a culture can be sampled and analyzed several times giving an accurate measure of any time-dependent changes in its kinetics. Second, the parameter values obtained are specific for a given microbial community because the amount of growth that occurs during the test is small enough to minimize changes in species predominance. Third, the procedure can be applied to any culture. This means that it can be used to obtain a "snapshot" of the kinetics associated with the sludge in a full-scale plant at any time and a series of such "snapshots" provides the engineer and operator with a moving picture of how the plant responds over time.¹³

Philbrook and Grady¹³ observed that even under carefully controlled conditions the kinetics of biodegradation of priority pollutants are subject to considerable variation. Additional research must be conducted to determine how best to minimize this variability. Application of the modified infinite dilution technique (MIDT), outlined by Philbrook and Grady,¹³ provides a rapid and effective way of evaluating variability. If the MIDT is employed on a routine basis during treatability studies, its use provides the engineer with statistical knowledge of the variability likely to be encountered in the full-scale system. Variability can then be considered quantitatively during design. When used on biomass from a full-scale plant, the MIDT can provide data both on the variability of the kinetic parameters and the impact of other waste constituents. Such data will lead to a better understanding of the factors affecting priority pollutant removal and will allow the operator to take corrective action to maintain the desired degree of removal.¹³

TREATMENT TECHNOLOGY

EFFICIENCY OF TREATMENT FOR METALS. General. Physical-chemical means are often used to remove metals from a hazardous waste stream, but aerobic suspended growth technology has been assessed in bench, pilot-, and full-scale activated sludge processes for the removal of heavy metals. Activated sludge processes are followed by secondary clarification, and the physical and chemical aspects of removal of metals must be considered.

Removal of metals from a waste stream by activated sludge depends on the individual metal, the wastewater matrix, and the operational characteristics of the treatment system. Metals may cause operational problems at an activated sludge facility by producing toxic effects; accumulating on sludge solids to an extent that the sludge becomes hazardous, thus complicating and restricting disposal. They can also pass through the plant, limiting the discharge or causing increased penalties.

Characteristics of the treatment process that may influence metal removal efficiency and mechanism include the mixed liquor suspended solids (MLSS) concentration; wastewater pH, temperature, and hardness; solids retention time (SRT); metal solubility; partitioning of the metal between soluble and insoluble fractions; and the presence of chelants or other complexing agents.

Removal Mechanisms. Stephenson *et al.*¹⁵ identified five basic types of metal removal mechanisms: direct settling of precipitated insoluble metals, interaction of insoluble metals with flocs of settling mixed liquor solids, activated uptake of soluble metals by the bacterial cells of sludge biomass,

adsorption of metals onto the biological solids, and volatilization of the metals. The latter is considered to occur to an insignificant extent.

The results of Elenbogen *et al.*¹⁶ differed from previous investigators in that no predictable correlation between SRT at 3 and 10 days and MLVSS metals concentrations was found. They concluded that control of SRT would not be a feasible operational tool for controlling mixed liquor metal concentrations.

Figure 5.3 provides a summary of the work by Stephenson *et al.*¹⁵ on the effects of solubility, removals, and SRT. Cadmium and copper removals were always greater than 75%, while nickel was less than 40%. From Figure 5.3 it can be seen that metals more soluble were less well removed. The SRT had little effect on overall metal removal. Solubilities of nickel were consistently close to 100%. The percentage solubilities of the three metals increased dramatically in the final effluent compared to settled sewage (primary effluent). It appears that insoluble metal was removed to a greater extent than soluble metal.

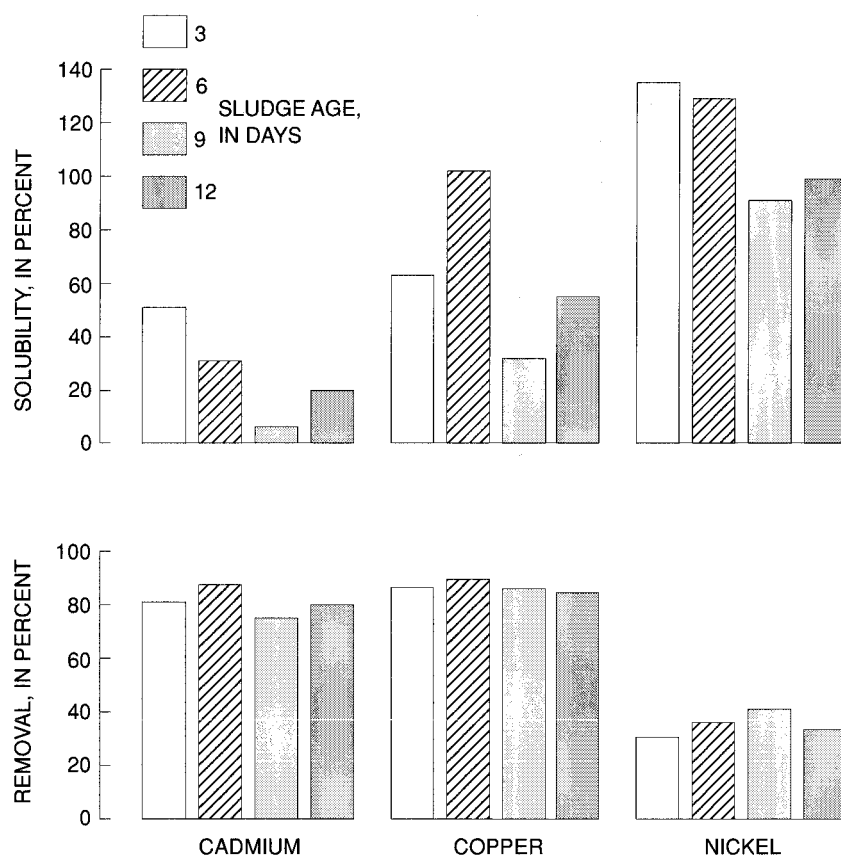


Figure 5.3 Percent removals and solubilities in final effluent in an activated sludge pilot plant for cadmium, copper, and nickel at 3-, 6-, 9-, and 12-day sludge ages.

For cadmium and copper, and to a lesser extent nickel, the removal of insoluble metal was responsible for most of the overall percentage removed. The metal was removed by its interaction with the settleable biological solids, a physical process that could occur in the secondary sedimentation tanks. Direct settling of particulate associated metal was of minor importance for cadmium and copper, but was slightly more significant for nickel which was always poorly removed.

Stephenson *et al.*¹⁵ concluded that the partitioning of metals between soluble and insoluble phases was important in determining the extent of removal during the activated sludge process. Metals that are most soluble in the influent settled sewage are least well removed.

Lowe and Gaudy¹⁷ evaluated removal of cadmium in a pilot extended aeration process. Changes in system pH of a few tenths of a pH unit in the range of 6 to 7 brought about substantial changes in cadmium solubility. The pH changes were the result of microbial activity. Kodukula and Patterson¹⁸ conducted batch activated sludge adsorption experiments and evaluated pH, adsorption, and precipitation effects. For affecting adsorption of metals to activated sludge solids, pH seems to be a controlling variable. The percent metal adsorption increased by more than 70% over 1 to 2 units of pH change. The effect of suspended solids on distribution of metals at a high pH level (8.0) seems to be minimal, but is quite significant in low-pH conditions. At pH levels below 7.0, the influence of suspended solids on metal distribution is pronounced. Thus, a combination of low pH levels and low suspended solids concentrations yields adverse results when high removals of metals, particularly nickel, are desired.

Removals of metals by activated sludge have been studied by numerous workers. Cormack and Hsu¹⁹ spiked a powered activated carbon (PAC) plug flow pilot plant influent with organic and inorganic pollutants. The removals of metals were compared with DuPont and U.S. EPA data. The EPA data were for biological treatment without PAC addition. These data are presented in Table 5.2.

The removal of inorganic pollutants ranged from 9% for arsenic to 82.9% for mercury. These were higher than those obtained in DuPont's PACT plant. This was reportedly due to the difference in the influent concentration. Influent concentrations of the inorganic pollutants in DuPont's PACT plant were all much lower than those observed by Cormack and Hsu.¹⁹ The percent removal obtained in their study was also slightly higher than the average national removal rate for secondary treatment processes published by the EPA. Cormack and Hsu¹⁹ believed this could also have been attributable to the use of carbon in the wastewater treatment process because activated carbon can adsorb inorganics, although the removal efficiency may not be as high as for organic compounds.

Table 5.2 Metal data for pilot-plant operation.

Metal	Priority pollutant		Range of effluent concentrations, (µg/L)	PACT removal, percent		
	Range of influent concentrations, (mg/L)	Detection limit, (µg/L)		Cormack and Hsu's study	DuPont	EPA secondary treatment
Arsenic		10	ND – 10	9	0	— ^b
Cadmium	ND ^a – 11	5	ND – 20	> 78.4	4	55
Chromium (T)	ND – 60	10	ND – 140	> 49.7	42	69
Copper	30 – 500	10	ND – 200	> 81.4	0	75
Lead	11 – 2100	50	ND – 480	> 59.1	52	63
Mercury	ND – 11.2	0.5	ND – 2.8	82.9	50	— ^b
Nickel	30 – 710	30	ND – 280	54.9	23	24
Silver	8 – 40	10	ND – 40	> 40.6	— ^b	76
Zinc	140 – 3400	20	30 – 700	79.1	40	70

^a ND = Not detected.

^b Not analyzed, or data not available.

Shock Loads and Acclimation. Inhibitory metal effects were evaluated by Lowe and Gaudy.¹⁷ They found the extended aeration biomass could retain extremely high concentrations of cadmium (in this study in excess of 2000 mg/L) without ill effects on the biochemical efficiency of purification of a synthetic waste. There was evidence that acclimation played a protective role in the system.

These results are of value because they demonstrate that relatively large concentrations of cadmium can build up in the sludge without hampering removal of soluble substrate, and they offer some indication that even higher levels of cadmium might be retainable in the sludge without ill effects. At levels up to 320 mg/L the system responded extremely well, and the results indicated that the process flow scheme for the biological removal and recovery of heavy metals (depicted in Figure 5.4) offers a viable alternative for treatment of wastes containing very high concentrations of heavy metals. The similarity between the process in Figure 5.4 with the contact stabilization process should be noted. Lowe and Gaudy¹⁷ concluded that long-term exposure to cadmium does select for a biomass that exhibits tolerance to rather high concentrations of the metal.

When the cadmium dosage was rather rapidly increased, eventually to 320 mg/L, there were no ill effects on the biochemical performance of the system. Previous long-term contact (1 year) at 1 mg/L may have imparted acclimation, permitting tolerance of the higher dosages.

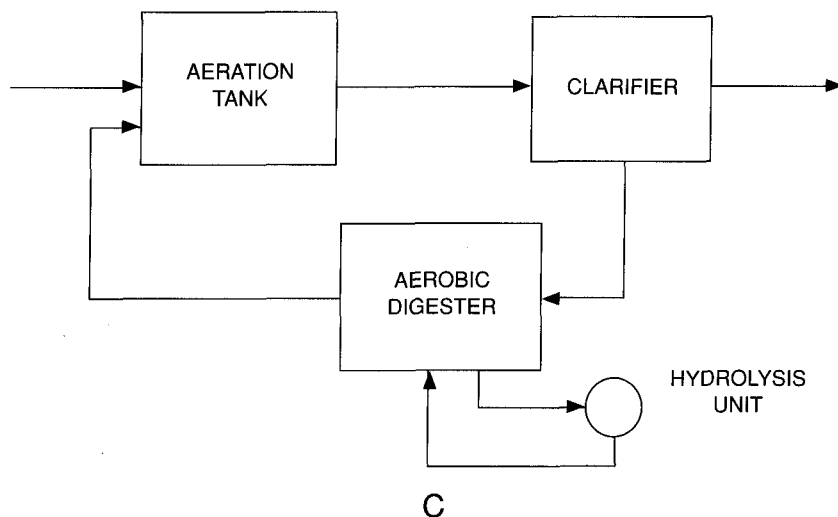


Figure 5.4 Schematic comparison of conventional extended aeration flow schemes with proposed modification incorporating external recycle and the hydrolytic assist.

Further evidence of the importance of acclimation was seen for the qualitative shock with copper of 100 mg/L on Day 385. Copper was chosen for the qualitative shock because it has been reported to have a greater affinity for, and toxicity to, sludge solids than cadmium, despite the fact that it is usually considered to be even less soluble than cadmium at neutral pH values. Regardless of solubility considerations, exposure of the nonacclimated biomass to copper resulted in prompt and severe deterioration of system operation. Therefore, it would appear acclimation played a role in the response of this system to heavy metals.

Variability. Unger and Claff²⁰ used statistical methods to evaluate percent removals from the EPA's 40 POTW Study.²¹ The data for all POTWs indicated that nickel, arsenic, and selenium were removed most poorly, while copper chromium, and zinc were removed to the greatest extent. They concluded percent removals of priority pollutants vary significantly among the 40 POTWs tested for both metals and organics. Metal removals in activated sludge plants ranged from 43 to 81%. Percent removals for a given priority pollutant were highly variable from plant to plant and even from sampling to sampling within a given treatment plant. Metal variability among plants ranged from 21 to 50%. The overall conclusion was percent removal data vary among POTWs and require evaluation on a plant-by-plant basis rather than on the mean percent removals derived from all treatment plants. This conclusion may be extrapolated from POTWs to treatment of hazardous

wastes in that generalizations about removal of a specific metal should not be made.

Comparison of Different Processes. Hannah *et al.*²² conducted a pilot study evaluating removals of toxic pollutants by six wastewater treatment processes. The aerated suspended growth units included were activated sludge, an aerated lagoon, and a facultative lagoon. Metal removals by these pilot processes were calculated from the average concentrations of Table 5.3 and are shown in Table 5.4. The activated sludge system and facultative lagoon showed the best removals for metals. The high-rate trickling filter system achieved percent removals for metals of from 28% for cadmium to 60% for copper. The metals were concentrated in the sludge. Copper, which exhibited the greatest percent removal, had the highest concentration in the sludge. Cadmium, which had the lowest percent removal, was also the least concentrated in the sludge. For all the metals used in this study, the percent removal in the trickling filter system increased as the degree of metal concentration in the sludge increased.

Table 5.3 Concentrations of metals in wastewater feed and effluents.

Metal	Wastewater feed		Activated sludge effluent		Aerated lagoon effluent		Facultative lagoon effluent	
	µg/L	σ	µg/L	σ	µg/L	σ	µg/L	σ
Chromium	221	88	40	18	65	106	46	34
Copper	345	119	61	40	89	61	71	46
Nickel	141	93	81	45	91	50	81	59
Lead	165	168	58	75	70	76	82	110
Cadmium	25	23	19	17	—	—	17	9

Table 5.4 Percent removal of metals by different processes.

Metal	Activated sludge	Aerated Lagoon	Facultative Lagoon
Chromium	82	71	79
Copper	82	74	79
Nickel	43	35	43
Lead	65	58	50
Cadmium	24	—	32

Chang *et al.*²³ studied the uptake of cadmium and copper in a three-stage rotating biological contactor (RBC). Cadmium concentrations of 5 and 20 mg/L, and copper concentrations of 1, 5, 10, 25, and 50 mg/L were used. The reactor consisted of three discs per stage, with a total surface area of 9120 cm². The flow rate was 50 L/d resulting in a 54.8 L/m² d surface load-

ing rate. The total detention time was 4 hours. The rotation speed was 25 rpm and the liquid volume:surface area ratio was 9.38 L/m².

The system was allowed to reach steady state with a feed consisting of sucrose and mineral supplements. A cadmium dose of 5 mg was added for 24 hours then discontinued. The organic removal efficiency decreased from 92 to 84% after the cadmium was added. The removal efficiency increased to 90% within 5 days after the cadmium addition was stopped. Cadmium was again added at a rate of 20 mg/L for 3 days. The substrate removal efficiency decreased from 90% to about 81 to 85%. The authors concluded that the initial cadmium shock with the addition of 5 mg/L for 1 day acclimated the system for the higher cadmium shock of 20 mg/L for 3 days.

The RBC system did not lose any efficiency when 1, 5, and 10 mg/L of copper were added. The organic substrate removal efficiency decreased by an average of about 10% when 25 mg/L of copper was added. The system efficiency returned to about 90% within 10 days after the copper feed was stopped. Copper was then added at a concentration of 50 mg/L. The efficiency declined an average of about 7%. Again, the conclusion was that the initial copper exposure acclimated the system for the subsequent higher copper loading.

During the copper addition, the biofilm color turned dark blue or black. The amount of sloughing also increased and the dry density of the biofilm increased. The authors attributed this to the adsorption of copper into the biofilm. The composition of the biomass was examined with a microscope to assess the population changes due to the copper addition. In general, the number of protozoa and rotifers decreased when 5 mg/L of copper were added.

EFFICIENCY OF TREATMENT OF ORGANICS. General. The removal of complex organic compounds by aerobic biological treatment of listed hazardous wastes has been evaluated in lab-, pilot-, and full-scale studies. These organics are measured and classified as the acid extractable, base-neutral extractable, volatile (purge and trap), and pesticide and PCB compounds.

Removal of these compounds by aerated suspended growth can be by biodegradation, air stripping, adsorption by biomass or polymers and incorporation into sludge, or other mechanisms or combinations of mechanisms not easily described or measured in a complex waste stream (for example, photo-oxidation).

Complex organics are degraded by microorganisms with low growth rates.^{24, 25} Processes that promote the growth of these types of organisms, therefore, would favor biological removal of complex contaminants. The microbial growth rate is inversely proportional to the solids retention time (SRT) in a biological reactor. Consequently, as the growth rate decreases, the SRT must increase. Control of the SRT and the maintenance of an optimum SRT will significantly impact slow-growing microorganisms that are impor-

tant in degrading complex contaminants. An SRT that is too low will result in slow-growth organisms being washed out of the system or being inhibited by other faster growing populations.^{24, 25} Biomass concentrations are also high in fixed-film processes promoting the removal of highly adsorbable compounds.²⁴

The removal of toxic trace contaminants from wastewater by fixed-film systems can be the result of stripping from solution, adsorption onto biological solids, precipitation from solution, and biological degradation.

Grady² defined characteristics of wastes as biodegradable, recalcitrant, or persistent. Biodegradability and recalcitrance are mutually exclusive intrinsic properties of organic compounds determined by their molecular structure. Consequently, each compound is either one or the other. A recalcitrant compound can never undergo biodegradation in a wastewater treatment system, no matter how that system is configured or operated. A biodegradable compound may or may not undergo biodegradation under any given condition, and that is where the concept of persistence arises. Persistence is a conditional property of a biodegradable organic compound in the sense that if the environment is not suitable for biodegradation to occur the compound will persist in spite of its inherent biodegradability.

According to a U.S. EPA report by Rogers²⁶ different organic compounds at the same concentration will have varying impacts on microbes with resultant levels of biodegradability depending on environmental and chemical conditions. Some, but not all, organisms have a preference for peptones, carbohydrates, and other forms of readily usable carbon sources over hydrocarbons or synthetic organic compounds. The sequential utilization of preferred substrates from a mixture has also been demonstrated for various classes of hydrocarbon and synthetic organic molecules. The following generalizations may be drawn concerning diauxic (two-phase) growth in mixed industrial wastes:

- Nonaromatic or cyclic aromatic compounds are preferred over aromatics.
- Materials with unsaturated bonds in their molecules, for example, alkenes, alkynes, tertiary amines, and so on, are preferred over materials exhibiting saturated bonding.
- The comparative stereochemistry of the molecules of certain compounds makes them more or less susceptible to attack by microbial enzymes. The *n*-isomers of the lighter weight molecules are preferred over branched isomers and complex, polymeric substances.
- Soluble organic compounds are usually more readily degraded than insoluble materials. Biological waste treatment is most efficient in removing dissolved or colloidal materials which are more readily attached by enzymes and transported through cell membranes. Readily dispersed compounds are usually degraded more rapidly because of

the increased surface area that is presented to the individual microorganisms.

- The presence of key functional groups at certain locations in the molecules can make a compound more or less amenable to biodegradation. Alcohols, for example, are often more readily degraded than their alkane or alkene homologues. On the other hand, halogenation of certain hydrocarbons may make them resistant to degradation.

Rogers²⁶ identified the following classes of wastes as generally resistant:

- Oil,
- Isoprene,
- Methyl vinyl ketone,
- Morpholine,
- Ethers,
- Ethylene chlorohydrin,
- Polymeric compounds,
- Polypropylene benzene sulfonates,
- Tertiary and volatile aliphatics,
- Aromatics,
- Alkyl-aryl groups,
- Tertiary aliphatic alcohols,
- Tertiary benzene sulfonates, and
- Trichlorophenols.

Biodegradability in complex waste mixtures is not identical to laboratory experiments. Some organic materials can polymerize or react in a synergistic manner on contact with other wastes. Acclimation of microorganisms can also affect biodegradability.

Ford *et al.*²⁷ determined the ratio of BOD₅ and COD of wastewater compounds. They used this ratio to indicate the fraction of dichromate-oxidizable materials amenable to biological degradation. A high ratio indicates that many of the dissolved organic materials can be degraded biologically, while a low value indicates the presence of a significant fraction of bioresistant organic constituents. Table 5.5 shows the measured BOD and COD for several classes of chemicals. The relatively high degradability of most unsubstituted aliphatic compounds should be noted.

Tabak²⁸ conducted biodegradability and acclimation studies on 96 organic priority pollutants using a static culture flask screening procedure. These included phenols, phthalate esters, naphthalenes, monocyclic aromatics, polychlorinated biphenyls (PCBs), halogenated ethers, nitrogenous organics, halogenated aliphatics, and organochlorine insecticides. Yeast extract was used as a synthetic medium and the test compounds were incubated for 7

Table 5.5 Comparisons of COD and BOD of selected organic chemicals.

Chemical group	Measured COD, mg/mg	Measured BOD ₅ , mg/mg	BOD COD, percent
Aliphatics			
Methanol	1.05	1.12	107
Ethanol	2.11	1.58	75
Ethylene glycol	1.21	0.36	30
Isopropanol	2.12	0.16	8
Maleic acid	0.80	0.64	80
Acetone	2.07	0.81	39
Methylethyl ketone	2.20	1.81	82
Ethyl acetate	1.54	1.24	81
Oxalic acid	0.18	0.16	89
Aromatics			
Toluene	1.41	0.86	61
Benzaldehyde	1.98	1.62	82
Benzoic acid	1.95	1.45	74
Hydroquinone	1.83	1.00	55
O-cresol	2.38	1.76	74
Nitrogenous organics			
Monoethanolamine	1.27	0.83	65
Acrylonitrile	1.39	nil	0
Aniline	2.34	1.42	61
Refractory			
Tertiary-butanol	2.18	0	0
Diethylene glycol	1.06	0.15	14
Pyridine	0.05	0.06	120

days at 25°C. This was followed by three weekly subcultures using domestic wastewater as the microbial inoculum. Although limited to screening since degradation and acclimation would differ greatly under process operating conditions, this method can be helpful in predicting compound treatability.

Observed Removal Efficiencies of Selected Organic Compounds.

PHENOLS. Hickman and Novak²⁹ evaluated removal of pentachlorophenol (PCP) in batch tests. They noted that removals of PCP in laboratory-scale tests have not been equaled in full-scale treatment plants. Among the acid extractables PCP is the most heavily chlorinated compound and has the highest octanol-water partition coefficient. Hickman and Novak²⁹ observed that the PCP concentration decreased from 12 to 13 mg/L to virtually zero after 30 days of feeding PCP, and then increased slowly. Apparently there was a shift in species composition to active PCP-degrading organisms at that time. After about 1 week of nearly complete PCP removal, PCP again began

to accumulate in the reactor. However, the activated sludge continued to remove PCP for the rest of the study. Hickman and Novak²⁹ stated that it was not clear why the PCP concentration began to increase; it was assumed that during the period of nearly complete degradation the PCP concentration was so low that there was no selective advantage for PCP degraders and their population declined.

PHTHALATE ESTERS AND NAPHTHALENE. Tabak²⁸ observed significant biodegradation, with rapid acclimation observed with the phthalate compounds. The phthalate esters, EHPE and DOPE, were the most persistent of the phthalates under the conditions of the static-flask-screening test.

MONOCYCLIC AROMATICS. Tabak²⁸ found significant biodegradation with rapid acclimation with benzene, toluene, and nitrobenzene.

POLYCYCLIC AROMATIC HYDROCARBONS. In the work by Tabak,²⁸ the polycyclic aromatic hydrocarbons (PAHs) demonstrated varied rates of biodegradation with different acclimation periods, depending on the test compound and the dose of substrate in culture media. The PAHs, in general, have been reported to be potentially biodegradable compounds, particularly by soil microorganisms and in soil systems which provide better conditions for biodegradation than aquatic systems. The biodegradability data have shown that the tricyclic aromatic hydrocarbons are more susceptible to biodegradative action than the tetracyclic and higher polycyclic hydrocarbons.

POLYCHLORINATED BIPHENYLS (PCBs). The individual PCBs vary widely in their susceptibility to biodegradation. The mono-, di-, and trichlorinated species may be significantly biodegraded or biotransformed, as well as volatilized. The PCBs with five or more chlorine atoms per molecule have a tendency to absorb suspended materials and sediments, bioaccumulate because of very low solubility, photodissociate, and are quite resistant to biodegradation.

In work by McDermott *et al.*,³⁰ PCB biodegradation was demonstrated in the laboratory using selected bacteria and naturally occurring bacteria. They found that the ability to degrade PCB ranges from very poor to outstanding, depending on the bacteria and the type of PCB.

HALOGENATED ETHERS. In Tabak's work,²⁸ the compounds *bis*-(2-chloroethyl) ether, 2-chloroethyl vinyl ether, and *bis*-(2-chloroisopropyl) ether are significantly biodegradable with slightly varied acclimation periods, whereas 4-chlorodiphenyl ether, 4-bromodiphenyl ether, and *bis*-(2-chloroethyl) methane demonstrated insignificant biodegradability.

NITROGENOUS ORGANIC COMPOUNDS. Tabak²⁸ showed that the diphenylnitrosamine, N-nitroso-N-phenylbenzamine (N-nitrosodiphenylamine) were easily biodegradable by microorganisms with rapid acclimation. Diphenylnitrosamine was reportedly more easily degraded by microorganisms than are dialkylnitrosamines.

HERBICIDES. Tabak²⁸ found that unsaturated ketone (cyclohexeneone) isophorone exhibited rapid degradation by microorganisms. The herbicide compound, acrylonitrile (vinyl cyanide) was easily degraded. Acrolein (an unsaturated aldehyde) was also shown to be easily dissimilated with rapid acclimation of microbiota to the substrate.

The work of Hill *et al.*³¹ using an activated sludge pilot plant showed that activated sludge treatment proved ineffective in removing chlorophenoxy herbicides (CPH) from settled wastewater. Statistical treatment of the data suggested neither adsorption nor catabolic biodegradation were responsible for those significant CPH removals. There was no evidence of acclimatization of the mixed liquor to the presence of CPH contaminants. Furthermore, there was no obvious effect of sludge age on the efficiency of CPH removal from settled wastewater.

ORGANOCHLORINE PESTICIDES. Tabak²⁸ observed poor removal efficiency for organochlorine pesticides. Aldrin, dieldrin, chlordane, p,p'-DDT, p,p'-DDE, p,p'-DDD, alpha-endosulfan, beta-endosulfan, endosulfan sulfate, heptachlor, heptachlor epoxide, endrin, hexachlorocyclohexane isomers (alpha, beta, and delta), and lindane compounds were shown to be recalcitrant to bio-oxidative activity by wastewater microbiota.

HALOGENATED ALIPHATICS. Tabak²⁸ reported on the biodegradation of halogenated aliphatics. Volatilization was accounted for by using controls where media were tested without biological inoculum. The chloroethane aliphatics, 1,1- and 1,2-dichloroethane and 1,1,1-trichloroethane are considered to be potentially biodegradable and will probably be destroyed during aerobic treatment after a considerable period of acclimation, whereas tetrachloroethanes will exhibit recalcitrance to microbial activity and might be bio-oxidized only after very extensive acclimation periods. Because of their lipophylicity, the dichloroethanes should not be bioaccumulated to a large extent, whereas the tri- and tetrachloroethanes, being lipophylic in nature, might have a tendency for accumulation.

In Tabak's work,²⁸ the halomethane aliphatics demonstrated different biodegradation rates and acclimation periods, depending on the test compound and substrate concentration in the culture media. Methylene chloride, bromochloromethane, and carbon tetrachloride were shown to exhibit rapid degradation, whereas chloroform shows significant dissimilation with gradual adaptation. The chloroethylene aliphatics, trichloroethylene, and

tetrachloroethylene were significantly biodegradable with gradual adaptation observed.

Variability of Removal. Unger and Claff²⁰ used statistical methods to evaluate data from the EPA study²¹ on the occurrence and fate of priority pollutants in 40 POTWs. Table 5.6 shows volatile, acid extractable, and base-neutral removals and the coefficient of variation (CV). The CV is an indication of the variability of removal efficiencies of priority pollutants. The observed percent removals varied significantly among the 40 POTWs tested. Organic removals ranged from 52 to 87%. Variability occurred from plant to plant and from sampling to sampling within a plant, ranging from 10 to 55%. It was concluded that because of large variations among POTWs, evaluations should be conducted on a plant by plant basis rather than on mean percent removals derived from all treatment plants.

Table 5.6 Mean percent removals and coefficients of variations for activated sludge plants.

Chemical group	Removal, percent	C.V.
Volatiles		
Benzene	74.7	28.2
1,1,1-trichloroethane	81.9	17.3
Chloroform	65.2	30.7
1,2- <i>trans</i> -dichloroethylene	68.7	31.4
Ethylbenzene	82.4	20.0
Methylene chloride	57.1	41.7
Tetrachloroethylene	72.2	33.4
Toluene	86.3	19.0
Trichloroethylene	84.8	19.0
Acid extractable		
Phenol	83.9	22.7
Base neutrals		
Naphthalene	68.9	33.3
<i>Bis</i> (2-ethylhexyl)phthalate	67.4	32.3
Butylbenzyl phthalate	67.9	33.1
Di- <i>n</i> -butyl phthalate	61.9	38.7
Diethyl phthalate	62.2	41.5
Anthracene	69.5	31.4
Phenanthrene	65.9	33.5
Pyrene	86.6	10.0

Marshall *et al.*¹² analyzed reactor performances and models, and attributed difficulties in fitting experimental data to empirical models to problems in estimating viable cell concentrations and achieving steady-state

conditions. In their study a considerable amount of day-to-day fluctuation was apparent in effluent TOC. Even greater fluctuations are present in measurements of MLVSS. Achievement of steady state was not demonstrated for any of the reactors, even after operating for periods equal to several residence times. Variability was attributed to a combination of inherent process variability; hydraulic variations (for example, HRT and SRT); environmental fluctuation (for example, pH and temperature); sampling error; and analytical error.

Stover and Kincannon³² presented figures showing the typical scatter of data used for determining biokinetic constants. All the individual data points from the 2-month operating period were shown to indicate the scatter normally observed during this type of analysis. The actual scatter presented could have been masked by plotting the average values at each sludge age. This is the approach normally used when presenting biological system data and conducting the data analysis, since this type of variability is inherent in biological systems.

The variability observed during these type of studies could have been due to several factors. For example, the wastewater that is very biodegradable yields very low effluent BOD₅, TOC, and COD values. Low effluent values create two problems. First, the precision, accuracy, and detection capabilities of the analytical test methods themselves become limited at the effluent levels observed. Second, these very low values allow no distinction to be made with respect to substrate removal. The initial substrate concentration is so large compared to the effluent concentration that the difference becomes negligible at different sludge ages. Variability could also be enhanced based on the amount of specific compound that was stripped on any given day. In the previous analysis the percent stripping was assumed to be constant; however, the amount of compound stripped could have varied on a given day due to fluctuations in the air flow rates to a given system.³²

Mechanisms of Removal. The mechanisms for removal of organic compounds in an aerobic treatment system are air stripping, biodegradation, adsorption onto biological solids, and removal by subsequent settling or photo decomposition. Removal can also occur by addition of polymers or coagulants into the aeration basin with the aim of removal during secondary clarification. Because this represents intentional action by physical-chemical means, it will not be considered here.

SORPTION. Mass balances done on the influent, effluent, and sludge streams of treatment plants will help determine the extent of removal of contaminants. Detection in the sludge generally indicates sorption of the contaminant has occurred.

A determination of the organic materials adsorbed onto the sludge indicates the degree of oxidation or stripping capability of the system. The type

and quantities of organic compounds identified in the sludge are an indication of the sludge as a sink for recalcitrant organics. Compounds identified in the sludge and not present in the influent are the breakdown products from the oxidation of other compounds, or the organics were adsorbed prior to sampling and were not degraded in the biological system, or the compounds were present at concentrations below the analytical detection limit and have accumulated to above that limit in the biological system.

Dobbs and Cheng³³ developed a correlation between sorption of toxic organics on biological solids and the octanol-water partition coefficient. The relationship was used to estimate removal of toxic organic compounds by sorption and predicting concentrations of compounds in various sludges. The octanol-water partition coefficient (K_{ow}) proved useful as a means for predicting soil adsorption, biological uptake, lipophilic storage, and biomagnification. The isotherms obtained for the toxic organic compounds studied showed a wide range of sorption capacities. Relevant Freundlich parameters for sorption on mixed-liquor solids were also determined. The data developed by Dobbs and Cheng³³ is a useful starting point for determining the degree of sorption.

STRIPPING. Stover and Kincannon³² measured and sampled off gases from complete mix bench-scale continuous flow activated sludge reactors. The reactors were fed a synthetic wastewater containing compounds present in chemical, plastics, petrochemical, and petroleum industry wastewaters. All are listed hazardous compounds.

Table 5.7 shows the percentage of each individual compound that was stripped from the biological systems. The amount of compound stripped varied from 0 to 99%, with five compounds showing no stripping, three compounds showing high levels of stripping, and four compounds showing

Table 5.7 Specific organic compound stripping characteristics.

Compound	Compound stripped from biological systems, percent
Tetrachloroethane	93
Nitrobenzene	0
2,4-dichlorophenol	0
Acrolein	0
Acrylonitrile	0
1,2-dichloropropane	99
Methylene chloride	5
Ethyl acetate	17
Benzene	15
1,2-dichloroethane	98
Phenol	0
1,2-dichlorobenzene	24

moderate levels of stripping. An important point to note is that several of the compounds that showed little or no stripping from the biological reactors were completely stripped under identical conditions without the biological population.

When the components of a waste stream are known, the degree of stripping that can be expected can be preliminarily screened using the ratio of the compound's vapor pressure to its solubility, or Henry's Law constant.

BIODEGRADATION. If stripping and adsorption phenomena can be accurately measured or predicted, and photochemical or chemical reactions are accounted for or neglected, the remaining removals may be assumed due to biodegradation. Biodegradation may not be complete, however. Intermediate compounds may be formed. Thus, reduction of a target hazardous compound may occur by biodegradation, but the breakdown products may also be hazardous and may or may not be amenable to further biodegradation. Determining the route of biodegradation or proving that biodegradation has occurred is a complex problem often conducted by analyses of metabolic intermediates by gas chromatography/mass spectrophotometry (GC/MS). Commercially available chemicals having the identical molecular formula compared with those of the samples in these GC/MS investigation.³⁴

In the work of Blackburn *et al.*,³⁵ the concentration of cells in an activated sludge system containing a gene known to participate in degradation of naphthalene was experimentally related to the biotransformation and mineralization of naphthalene. The ability to enumerate a critical genotype and relate it to enzymatic activity in a mixed culture suggests an improved capability for system understanding at the ecological level and the potential for process control at the genotype level. Thus, if the cells that carry out the degradation (or their genotype) are identified, isolated, and made available for use, biodegradation of specific compounds may be hastened. Blackburn *et al.*³⁵ concluded that their method permits dynamic *in situ* investigations of the microbial ecology of mixed culture systems. They felt the ability to discern the relative effects of ecological factors, population dynamics, genotype concentrations, and enzyme synthesis on the system's performance may emerge with further work.

Hill *et al.*³¹ discussed the role of co-metabolism in biodegradation of CPHs. They stated co-metabolism may have been important in CPH removal, particularly if the concentration of each compound is relatively low. Co-metabolism supposedly involves the breakdown of chemical compounds by organisms, usually via fairly nonspecific enzyme pathways, but does not yield useful energy to the organism. As a result, the chemical compound in question does not exert a selection pressure on the microbial community and therefore, although degradation may commence immediately after the substrate is added to the system, the extent of degradation will tend to be small and the degradation rate will remain relatively constant.

TREATMENT METHODS

AEROBIC SUSPENDED GROWTH. Alternate Suspended Growth Reactors. Besides the complete mix and plug flow activated sludge reactors, alternate modes of aerobic suspended growth reactors have been used successfully or pilot- and full-scale treatment of waste streams containing hazardous wastes. The processes include facultative and aerobic lagoons, PAC addition to activated sludge, and SBRs.

COMPARING PROCESSES. Hannah *et al.*²² compared the treatment efficiencies of six wastewater treatment processes for the removal of 21 priority pollutants. Table 5.8 presents a summary of their volatile organic data comparing removal efficiencies and effluent concentrations observed for activated sludge, aerated lagoons, and facultative lagoons. Table 5.9 shows results for semivolatile organics for activated sludge, aerated lagoon, and facultative lagoon systems.

Table 5.8 Concentrations and standard deviations of volatile organics in wastewater feed and effluent and their percent removals.

Compound	Waste-water feed		Activated sludge			Activated lagoon			Facultative lagoon		
			Effluent		Removal, percent	Effluent		Removal, percent	Effluent		Removal, percent
	μ/L	σ	μ/L	σ		μ/L	σ		μ/L	σ	
Carbon tetrachloride	69	33	13	3	74	15	9	70	11	4	77
1,1-dichloroethane	144	24	8	3	94	45	10	68	19	6	87
1,1-dichloroethylene	212	72	14	11	92	83	59	60	35	49	85
Chloroform	135	16	18	10	86	53	17	61	31	18	80
1,2-dichloroethane	153	44	22	14	84	45	22	70	15	11	90
Bromoform	90	35	29	10	65	15	6	80	22	26	84
Ethylbenzene	111	21	6	10	93	27	15	70	12	27	96
Mean for all volatiles	—	—	—	—	84	—	—	68	—	—	86

Hannah *et al.*²² concluded that the activated sludge process provided the best removals of both conventional pollutants and toxic priority pollutants. The facultative lagoon with its long detention time was the most successful alternative process. The aerated lagoon with a shorter detention time was less

Table 5.9 Means and standard deviations of influent, effluent, concentrations, and percent removals for semivolatile organics.

Compound	Wastewater feed		Activated sludge				Activated lagoon				Facultative lagoon			
			Effluent		Removal, percent		Effluent		Removal, percent		Effluent		Removal, percent	
			$\mu\text{g/L}^a$	σ	mean	σ	$\mu\text{g/L}^a$	σ	mean	σ	$\mu\text{g/L}^a$	σ	mean	σ
<i>Bis</i> (2-ethylhexyl) phthalate	168	74	18	22	87	16	34	43	77	29	30	46	80	31
Dibutylphthalate	73	26	7	7	88	17	44	12	40	20	14	7	78	13
Naphthalene	108	34	4	1	97	1	36	5	64	12	13	6	87	8
Phenanthrene	95	24	4	1	95	2	40	12	55	19	16	13	82	19
Pyrene	104	18	5	2	95	2	36	11	63	14	25	11	75	12
Fluoranthene	104	19	5	2	95	2	36	10	64	15	23	10	77	11
Isophorone	89	30	2	1	98	1	68	29	22	37	62	18	25	32
<i>Bis</i> (2-chloroethyl) ether	143	51	30	48	80	31	102	41	23	31	78	28	43	14
<i>p</i> -dichlorobenzene	93	17	5	3	94	3	31	7	65	13	12	6	87	6
Phenol	126	49	14	6	86	9	84	55	30	42	18	19	86	11
2,4-dichlorophenol	228	178	1	1	99	1	155	202	48	46	65	95	73	38
Pentachlor <i>o</i> -phenol	84	46	3	2	96	2	57	48	37	36	20	8	74	12
Lindane	39	6	31	2	18	16	22	1	42	12	7	2	80	4
Heptachlor	39	3	13	1	65	3	13	2	66	5	13	1	62	6

^a Mean

effective than the facultative lagoon. Nonetheless, a modified design that permits higher aeration rates should increase the efficiency of organic priority pollutant removal, particularly that of volatiles.

In general, the alternative processes do not produce overall toxics removals comparable to activated sludge treatment. However, selected alternative processes may be acceptable in site-specific situations, where toxic removal requirements are limited because of consistently low influent concentrations of toxic chemicals and where water quality criteria are not overly restrictive.

POWDERED ACTIVATED CARBON. The use of PAC addition to suspended growth reactors reportedly has the advantage that the PAC modifies the process and affects its general performance not only through its effect on inhibitory substances, but also by sharing the total organic load with the biomass.³⁶

Grady² stated that studies to date have shown that the main impact of the activated carbon on the removal of highly biodegradable compounds is to enhance removal during acclimation. Powdered activated carbon's major impact is on those compounds that are less readily degradable and also volatile. In this case, the addition of the activated carbon can reduce the discharge of the pollutant to both the atmosphere and the receiving water. Adsorption of nondegradable organics can also stimulate biological processes that are sensitive to their presence in the liquid phase. Thus, there appears to be a benefit associated with the addition of PAC to biological processes.

SEQUENCING BATCH REACTORS (SBR.) Herzbrun *et al.*³⁷ used a SBR to treat a hazardous waste containing phenol concentrations of up to 570 mg/L. Nine bench-scale SBRs were operated over 1 year, and HRTs of 1.25 to 10 days were evaluated. Table 5.10 presents performance data for the control reactor and a reactor operated on an energy conservation strategy (ECS).

Table 5.10 Performance data for a sequencing batch reactor treating a hazardous waste.

Parameter	Control	Energy conservation
Detention time, days	5	5.5
Influent TOC, g/m ³	1620	1620
Effluent TOC, g/m ³	340	400
TOC degraded, percent	79	75
Effluent phenol, g/m ³	0.4	0.4
MLSS, g/m ³	3760	3620
MLVSS, g/m ³	3240	3020
Effluent SS, g/m ³	150	160
SVI, mL/g	50	60

Performance in the reactor on ECS was almost identical to the control with respect to TOC degradation, phenol degradation, SVI, and effluent suspended solids. Although TOC degradation was slightly better in the control, it must be noted that the 6 hours of anoxic feed represented an approximate 30% overall energy savings. One potential problem with anoxic feed is an elevated odor that could make anoxic conditions in the full-scale impractical. The SBR was built in full scale and phenol removal efficiencies were 99% during the first month of operation.

Bell and Hardcastle³⁸ used a modified pilot SBR to treat a synthetic munitions wastewater with an average COD of 2560 mg/L. They used a continuously fed, intermittently operated system. It differed from a true sequencing batch reactor only in the influent flow pattern. During the entire study the system was operated on four cycles per day. In all cycles, the settling time was 45 minutes and the decant time was 15 minutes. The remaining 5 hours of each cycle were divided into aerobic and anoxic periods of various durations. In all cases, the single aerobic period was followed by a single anoxic period, settling, and decant. The activated sludge system was operated treating a high-strength industrial waste containing organic solvents and approximately 44 mg/L hexamine for more than 30 months. Various operating protocols were used. Organic removal was consistently high (92 to 94%) and nitrification and denitrification were essentially complete. Because of the light nitrogen loading, nitrification and denitrification rates were minimum. Solids separation was good throughout the study when DO was sufficient during aerobic periods. The following conclusions were drawn:

- Continuously fed, intermittently operated activated sludge systems seemed highly suitable for the treatment of high-strength industrial wastes containing organic solvents.
- Complete nitrification and denitrification was achieved.
- When DO was sufficient, SVI values were low at 101 to 150 mL/g under aerobic F:M ratios from 0.20 to 0.44 g COD/g MLVSS d.
- The system was highly stable and extremely tolerant of changes in operating conditions, including shocks from power outages, mixer failure, and accidental overfeeds.

AEROBIC FIXED FILM. Trickling Filters. The trickling filter has been used to treat industrial wastewater containing hazardous chemicals. Trickling filters have a packed bed of crushed rock or synthetic media on which a biological slime grows. Organics in the influent stream diffuse into the biological mass and are oxidized. Synthetic media allow for greater filter depths due to the lower bulk weight. Higher organic and hydraulic loadings, therefore, are possible. Design variables include media type, characteristics of the organic waste, organic and hydraulic loadings, and ventilation.

Hannah *et al.*²² investigated the removal of volatile and semivolatile organic priority pollutants and five metals that are often found in municipal wastewaters. The high-rate trickling filter treatment system was operated for 30 days to allow the biomass to acclimate to the spiked contaminants. The average concentrations of conventional wastewater pollutants in the feed solution were 164 mg/L total suspended solids (TSS), 344 mg/L total chemical oxygen demand (COD), 172 mg/L soluble COD, 20.9 mg/L total kjeldahl nitrogen (TKN), 12.7 mg/L ammonia nitrogen, and 3.6 mg/L total phosphorus.

The high-rate trickling filter system was sized to handle 8.2 m³/d and included a primary clarifier, a trickling filter containing crushed slag media, and a final clarifier. The surface loading rate to the trickling filter was 12.4 m³/m² d and the media loading rate was 6.6 m³/m³ d. The trickling filter system removed 76% of the TSS, 47% of the total COD, 26% of the soluble COD, 14% of the TKN, and 39% of the total phosphorus.

Influent, effluent, and sludge samples to be analyzed for volatile organic compounds (VOCs) were collected three times a day and composited into one daily sample for analysis. Similar samples for semivolatile organic compounds were collected six times a day and composited into one daily sample for analysis. These samples were taken for 2 to 3 consecutive days at 6 week intervals.

The removal efficiencies ranged from 25% for chloroform to 71% for ethylbenzene. The average percent removal for all the VOCs studied was 48%. The percent removals were calculated from 14 matched pairs of influent and effluent samples then individual percent removals were averaged to determine the overall percent removal.

Percent removal for all semivolatile organics except lindane and heptachlor was calculated from 11 matched pairs of influent and effluent samples. Three matched pairs were used to determine the percent removal for lindane and heptachlor. Seventy-five percent of *bis*-(2-ethylhexyl) phthalate was removed from the influent in the trickling filter system, whereas only 26% of the dibutylphthalate was removed. For the phenols, the percent removal decreased as the degree of chlorination increased. Phenol was removed the most, followed in order by 1,2-dichlorophenol and pentachlorophenol.

In general, the amount of volatiles in sludge was similar to the concentration of volatiles in the effluent. No accumulation of VOCs was observed in the sludge, therefore the reduction in VOC concentration was attributed to biodegradation.

Contrary to the results found with volatiles, the semivolatiles tended to concentrate in the sludge. In general, the percent removal of the semivolatiles from the influent increased as the concentration of semivolatiles in the sludge increased. *Bis*-(2-ethylhexyl) phthalate had the highest concentration in the sludge, which accounts for its high percent removal from the influent. These results indicate that there may be a limited amount of biodegradation of the

semivolatile organics in the trickling filter system or biodegradation takes place following adsorption onto the biomass.

Rotating Biological Contactors. Rotating biological contactors (RBCs) also employ an attached growth system to treat organic wastes. The RBC has not been widely used due to past operational problems. The RBC does have certain advantages. It uses less energy than activated sludge systems. It is also reported that the resulting sludge has good settling and dewatering properties. Bulking, foaming, and floating sludge is also minimized in the RBC system.³⁹

Tokuz³⁹ investigated the degradation of a phenolic wastewater by an RBC system. A four-stage unit involving 0.5-m diameter discs constructed of high-density polyethylene was used. The rotation speed was 4 rpm and the hydraulic loading rate was varied between 0.04 m³/m² d and 0.08 m³/m² d. The total surface area was about 23.23 m². The results of the study indicated that the removal efficiencies decreased as the hydraulic loading increased. The removal of pentachlorophenol and 2,4,6-trichlorophenol was affected most by the changes in hydraulic loading. The 2-chlorophenol was affected the least by changes in hydraulic loading.

Glaze *et al.*⁴⁰ examined the use of RBCs for removal of naphthalene. Radiolabeled naphthalene was introduced into the treatment system. Biofilm and sludge samples were analyzed for unreacted naphthalene and metabolic products.

The pilot-scale unit was composed of four stages, each with six rotating polyethylene discs. The rotation speed was 6 rpm, the surface area of the discs was 116 m², and the liquid volume of the reactor was 0.53 m³. A flow rate of 0.23 m³/h resulting in a 2.3-hour detention time was used. The reactor was covered to trap and analyze naphthalene in the headspace. The influent characteristics were as follows: 520 mg/L COD, 95 mg/L total oxygen demand, 161 mg/L BOD₅, pH 9.6, 29 mg/L oil and grease, 49 mg/L TSS, 14 mg/L ammonia nitrogen, and 2.4 mg/L total phosphorus.

The BOD₅ removal for the system ranged from 75 to 80%. The total recovery of ¹⁴C activity was 133%. This was considered within an acceptable range for the analytical equipment. Twenty-three percent of the radiolabeled naphthalene was detected in its original form in the biofilm. Ninety-five percent of the ¹⁴C activity was detected in the biofilm. Only 12% of the unreacted naphthalene was measured in the effluent. The results of the study indicated that most of the influent naphthalene was adsorbed into the biofilm and subsequently biodegraded.

Huang *et al.*⁴¹ examined the removal of phenol-formaldehyde resin wastewater with RBCs. Two system configurations were used in the study. The first consisted of a one-shaft, four-stage unit and the second system used a three-shaft, three-stage configuration. The one-shaft, four-stage unit contained 50 polyethylene discs. The three-shaft, three-stage unit consisted of 54 discs.

Five experimental conditions were used to evaluate the treatment of phenol-formaldehyde resin wastewater. The first condition used a medium strength wastewater containing less than 300 mg/L phenol. The hydraulic detention times used were 4.2 and 2.8 hours. Only the four-stage unit was used for the first operating condition. For the 4.2-hour detention time operation, the influent COD was 680 mg/L and phenol was 113 mg/L. The effluent COD was 176 mg/L and phenol was 0.73 mg/L, indicating 74.1% COD and 99.35% phenol removal.

the influent loading conditions were as follows:

- Phenol surface loading rate: $2.6 \text{ g/m}^2 \text{ d}$;
- Phenol volumetric loading: $0.63 \text{ kg/m}^3 \text{ d}$;
- Hydraulic surface loading: $0.021 \text{ m}^3/\text{m}^2 \text{ d}$;
- Hydraulic volumetric loading: $5.73 \text{ m}^3/\text{m}^3 \text{ d}$;
- COD surface loading: $11.54 \text{ g/m}^2 \text{ d}$; and
- COD volumetric loading: $2.85 \text{ kg/m}^3 \text{ d}$.

For the 2.8-hour detention time condition, the influent contained 1293 mg/L COD and 192 mg/L phenol. The resulting effluent contained 322 mg/L COD and 1.5 mg/L phenol which represented a 75% COD removal and a 99.2% phenol removal. An analysis of effluent from each stage indicated that the majority of the phenol was removed in the first stage.

Subsequent RBC operating conditions indicated that effective phenol and formaldehyde removal could be achieved at the following operating conditions:

- Phenol surface loading: $6.54 \text{ g/m}^2 \text{ d}$;
- COD surface loading: $33.3 \text{ g/m}^2 \text{ d}$;
- Formaldehyde surface loading: $6.4 \text{ g/m}^2 \text{ d}$; and
- Hydraulic loading: $35 \text{ L/m}^2 \text{ d}$.

Biological Fluidized Beds. Biological fluidized beds have been pilot tested or successfully applied to industrial wastewaters containing complex organics. Melcer *et al.*⁴² demonstrated the use of biological fluidized beds in a denitrification-nitrification mode. The waste stream consisted of a mixture of blast furnace scrubber water and coke plant wastewater typical of the iron and steel industry. The scrubber water contains ammonia, phenols, and cyanides. Treated alone, this scrubber water does not usually contain enough organic compounds to support the growth of a biological population. The coke plant wastewater, however, contains ammonia, phenols, cyanides, polynuclear aromatic hydrocarbons, and heterocyclic nitrogenous compounds. The mixture of these two waste streams was the subject of the study.⁴²

The results of the study indicated that the combined waste stream could be effectively treated to 90% removal consistently. The hydraulic detention time

of the system was 4.5 hours. Design SRTs were not determined under steady-state conditions, however, the calculated SRTs were based on pseudo-steady-state conditions. These SRT values were in excess of the required SRT for suspended growth processes studied in a separate experiment. In addition, the hydraulic detention time for the suspended growth system (16 hours) was greater than was needed for the fixed-film process.

ANAEROBIC PROCESSES. General. Anaerobic treatment is a biological process employing facultative and strictly anaerobic bacteria to decompose complex organic matter in the absence of free oxygen. Proper application of anaerobic treatment results in virtually complete destruction of putrescible organics, significant reduction in pathogens, conversion of hydrophilic solids to water, minerals, a valuable gas, and a humus-like residue, and favorable alteration of the dewaterability of the sludge.⁴³ As a result of its successful application for municipal sludge treatment and its several important advantages (detailed below), anaerobic treatment is being used for treatment of industrial and hazardous wastes.

Advantages and Disadvantages of the Anaerobic Treatment Process.

ADVANTAGES. The advantages of the anaerobic treatment process include

- Oxygen transfer is not a limiting factor and therefore anaerobic treatment is amenable to high-strength organic waste. For high-strength industrial wastewaters with BODs exceeding 5000 mg/L, oxygen transfer is impractical and prohibitively expensive.
- Very low cell yield and less sludge production.
- Methane gas is produced.
- Good dewaterability.

DISADVANTAGES. The disadvantages of the anaerobic treatment process include

- It requires a longer MCRT to maintain stability. This means a larger reactor volume which accounts for the very high initial cost.
- Heat input is required.
- Oxidizing agents are toxic.
- The reaction chemistry is still mysterious.
- It is highly sensitive to upsets and environmental changes.

Factors Affecting the Performance of Anaerobic Treatment. The following is a discussion on some of the important parameters governing anaerobic treatment. The reader should refer to the references for additional information. Toxicity is discussed separately because of the relevance between hazardous waste treatment and toxicity.

COEXISTENCE OF TWO GROUPS OF BACTERIA. Anaerobic processes are basically unstable. This results from the necessity for the two main groups of bacteria to coexist in one reactor. Under the environmental conditions normally imposed, the nonmethanogenic populations can respond more rapidly to environmental changes than can the methanogenic populations.

pH. Acetate and fatty acids produced during anaerobic treatment tend to lower the pH of the liquid medium. However, the ion bicarbonate equilibria of the carbon dioxide in the reactor exert substantial resistance to pH change. Thus the presence of bicarbonate can help prevent adverse effects on methanogens resulting from low pH from excessive production of fatty acids during biodegradation.

Most anaerobic microorganisms grow best under neutral pH conditions, since other pH values may adversely affect metabolism by altering the chemical equilibrium of enzymatic reactions, or by actually destroying the enzymes. The methanogenic group of organisms is the most pH sensitive.

TEMPERATURE. The metabolic and growth rates of chemical and biochemical reactions tend to increase with temperature, within the temperature tolerances of the microorganisms. Microorganisms exhibit optimum growth and metabolic rates within a well-defined range of temperatures that are specific to each species.

Methanogenic bacteria are more sensitive to changes in temperature than other organisms. All bacterial populations in the reactor are fairly resilient to short-term temperature upsets of up to about 2 hours. They will rapidly return to normal gas production rates when the temperature is restored. However, numerous or prolonged temperature variations can result in unbalanced populations resulting in damage to the biological activities.

Temperature drops as small as 2°C can have adverse effects on mesophilic (~35°C) digestion or 0.5°C with thermophilic (~55°C) digestion. The usual causes of temperature decrease in an anaerobic treatment system are failure of the heating system or rapid introduction of a large quantity of cold feed.

TOXICITY. Table 5.11 gives data on the concentration ranges in which various substances exert toxicity in anaerobic waste treatment systems. As can be seen in Table 5.11, the concentration of any heavy metal that will produce toxicity is 1 mg/L or less; however, much higher levels of heavy metals in anaerobic waste treatment systems have been reported with no ill effects. This is because sulfides remaining from the breakdown of proteins and sulfates form insoluble metal sulfides and precipitate the heavy metals. If sufficient sulfide is not present to precipitate the heavy metals (0.5 mg/L S₂ per mg/L metal) toxicity will result. Sodium sulfide and ammonium sulfate have been successfully added to avoid toxicity.⁴⁴

The method of toxicity control is removal of the toxic material from solution. Other examples of the use of precipitation to remove a toxicant is the use of cationic detergents to precipitate anionic detergents, and calcium to precipitate long-chain fatty acids.⁴⁵ Another version of this technique is the use of gas stripping to remove volatile substances such as chloroform and sulfide.⁵

Table 5.11 Toxic concentrations in anaerobic digestion.

Substance	Nonacclimated	Antagonists present	Acclimated	Acclimated and antagonists present
Iron	200	—	200	—
Sodium	4500	8000 – 10 000	8000	10 000
Potassium	4000	6000 – 8000	5500	15 000
Ammonium	1700	4000	—	—
Calcium	2800	4500 – 5500	5500	8000
Magnesium	1200	3000	1500	3500
Ammonia	30 – 60	—	50 – 100	—
Sulfide	100	—	200	—
Long-chain fatty acids	—	—	500	—
Heavy metals	1	—	1	—
Anionic detergents ^a	15 000	—	20 000	—
Chlorinated hydrocarbons ^a	10	—	15 – 30	—

mg substance/kg dry sludge solids.

BIODEGRADATION OF HAZARDOUS WASTES IN SOILS AND SLUDGES.

Introduction. Soils and sludges can be biologically treated either under solid phase or slurry phase. Composting is one form of solid-phase biodegradation, but has conventionally been used for nonhazardous solid wastes.

Organic contaminants in sludges and soils can be biologically treated *in situ* or excavated and treated by solid- and slurry-phase bioremediation processes. Solid-phase processes are being developed, and in some cases have been used to treat a wide range of contaminants such as pesticides, diesel, gasoline, fuel oil, creosote, pentachlorophenol, and halogenated volatile organics. Enhanced *in situ* biodegradation is being used for sites having soil and groundwater contaminated with readily biodegradable organics such as gasoline and diesel. This technology is being developed for contaminants that are more difficult to degrade.⁴⁶

Solid-Phase Treatment. Solid-phase soil bioremediation is a process that treats soils in an above-grade system using conventional soil management practices to enhance the microbial degradation of contaminants. The system can be designed to contain and treat soil leachate and VOCs. Typically this system consists of a treatment bed that is lined with a high-density liner with heat-welded seams. Clean sand is placed on top of the liner to provide protection for the liner and proper drainage for the contaminated water as it leaches from the contaminated soils placed on the treatment bed. Lateral perforated drainage pipe is placed on top of the synthetic liner in the sand bed to collect the soil leachate. If volatile contaminants must be contained, the lined soil treatment bed is completely covered by a modified plastic-film greenhouse. An overhead spray irrigation system contained within the greenhouse provides moisture control and a means of distributing nutrients and microbial inocula to the soil treatment bed.⁴⁶

Volatile organic compounds that are released from the soil during processing are swept through the structure to an air management system. Biodegradable VOCs can be treated in a vapor-phase bioreactor. Nonbiodegradable VOCs can be removed from the effluent gas stream by adsorption on activated carbon, or by incineration.

Contaminated leachate that drains from the soil is transported by the drain pipes and collected in a gravity-flow lined sump and then pumped to an on-site bioreactor for treatment. Treated leachate can then be used as a source of microbial inocula and reapplied to the soil treatment and other environmental parameters.

EPA evaluated the solid treatment potential of soil for 56 chemicals identified as hazardous.⁴⁷ These chemicals were organized into four categories of substances: polynuclear aromatic hydrocarbons (PAHs), pesticides, chlorinated hydrocarbons, and miscellaneous chemicals. Treatability screening studies were conducted to determine: degradation rates, partition coefficients among air, water, soil, and oil phases, and transformation characteristics.

The quantitative information developed for a subset of the tested chemicals was input into two mathematical models (RITZ and VIP) specifically designed to describe the soil treatment process. Results of the fate and transport predictions for the models were compared with laboratory and literature results to evaluate the ability of the models to predict the behavior of the selected chemicals in a soil system.

The experimental approach used was designed to characterize degradation, immobilization, and transformation potentials for the hazardous substances evaluated. Results indicated that the significance of volatilization and abiotic loss processes in influencing "apparent loss rates" of substances from soil depends on the class of substance.⁴⁷ These processes were insignificant for the majority of PAH compounds, biodegradation appears to be the major process for the loss of PAH compounds from soil systems. However, abiotic

loss may also be an important process for certain pesticide substances. Volatilization was found to play the major role in influencing loss rates of volatile chemicals from soil. Very little leaching or air emissions were predicted by either mathematical model for the subset of pesticides selected under the simulated test conditions.

Slurry-Phase Treatment. A second biodegradation technology involves the treatment of contaminated soil or sludge in a large mobile bioreactor. This system maintains mixing and contact of microorganisms with the hazardous compounds and creates the appropriate environmental conditions for optimizing microbial biodegradation of target contaminants.⁴⁶

The first step in the treatment process is to create the aqueous slurry.

During this step stones and rubble are physically separated from the waste, and the waste is mixed with water, if necessary, to obtain the appropriate slurry density. The water may be contaminated groundwater, surface water, or another source of water. A typical soil slurry contains about 50% solids by weight; a slurried sludge may contain fewer solids. The actual percent solids is determined in the laboratory based on the concentration of contaminants, the rate of biodegradation, and the physical nature of the waste. The slurry is mechanically agitated in a reactor vessel to keep the solids suspended and maintain the appropriate environmental conditions. Inorganic and organic nutrients, oxygen, and acid or alkali for pH control may be added to maintain optimum conditions.

Microorganisms may be added initially to seed the bioreactor, or added continuously to maintain the correct concentration of biomass. The residence time in the bioreactor varies with the soil or sludge matrix, the physical and chemical nature of the contaminant (including concentration), and the biodegradability of the contaminants. Once biodegradation of the contaminants is completed, the treated slurry is dewatered. The residual water may require further treatment prior to disposal.

Depending on the nature and concentration of the contaminants and the location of the site, any emissions may be released to the atmosphere, or treated to prevent emission. Fugitive emissions of VOCs, for instance, can be controlled by modifying the slurry-phase bioreactor so that it is completely enclosed.

Aside from the biodegradability of a particular compound, other limiting factors include the presence of inhibiting compounds and operating temperature. Heavy metals and chlorides may inhibit microbial metabolism because of their toxicity. The operating temperature range is approximately 15 to 70°C. Dissolved oxygen is also critical and must be monitored along with pH, nutrients, and waste solubility.

One advantage of treatment in a contained process is that a remediation system can be designed to pretreat waste contaminated with heavy metals as well as biodegradable semivolatile compounds. Soil washing and extraction

of metals using weak acids and chelating agents can be combined with biological treatment by coupling two separate slurry-phase reactors in series.

Composting. Composting involves the storage of highly biodegradable structurally firm material (for example, chopped hay, wood chips, and so on) with a small percentage (%) of biodegradable waste. Composting is enhanced by waste size uniformity. Adequate aeration, optimum temperature, moisture, and nutrient contents, and the presence of an appropriate microbial population are necessary to enhance decomposition of organic compounds.

There are three basic types of composting: open windrow systems, static windrow systems, and in-vessel (reactor) systems. The open windrow system consists of stacking the compost into elongated piles. Aeration is accomplished by tearing down and rebuilding the piles. The static windrow system also involves long piles of compost. However, the piles are aerated by a forced air system, that is, the piles are built on top of a grid of perforated pipes. Finally, the in-vessel system involves placing the compost into an enclosed reactor. Aeration is accomplished by tumbling, stirring, and forced aeration. In general, compared to *in situ* biodegradation, composting is relatively insensitive to toxicants. The optimum temperature range for composting is between 10 and 45°C. When treating hazardous wastes, it is necessary to collect leachate and runoff water from the composting beds. Composting has not been widely used, but is potentially applicable to both hazardous sludges and soils.

Co-Composting with Solids Wastes. Co-composting of sludges and municipal solid wastes usually does not require that sludge be dewatered. Feed sludges contaminated with hazardous wastes may have a solids content ranging from 5 to 12%. A 2 to 1 mixture of solid wastes to sludge is recommended; in fact, any amount of sludge can be mixed with solid wastes for composting, provided that the sludge is dewatered adequately. The solid wastes should be presorted and pulverized in a hammermill prior to mixing with sludge.⁴⁸ Practical application of this method was not, however, found in the literature.

S *CALE UP AND CASE STUDIES*

AEROBIC SUSPENDED GROWTH. Biological treatment of hazardous wastes in aerobic suspended growth reactors has been done successfully at low and high organic loading rates, high compound loading rates, and variable microbe concentrations, SRTs, and HRTs. Table 5.12 presents selected data from plants treating hazardous wastes. From Table 5.12 it is apparent that generalizations about operating conditions are not possible, and that

determination of operational characteristics must be done on an individual basis depending on the waste components and treatment capabilities.

Aitken and Irvine¹ stated the primary objective of a treatability study was to provide information to be used in determining the technical and economic feasibility of scale-up, or information to be used directly in design. It also may be useful to continue operation of bench or pilot systems beyond the evaluation stage to provide more accurate information during design or to evaluate operating strategies before they are implemented in the field.

A summary of the information needed to complete a feasibility evaluation is given below:

Table 5.12 Selected operational conditions for treatment plants receiving hazardous wastes.

Waste treated	Units	Value	Reference
Food:micro-organism ratio			
2500 mg/L COD	g COD/g MLVSS•d	0.4 – 0.5	Bell and Hardcastle, 1984
88 000 mg/L COD, cellulosives		0.1 – 0.6	Brown and Weintraub, 1982
Full scale, organic solvent; 1900 – 10 900 mg/L COD		0.2	Marston and Woodward, 1986
DMF	g BOD/g MLSS•d	0.04	Carter and Young, 1984
Phenols, 5600 mg/L COD3		0.04 – 0.38	Tsai, <i>et. al.</i> , 1984
Organic loading			
DMF	lb BOD/1000 cu ft•d	40	Carter and Young, 1984
Compound loading			
DMF	DMF/1000 cu ft	40	Carter and Young, 1984
DMF	MLSS, mg/L	14 800	Carter and Young, 1984
		2470 – 4200	Bell and Hardcastle, 1984
		2500	Powell and Reitano, 1982
Full scale, organic solvent; 1900 – 10 900 mg/L COD		5300 – 9650	Marston and Woodard, 1986
Refinery waste	SRT, days	31 – 105	Bell and Hardcastle, 1984
		57 – 380	Tsai, <i>et. al.</i> , 1984
	HRT, days	4.4	Powell and Reitano, 1982
		2.6 – 7.1	Tsai, <i>et. al.</i> , 1984
		0.4 – 1.5	Brown and Weintraub, 1982

- The need for pretreatment. The presence of an inhibitory inorganic may not be known until the biological treatability study is underway. Steps to remove such species would be necessary before attempting further biological treatment studies.
- The need for pH control. It should be noted that improper pH control in the bench or pilot study can lead to data that are unreliable for scale-up, or to false conclusions that stable operation is not possible.
- The need for nutrient supplementation. Nitrogen and phosphorus are the two most common nutrients that may be deficient in a waste. Sulfur may also be important in anaerobic systems. Metals, iron in particular, can be limiting nutrients as well. Determining the quantity of a nutrient to be added should be done in consideration of growth requirements, which will vary depending on the reactor being used and the manner in which it is operated. Overdosed nutrients can sometimes be evaluated by observing abnormally high concentrations in the effluent.
- Mass balances on the major constituents of interest. Nonbiological removal mechanisms must be taken into consideration.
- The reliability of process performance. Inconsistent performance in meeting final treatment objectives or the inability of the biological process alone to remove all of the target organics indicate that a polishing step will be needed after biological treatment.
- Kinetics and stoichiometry or organic removals.
- Organic and hydraulic loading criteria.

Standard engineering practice can be used to combine the above information for a feasibility evaluation and for comparison to other waste management alternatives. Several examples of scale up for full-scale treatment of hazardous wastes are discussed below.

Marston and Woodard⁴⁹ conducted a pilot study for the treatment of high-strength solvent containing wastewaters. Influent solvents included glycerin, methanol, ethanol, butanol, acetone, DMAC, DMSO, and formamide. The BOD concentration averaged 3150 to 3310 mg/L in the pilot study, where consistent removals of greater than 90% were achieved.

Important considerations in the design of the pretreatment facility included

- Wastewater volume and strength varied throughout the day. A tank for flow and concentration equalization was required.
- The waste streams to be collected for pretreatment contained only solvents from the manufacturing processes. Chemical feed equipment to add nutrients was required.
- Cleaning compounds were in the wastewater that could cause foaming problems. A foam spray system in the aeration tank was required.

- Very little space for a pretreatment system was available. A deep aeration tank and common wall construction between the equalization tank, aeration tank, and clarifier were used to keep the system compact.
- The proximity of a residential area required minimization of the noise generated by the plant.
- There were no maximum limits for suspended solids; therefore, waste activated sludge could be discharged directly to the sewer. This eliminated the need for sludge handling facilities and minimized the clarifier size required.

Design criteria are presented in Table 5.13 for the full-scale plant. Performance and loading are shown in Tables 5.14 and 5.15 for October through December 1983.

As shown in Tables 5.14 and 5.15, the pretreatment system removed an average of 94% of the COD and 99% of the solvents contained in the concentrated waste streams treated. The pretreatment system achieved consistently high removal rates in spite of significant variations in loading; however, on the average, the system is loaded at less than 50% of design capacity.

Table 5.13 Design criteria for a full-scale plant.

Flow	43 000 gal/day (average) 50 000 gal/day (maximum)
Solvent load	800 lb/day (average) 1200 lb/day (maximum)
Solvent removal	90+%
F:M	0.5/day (maximum)
Oxygen required	911 lb/day (average) 1352 lb/day (maximum)
MLSS	5000 mg/L
Influent temperature	100° F (maximum)

Table 5.14 Plant loading and performance for a full-scale activated sludge plant treating a hazardous waste.

Flow	average range	15 000 gpd 5000 – 22 000
Influent COD	average range	6700 mg/L 3100 – 10 000
Influent solvents (Total)	average range	4230 mg/L 1900 – 10 900
Effluent COD	average range	435 mg/L 70 – 1000
Effluent solvents (Total)	average range	<42 mg/L <42 – 80

Table 5.14 Plant loading and performance for a full-scale activated sludge plant treating a hazardous waste (continued).

F:M ^a	average	0.2/day
	range	0.04 – 0.4
MLSS	average	7850 mg/L
	range	5300 – 9652 mg/L

Table 5.15 Solvent removal.

		Influent, mg/L	Effluent, mg/L
Methanol	average	1140	<4
	range	180 – 2900	<4 – 20
Ethanol	average	1458	<8
	range	240 – 4400	<8 – 17
Butanol	average	958	<2
	range	190 – 2000	none
Acetone	average	571	<8
	range	49 – 2700	none
DMAC ^a	average	80	<5
	range	5 – 220	<5 – 29
DMSO ^b	average	<10	<10
	range	none	none
DMF ^c	average	23	<5
	range	<5 – 190	none

^a DMAC = Dimethylacetamide.

^b DMSO = Dimethylsulfoxide.

^c DMF = Dimethylformamide.

Herzbrun *et al.*³⁷ operated sequencing batch reactor pilot units to treat a wastewater with over 500 mg/L phenol. Results from the bench-scale studies were used to design a full-scale demonstration facility.

Construction of the 1900 m³ (67 000 CE) unit was completed and TOC and phenol degradation averaged 76 and 99%, respectively, during the first month of operation. Table 5.16 presents full-scale performance data. The data for phenol, TOC, effluent suspended solids, and sludge volume index (SVI) all indicate acceptable treatment as anticipated from the bench-scale

reactors. In addition, TOC degradation decreased from 86% in Week 2 to 72% in Week 5. Such results were expected because lab reactors typically require 4 to 8 weeks for treatment to stabilize fully.

AEROBIC FIXED FILM. EPA 21 conducted a study of 40 POTWs to determine the levels of VOCs, semivolatile organics, pesticides, and metals

Table 5.16 Performance data from a full-scale SBR.

Influent TOC, g/m ³	1100
Effluent TOC, g/m ³	260
TOC degraded	76%
Influent phenol, g/m ³	39.6
Effluent phenol, g/m ³	0.4
Phenol degraded	99.0%
MLSS, g/m ³	1100
MLVSS, g/m ³	930
Effluent SS, g/m ³	80
SVI, mL/g	60

in the influent, effluent, and sludge. Seven of the POTWs used trickling filters and one used RBCs. The trickling filter plants were numbered 11, 15, 21, 24, 29, 39, and 40. Plant 33 was the RBC facility.

Plant 11 received about 4% of its 38.5-mgd average daily flow from food products and fabricated metal machinery industries. Volatile organics detected in the influent were effectively removed. The lowest removal observed was 77% for methylene chloride. The combined primary and secondary sludge generally showed higher concentration of VOCs than were contained in the effluent. Chloroform, 1,1,1-trichloroethane, tetrachloroethylene, and trichloroethylene were the exceptions. The VOC concentration in the secondary sludge was only slightly higher than the influent and effluent concentrations. Eighty-eight percent of the oil and grease was removed and like the VOCs tended to concentrate in the combined sludge more than the secondary sludge.

The few semivolatiles detected in Plant 11 were not significantly removed. *Bis*-(2-ethylhexyl) phthalate concentrated primarily in the combined sludge and less so in the secondary sludge. Metal removal ranged from 11% for cadmium to 75% for copper and mercury. The metals were highly concentrated in the combined and secondary sludges.

Plant 15 averages 6.6 mgd daily, 25% of which comes from fabricated metal products, electroplating, and electrical component industries. Eighty-nine percent of the oil and grease was removed, but the primary and combined sludges contained more than 100 times the level of oil and grease. The primary volatile organic detected in the influent was 1,1,1-trichloroethane.

The treatment process removed 97% of the influent 1,1,1-trichloroethane with none of the volatiles detected in the sludges. The other volatiles detected in the influent were also effectively removed.

As in Plant 11 the primary semivolatile detected at Plant 15 was *bis*-(2-ethylhexyl) phthalate. Di-N-butyl phthalate was 60% removed by the system and was much less concentrated in the sludges as compared to *bis*-(2-ethylhexyl) phthalate. Metal removal ranged from 59% for copper to 85% for nickel. As discussed previously, the metals concentrated in the primary and combined sludges.

The data for Plants 21, 24, 29, 33, 39, and 40 indicate similar trends as has been discussed for Plants 11 and 15. In general the volatile organics were effectively removed and did not concentrate in the sludges indicating significant removal by biological degradation. The semivolatile compounds were not as efficiently removed and tended to concentrate in the sludge. These compounds may then be subject to biological degradation, but this possibility was not addressed in the report. The metals also concentrated in the sludges.

ANAEROBIC PROCESSES. Phenols and Coal Gasification Wastes.

Phenolic compounds are often the major pollutant in aqueous effluents from coal gasification facilities, coke oven batteries, oil refineries, and some petrochemical plants. The liquid wastewaters from industrial operations that use phenolic compounds as raw manufacturing materials also contain phenolic pollutants.

The use of anaerobic activated carbon filters to remove phenolic compounds has been studied by a number of researchers. Granular activated carbon anaerobic treatment processes combine the advantages of the energy-efficient anaerobic filter and the adsorptive capability of activated carbon for extended retention of toxic or less readily biodegradable compounds. Activated carbon protects microorganisms from shock loading through rapid initial adsorption into pores and slow subsequent release by desorption. This desorption phenomena, accompanied by biodegradation of the desorbed compounds, has been frequently referred to as bioregeneration.

O'Barsky *et al.*⁵⁰ concluded that by pretreating polysulfide rubber wastewater, 80% sulfur removal could be achieved even when sulfate concentration exceeded 500 mg/L. The results obtained from running a GAC reactor⁵¹ for approximately 200 days (starting with fresh GAC) indicated that contributions of biogas production, adsorption, and biomass production were all important in the removal of phenol. Among them, the biogas production was most important. Bioregeneration occurred as adsorbed phenol was desorbed because of reduced influent phenol concentration. This was also shown by increased biogas production during the same period.

Wang *et al.*⁵² concluded that the organic removal efficiency of an expanded-bed anaerobic reactor using GAC as a biological attachment

medium was very high when subjected to a wide range of feed phenol concentrations. During 588 days of continuous operation, four steady-state conditions were obtained under feed phenol concentrations of 358, 716, 1432, and 2864 mg/L. Steady-state phenol, COD, and DOC removal efficiencies exceeded 99.9, 92, and 93%, respectively, even for the highest loading conditions. By the end of this study, 87.5% of the feed COD was converted to methane gas; only 6% of the feed COD escaped in the aqueous effluent from the anaerobic reactor. The high conversion to methane and the low retention of COD within the reactor demonstrate that biological utilization was the major removal mechanism and the net growth of bacteria in the reactor was low. The major conclusion of this study was that the GAC expanded-bed reactor achieved nearly 100% removal of phenol when the surface loading ranged from 0.028 to 0.23 mg/cm² d COD.

The expanded-bed reactor responded favorably to the sudden doubling of feed concentration. Gas production from the reactor increased rapidly immediately after the increase in organic load. Gas production doubled within 1 week after the feed phenol concentration was doubled, but increases in effluent phenol concentrations were small. The use of partially saturated GAC media and phenol-acclimated activated carbon inocula enabled biological utilization of phenol to start in 8 days.

In another study in Canada, Fedorak *et al.*⁵³ diluted high-strength wastewater (7600 mg/L phenolics) from the H-coal liquefaction process and fed to anaerobic methane-producing cultures. Total phenolic concentrations of 150 and 300 mg/L were added to 50 mL semicontinuous cultures with hydraulic retention times of 12.5, 16.7, and 25 days. The rates of methane production and effluent concentrations of three fermentable phenolics (phenol, *p*-cresol, and *m*-cresol) were monitored over a 188-day period. After acclimation to the wastewater, stable periods followed during which each of the six cultures removed essentially all of these fermentable phenolics. The duration of the stable periods decreased with increasing phenolic mass loading rates. The first phenolic to appear in the effluent was *m*-cresol, and its presence served as the first indicator of reduced phenolic removal capability. The effluent *m*-cresol concentrations from cultures receiving 300 mg/L total phenolics followed simple washout curves suggesting that its degradation stopped abruptly. Later *p*-cresol and ultimately phenol appeared in the effluents from the cultures that received the highest phenolic mass loadings.

A mathematical model was developed by Mack *et al.*⁵⁴ to represent specific phenol utilization by anaerobic process. This model indicated a maximum specific utilization rate by anaerobic process at a phenol level of 700 mg/L with process instability occurring at phenol levels in excess of this value. Methane was not produced during these experiments.

Chlorinated Solvents. Many environmentally important anthropogenic compounds are halogenated.⁵⁵ The list of these species includes pesticides, plas-

ticizers, solvents, and trihalomethanes. Of the halogenated compounds, the best known and most studied are the chlorinated compounds.⁵⁶

Anaerobic studies with halogenated compounds have shown several of these compounds are biodegradable. It has been shown that transformations of trihalomethanes can occur under anaerobic conditions. The biotransformation of some haloaliphatic compounds suggests a series of reductive dechlorination reactions.⁵⁷

There is great interest in biodegradation of chlorinated compounds by anaerobic digestion. The disadvantages are long start-up time and incomplete understanding of the microbiology involved. There is more evidence for biodegradation of chlorinated compounds in anaerobic systems. Recently, researchers have shown that 1- and 2-carbon halogenated aliphatic organic compounds are biodegradable under methanogenic conditions. There is also field evidence for the long-term transformation of halogenated compounds under anaerobic conditions. No specific research has been done to establish the actual degradation mechanism or the affected group of microorganisms.⁵⁷

In a study by Vargas and Ahlert,⁵⁵ the biodegradability of 1,1,1-trichloroethane (TCA), 1,1-dichloroethane (DCE), and dichloromethane (DCM) under anaerobic conditions was investigated. The acclimation potential of a mixed anaerobic culture to these compounds was also accessed.

The build-up of acetic acid lowers pH, making conditions unfavorable for the methanogens. Also, increased hydrogen partial pressure inhibits the acetogens.⁵⁸ If the acetogens were inhibited, recovery was more likely. During the lag phase, no gas production was observed because the acetogens were inhibited and ethanol was not broken down for use by the methanogens. Once the methanogens degrade the toxicant to less than inhibition levels, acetogens start utilizing ethanol, and gas production resumes. Studies with separate anaerobe populations indicate that the methanogens, known for extreme sensitivity, may be responsible for degradation of chlorinated compounds. There is some indirect evidence to support these results.

Johnson and Young⁵⁹ conducted laboratory tests to study the inhibition of anaerobic cultures by toxic organic chemicals and to examine the conditions affecting recovery from this inhibition. Screening tests were used in Phase 1 to isolate organic compounds that had severe inhibitory effects on anaerobic biological reactions. The nature of the recovery of anaerobic cultures from inhibitory effects was studied in Phase 2, and Phase 3 was designed to identify inhibition contributory factors. Concentrations of 100 mg/L of hexachloroethane, hexachlorocyclopentadiene, hexachloro-1,3-butadiene, 4-nitrophenol, nitrophenol, 2,4-dichlorophenol, and nitrobenzene inhibited anaerobic cultures at 37°C. Acclimation adsorption and the concentration of toxic compounds were found to be effective factors in the reduction of toxicity.

Nitrogen-Substituted and Sulfonated Benzene Aquifer Contaminants. A literature survey of groundwater contaminants by indicated that aquifers are repositories for hazardous wastes, including N'- and S-substituted benzene derivatives. They examined the susceptibility of several anilines, benzamides, benenesulfonic acids, and benenesulfonamides to anaerobic metabolism by aquifer microorganisms. Under sulfate-reducing and methanogenic conditions the carboxylated anilines were biotransformed within 1 or 3 months while unsubstituted or methylated anilines required longer incubation times. Benzamide as well as an arylmethyl and an N-methyl derivative were biodegraded under redox conditions. The anaerobic degradation of the N-methylated benzamide was favored in sulfate-reducing rather than methanogenic incubations. However, the addition of a second N-alkyl group rendered the resulting compounds resistant to anaerobic decay. Only one of seven benenesulfonates and two of five benenesulfonamides proved amenable to anaerobic metabolism.⁶⁰

***E*MERGING TECHNOLOGIES**

A number of new technologies have recently emerged and have shown promise for the treatment of hazardous wastes. Although existing experience is mostly limited to laboratory and pilot reactors, further research and future full-scale applications may prove these technologies have advantages over current methods of biological hazardous waste treatment.

Immobilized bacterial cells have been used for biodegradation of toxic wastes. The microorganisms are trapped on a media that is then fed a wastewater containing the target hazardous compounds. In this technique, bacterial cultures are centrifuged to concentrated pellets and immobilized on a gel of sodium alginate. Other larger cells, such as plant cells, animal cells, and high molecular weight enzymes, can also be immobilized.

Due to the low solubility of oxygen in water and the high local cell density, oxygen transfer is often the rate limiting factor in the performance of aerobic immobilized cell systems. Another disadvantage is the difficulty in assessing the biomass concentration (as is true in more conventional fixed-film processes). Immobilization has advantages over the conventional free cell systems. Prevention of washout of biomass in continuous-flow reactors, easy separation, and a greater degree of operational flexibility have been reported.⁶¹ Immobilized cells can also be much more resistant to high concentrations of toxic chemicals. The cell density of immobilized cells can be much higher than that of the free cells, resulting in higher rates of biodegradation per unit volume of the reactor. Moreover, the immobilized cells can also be dried and stored as a convenient and accessible source of reproducible biomass.

In a study by Lakhwala *et al.*,⁶¹ activated sludge from a municipal wastewater treatment plant was acclimated in a nongrowth medium with phenol (100 mg/L) and with continuous aeration. The immobilized microorganisms could withstand concentrations of 5,000 mg/L of 2-chlorophenol while concentrations of 750 mg/L were fatal to acclimated free microorganisms. Thus, the immobilized cells were more resistant to higher concentrations of the toxic compound studied.

Aitken and Irvine¹ presented an overview of the use of fungi for biodegrading xenobiotics (meaning foreign to the biological system, without regard to the biological response). Aitken and Irvine¹ list over 30 citations conducted mostly in the laboratory for which fungi-degraded aromatics, polynuclear aromatics, dyes, chlorinated lignins, cyanides, PCBs, PCP, 2,3,7,8-TCDD, and lindane.

An example is a study by Lewandowski *et al.*⁶² where white rot fungus was used for the degradation of 2-chlorophenol. They combined the fungi with immobilized bed technologies using both a packed-bed reactor employing a silica-based porous support for the fungus, and a well-mixed reactor employing alginate beads as the immobilizing medium.

In addition, balsa wood chips were also used as a support for the fungi. Influent concentrations of 520 mg/L of 2-chlorophenol were reduced from 0.1 to 170 mg/L in the immobilized packed bed and were reduced to 0.1 to 210 mg/L in well-mixed reactors, with immobilized cells, respectively. The degree of removal was dependent on the influent flow rate to the bench-scale reactors, with better removals at lower flow rates. The most important external factors affecting the activity of the fungi were reportedly temperature, pH, DO concentration, and fixed nitrogen concentration.

Aitken and Irvine¹ reviewed the use of algae for removal of xenobiotics. However, means other than biological degradation were reportedly responsible for the removals observed. Sloan *et al.*⁶³ identified a sequestering phenomenon that produced the removal of metal ions by the green alga, *Chlorella pyrenoidosa*. The uptake of metals by the alga was dependent on the ionic strength of the solution and the metal ion concentration. Their results suggested the rapid uptake of metal ions (cadmium, copper, and lead) was by ion exchange, independent of the alga cell's metabolism. The alga cell's uptake was found to be best modeled as a weakly acidic cation exchange resin.

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Chapter 6

Physical Treatment of Hazardous Wastes

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*I*NTRODUCTION

Physical treatment processes were derived from observations of the physical forces of nature. These operations are widely used by themselves or in conjunction with other treatment technologies as pre or posttreatment. For example, physical treatment can be used to prepare waste streams for treatment by removing metals or VOCs. Physical treatment is basically a separation process that, when applied, results in the separation and/or concentration of the contaminant to reduce the volume of material requiring further treatment or disposal.

Physical separation can be used to treat wastes composed of combinations of liquids, solids, and gases via concentration, recovery, dewatering, separation, pulverization, and solidification. This chapter presents an overview of the various physical separation treatment processes that are used for the treatment of hazardous waste. The most commonly considered unit operations are discussed in greater detail in this chapter. These discussions will present

process description, application for treatment of hazardous waste, expected performance, fundamentals involved, and other relevant and important factors. Unit operations currently used in the chemical processing and wastewater industry will be defined and described.

WASTE CHARACTERIZATION AND TREATABILITY TESTS. All hazardous wastes should be characterized prior to considering the type of treatment methods to apply. Hazardous wastes containing only organics, toxic anions, heavy metals, or combinations thereof will be treated differently. It is important to note whether the waste can be characterized as a liquid, oily liquid, sludge, slurry, soil, solid, or tar. Most treatment processes are generally limited to treating three or fewer of these conditions.

Chemically characterizing a hazardous waste will help determine the strategy for treatment. The final decision to select particular treatment processes to handle hazardous waste generally should be based on bench- or pilot-scale treatability studies. These studies are necessary for both demonstrated technologies (key design criteria and efficiencies are known) and innovative technologies. Bench- and pilot-scale studies for innovative technologies will take 2 to 5 times as long and cost considerably more.

Whether to use bench- or pilot-scale testing depends on several factors, including regulatory requirements, time, degree of certainty relative to the technology, and cost and waste application of innovative technology such as reverse osmosis or solvent extraction. The cost of a particular process may be prohibitive. Time constraints may limit testing to short bench-scale testing. To ensure that a particular treatment technology will work, pilot-scale testing is advised. Full-scale testing may be required for hazardous wastes of unknown compounds and/or byproducts.

PHYSICAL TREATMENT PROCESSES. The application of biological and chemical processes to treat liquid, hazardous, organic, and inorganic wastes produces a mixture of solids and liquids. Metal hydroxides and biological solids must be removed by physical treatment to produce a pollutant-free liquid for reuse or discharge. Clarification may include the following processes, depending on the effluent limits required:

- Coagulation,
- Flocculation,
- Sedimentation, and
- Filtration.

Treatment of hazardous wastes by a chemical process such as metal precipitation is usually followed by coagulation, flocculation, sedimentation, and filtration. Each process further reduces the concentration of particulate metals in the effluent stream. Treatment of hazardous waste by biological

processes includes sedimentation and often filtration. Coagulation and flocculation of biological solids usually take place in the biological reactor, although supplemental coagulation and flocculation can be enhanced by further chemical addition in the clarifier.

Sedimentation uses gravitational forces to physically separate suspended solids from the treated hazardous waste mixture. Its use is restricted to solids removal that is generally more dense than water and is not suitable for wastes consisting of emulsified oils. Filtration uses a medium to physically restrain and/or capture the solids. Operation of clarifiers results in the production of three streams: effluent, sludge, and skimmings. Sludge and skimmings are often combined and further treated prior to disposal. The treatment of hazardous waste is not complete until all three streams are dealt with.

The volume of sludge produced from clarifiers can range from approximately 3 – 25% of the influent flow. Operation of through-flow filters treating hazardous waste will result in the production of product water and backwashes. Backwash volumes can range from 1 – 5%. Backwashes are usually recirculated to the influent of the hazardous waste treatment facility. Permeate (product water) and concentrates are produced from operating cross-flow filters. The concentrates can be further treated or sometimes recycled if the concentrated pollutants can be reused.

Coagulation and Flocculation. PROCESS DESCRIPTION. Coagulation and flocculation processes are used to promote the settleability and filterability of suspended solids in treated and nontreated hazardous wastes. It is not recommended for waste streams with high viscosity because it affects settling of agglomerated solids. Coagulation is a process wherein the charges on particles suspended in a liquid are neutralized. Coagulation results in the destabilization of the particles in the liquid. Flocculation refers to the agglomeration and entrapment of the neutralized particles into a large solid network. These processes are used when treating hazardous wastes containing heavy metals. Coagulation and flocculation of suspended solids take place in five steps:

- pH adjustment and rapid mixing,
- Rapid mixing of coagulants into the waste stream,
- Destabilization,
- Addition and mixing of flocculants, and
- Agglomeration of neutralized particles.

Coagulants and flocculants are added to the hazardous waste stream to promote destabilization and agglomeration. There are two main classes of coagulants and flocculants—inorganic and organic. The organic chemicals are generally referred to as polyelectrolytes or polymers. A list of inorganic

coagulants and flocculants used to treat hazardous wastes is shown in Table 6.1. The use of inorganic coagulants results in an increase in sludge production.

Patterson and Voice review in detail the use of coagulants and flocculants used to treat metal-containing wastes.^{1,2}

Polymers are organic macromolecules composed of many monomers joined together. Polymers are usually classified by the following characteristics:

- Type (anionic, non-ionic, or cationic),
- Molecular weight,
- Basic molecular structure,
- Charge density, and
- Suitability for water treatment.

Polymer molecular weights can range from 50 000 to 10 000 000 or more. Polymer dosages, used to treat hazardous wastes, can range from 1 – 1000 mg/L. Coagulants and polymers can be used to remove oil from hazardous wastes.

DESIGN PARAMETERS. The design of coagulation and flocculation processes necessitates determining the following design parameters:

- Proper pH,
- Proper coagulant and flocculant dose,
- Chemical feed concentrations,
- Feed points,
- Mixing energies,
- Mixing and flocculation times,
- Order of chemical addition, and
- Settling rates.

Most inorganic coagulants require a specific pH for optimum results. Flocculation with anionic polymers is less pH dependent and usually does not require additional pH adjustment. Selection of the proper chemical dose and feed concentration is critical. Over-feeding of coagulants and flocculants will result in a less efficient treatment system.

The intensity and time of mixing during flocculation is an important parameter because too high an intensity or too short a time will result in poor flocculation of particles. In some cases, the order of chemical addition is important to formation of the floc particle. Typical mixing times for rapid mix and flocculation are 1 – 2 minutes and 3 – 10 minutes, respectively.

Jar testing is the most widely used procedure for determining the design parameters above for a coagulation/flocculation process. The traditional jar test unit (six stirrers), when used with the newer Camp or Gator jars,

Table 6.1 List of inorganic coagulants and flocculants.

Compounds	Formula	Commercial strength	Grades available	Weight (g/m ³)	Suitable handling materials	Remarks
<i>Coagulants:</i>						
Aluminum sulfate	Al ₂ (SO ₄) ₃ •18H ₂ O	17% Al ₂ O ₃	Lump Powder Granules	Powder: 0.61 – 0.72 Other: 0.91 – 1.07	Lead Rubber Silicon Iron	Coagulation and sedimentation systems; prior to pressure, filters for removal of suspended matter and oil.
Sodium aluminate	Na ₂ Al ₂ O ₄	55% Al ₂ O ₃	Crystals	0.80 – 0.96	Iron Steel Rubber Plastics	Usually added with soda ash to softeners.
Ammonium alum	Al ₂ (SO ₄) ₃ (NH ₄) ₂ SO ₄ •24H ₂ O	11% Al ₂ O ₃	Lump Powder	0.96 – 1.09	Lead Rubber Silicon Iron Stoneware	Coagulation systems— not widely used.
Potash alum	Al ₂ (SO ₄) ₃ •K ₂ SO ₄ •24H ₂ O	11% Al ₂ O ₃	Lump Powder	1.02 – 1.09		Coagulation systems— not widely used.
Copperas	FeSO ₄ •7H ₂ O	55% FeSO ₄	Crystals Granules	1.01 – 1.06	Lead Tin Wood	Suitable coagulant only in pH range of 8.5 to 11.0.

Table 6.1 List of inorganic coagulants and flocculants (continued).

Compounds	Formula	Commercial strength	Grades available	Weight (g/m ³)	Suitable handling materials	Remarks
Chlorinated copperas	FeSO ₄ •7H ₂ O + 1/2 Cl ₂	48% FeSO ₄				Ferrous sulfate and chlorine are fed separately.
Ferric sulfate	Fe ₂ (SO ₄) ₃	90% Fe ₂ (SO ₄) ₃	Powder Granules	0.96 – 1.12	Lead Rubber Stainless steel Plastics	Coagulation—effective over wide range of pH, 4.0 to 11.0.
Ferric chloride hydrate	FeCl ₃ •6H ₂ O	60% FeCl ₃	Crystals		Rubber Glassware Stoneware	Coagulation—effective over wide range of pH, 4.0 to 11.0.
Magnesium oxide	MgO	95% MgO	Powder	0.40 – 0.56	Iron Steel	Essentially insoluble—fed in slurry form.
<i>Coagulant aids:</i> ^a Bentonite			Powder	0.96	Iron Steel	Essentially insoluble—fed in slurry form.
Sodium silicate	Na ₂ O(SiO ₂) _{3–25}	40 Bé solution	Solution	1.37	Iron Steel Rubber	

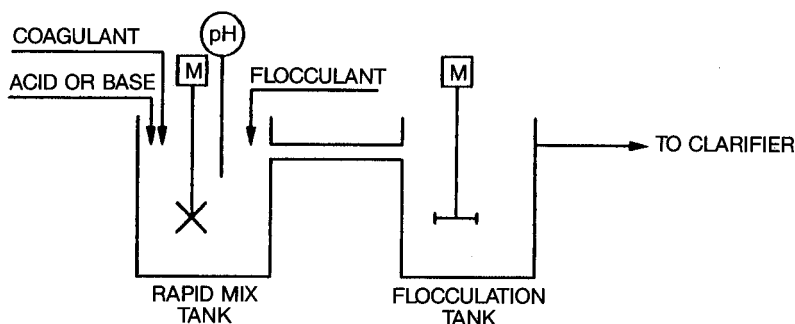
Table 6.1 List of inorganic coagulants and flocculants (continued).

Compounds	Formula	Commercial strength	Grades available	Weight (g/m ³)	Suitable handling materials	Remarks
<i>pH adjusters:</i>						
Lime, hydrated	Ca(OH) ₂	93% Ca(OH) ₂	Powder	0.40 – 0.80		pH adjustment and softening.
Soda ash	Na ₂ CO ₃	99% Na ₂ CO ₃	Powder	0.54 – 0.83		pH adjustment and softening.
Caustic soda	NaOH	98% NaOH	Flake Solid Ground Solution			pH adjustment, softening, oil removal systems.
Sulfuric acid	H ₂ SO ₄	100% H ₂ SO ₄	Liquid			pH adjustment.

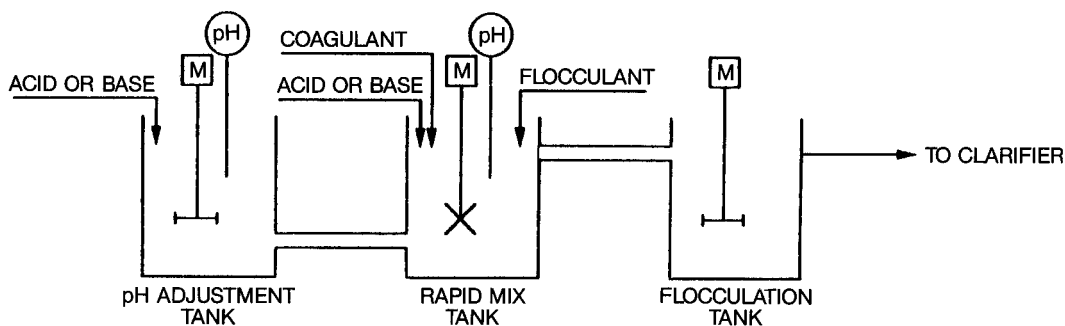
^a Other compounds, for which no information is available, suitable as coagulant aids are activated silica, clay, activated carbon, causticized starches, and ethyl cellulose.

provides the engineer with design data on mixing requirements and settleability. A jar test can also provide information on the quantity and quality of sludge generated and whether there is a tendency towards scum buildup in the downstream clarifier. Adams *et al.* describe a jar test procedure for developing design and operating criteria for treating hazardous liquid wastes.³

TYPES OF EQUIPMENT. Coagulation and flocculation of inorganic hazardous waste solids usually takes place in a two- or three-stage system. Each stage includes a tank, mixer, and the required instrumentation. Figure 6.1 illustrates two- and three-stage systems. The first stage usually consists of pH adjustment and coagulant addition. The second stage consists of flocculant addition and flocculation. A high or low influent pH may require the use of another pH adjustment stage to assure system reliability.



TWO STAGE SYSTEM



THREE STAGE SYSTEM

Figure 6.1 Two and three stage coagulation/flocculation systems.

Tanks used for rapid mixing and flocculation can either be made of metal or fiberglass-reinforced plastic (FRP). Two separate tanks or one tank with a

baffle and two mixers can be used. Access to the tanks is required for safety, maintenance, and sampling. Sometimes a static mixer is used to mix chemicals and wastewater.

Chemical feed systems are required to feed inorganic coagulants and polymers. Polymers can be fed as dry, solution, or emulsion. The type selected will be determined by the jar test.

Safety considerations are important during the design and operation of coagulation/flocculation systems. Proper handling techniques of chemicals and their material safety data sheets (MSDSs) should be posted at the hazardous waste treatment facility. Polymer feeding and storage areas should be kept dry at all times. Polymer solutions and sludges containing polymers are slippery and should not be allowed to remain standing if spilled.

Sedimentation. PROCESS DESCRIPTION. The sedimentation process has been used in liquid hazardous waste treatment for the removal of oil, biological solids, and chemically precipitated solids. The concentration of solids and their characteristics determines the type of settling. Settling of hazardous waste solids can be divided into three classes:

- Discrete settling,
- Flocculant settling, and
- Hindered or zone settling.

Hudson and Benefield *et al.* describe in detail the sedimentation theory behind each class.^{4,5}

Systems containing high concentrations of suspended solids will exhibit hindered settling. Hindered settling is associated with biological treatment of hazardous wastes and coagulated and flocculated metal hydroxides. Hindered settling is characterized by the formation of a distinct interface between the sludge blanket and the clarified waste. Any solids remaining above the interface exhibit discrete or flocculant settling.

DESIGN PARAMETERS. Sedimentation basins can be circular, rectangular, or square. In each case the design parameters are based on the quality and quantity of the hazardous waste to be treated. Clarifiers, which treat biologically treated hazardous wastes, are designed using the following criteria:

- Surface loading or hydraulic loading rate, $\text{m}^3/\text{m}^2\cdot\text{d}$,
- Solids loading rate, $\text{kg}/\text{m}^2\cdot\text{d}$,
- Flow-through velocity, m/s ,
- Weir overflow rate, $\text{m}^3/\text{m}\cdot\text{d}$, and
- Retention time of settled solids (hours).

Average and peak design flows should be considered when calculating the actual design parameters. Table 6.2 gives recommended design criteria for secondary clarifiers and is applicable to treating organic hazardous wastes. Surface overflow rates for clarifiers associated with rotating biological contactors can range from 20 – 48 $\text{m}^3/\text{m}^2 \cdot \text{d}$. Clarifiers treating organic hazardous waste by activated sludge and powdered activated carbon (PAC) exhibit surface overflow rates of about 30 – 50 $\text{m}^3/\text{m}^2 \cdot \text{d}$ and solids loading rates of approximately 70 – 100 kg. Clarifier effluent suspended solids concentrations can range from 10 – 50 mg/L during normal operating periods. Design parameters for clarifiers treating biologically treated hazardous wastes are developed during bench-and pilot-scale biological treatability studies. These studies include settling tests that will determine the design parameters. If chemical addition is necessary to promote settling, the additional solids loading should be considered.

Table 6.2 Typical design information for clarifiers.⁶

Type of treatment	Overflow rate, $\text{m}^3/\text{m}^2 \cdot \text{d}$		Loading, $\text{kg}/\text{m}^2 \cdot \text{h}$		Depth, m
	Average	Peak	Average	Peak	
Settling following trickling filtration	16 – 24	40 – 48	3.0 – 5.0	8.0	3 – 4
Settling following air-activated sludge (excluding extended aeration)	16 – 32	40 – 48	3.0 – 6.0	9.0	3.5 – 5
Settling following extended aeration	8 – 16	24 – 32	1.0 – 5.0	7.0	3.5 – 5

To design clarifiers to settle out chemically precipitated solids such as metal hydroxides, average and peak design flows and surface overflow rates are used. The surface overflow rate is usually expressed as $\text{L}/\text{m}^2 \cdot \text{s}$ or $\text{m}^3/\text{m}^2 \cdot \text{d}$. Typical surface overflow rates used to settle out chemically precipitated metal hydroxide solids range from 0.10 – 0.50 $\text{L}/\text{m}^2 \cdot \text{s}$. Clarifier effluent suspended solids concentrations can range from 10 – 30 mg/L.

As previously discussed, the jar test can be used to develop design and operational criteria for clarifiers. A settling test, using the Gator jar, is a convenient method for calculating the required surface loading rate. The jar test can be used to determine the efficiency of the clarifier by calculating the percent solids removal at a particular surface loading rate. Clarifier performance is affected by several factors:

- Short-circuiting,
- Density currents,
- Turbulence, and
- Losses at inlet and outlet structures.

Short-circuiting occurs when the actual detention time is less than the design detention time. Density currents occur due to a temperature difference between the clarifier contents and the influent. Turbulence is caused mainly by high inlet velocities. These high velocities scour solids off the clarifier bottom. Improperly designed inlet and outlet devices cause high velocities and turbulence.

TYPES OF EQUIPMENT. Most clarifiers have four zones: inlet, settling, sludge, and outlet zones. Different clarifier geometries and manufacturers exhibit various ways to structure the four zones. Clarifiers are classified as either horizontal-flow, solids-contact, or inclined-surface. The advantages and disadvantages of each clarifier are discussed in Table 6.3. Clarifier selection is based on weighing the following factors:

- Flow and quality variation of hazardous waste,
- Solids-settling rates,
- Type of hazardous waste,
- Land area available, and
- Economics.

Table 6.3 Clarifier types — advantages and disadvantages.⁷

Rectangular clarifier — chain drive scraper

Advantages	— Requires less land area than circular clarifiers when multiple units are used.
	— Common wall for meeting with other clarifiers or treatment units.
	— Easier to cover than circular clarifiers.
	— Small units have less short circuiting than comparable circular clarifiers.
	— Lower inlet–outlet losses.
	— Power consumption of endless chain sludge removal mechanism less than that of other mechanisms.
Disadvantages	— Adversely affected by flow surges.
	— Restricted in width by collection equipment.
	— Requires multiple weirs to maintain low overflow rates.
	— High maintenance costs of the chain and flight sludge removal mechanism.
	— Tank must be dewatered for gear or chain repair.

Rectangular clarifier — bridge drive scraper

Advantages	— Requires less land area than circular when multiple units are required.
	— Common-wall construction is possible.
	— Low inlet–outlet losses.
	— Good hydraulic performance.
	— Small units have less short circuiting than comparable circular clarifiers.
	— Lower maintenance cost than chain-type designs.
	— No width restrictions as with chain-type designs.

Table 6.3 Clarifier types — advantages and disadvantages (continued).⁷

Rectangular clarifier — bridge drive scraper (continued)

Advantages	— Tank dewatering not required for service or replacement.
(continued)	— Unit will operate with “light” icing conditions.
	— Longer mechanical life with no underwater bearings or gears.
	— Standard design permits scraper repair or replacement without tank dewatering.
Disadvantages	— These units will not operate with heavy ice-covered tank.

Rectangular clarifier — bridge drive suction

Advantages	— Require less land area than circular when multiple units are required.
	— Common-wall construction is possible.
	— Low inlet–outlet losses.
	— Good hydraulic performance.
	— Small units have less short circuiting than comparable circular clarifiers.
	— Lower maintenance cost than chain-type designs.
	— No width restrictions as with chain-type designs.
	— Tank dewatering not required for service or replacement.
	— Optimum control of sludge residence time is possible.
	— Better pickup of light sludges than scraper-type mechanisms.
	— Lower cost tank construction.
Disadvantages	— These units will not operate with ice-covered tank.

Centerfeed peripheral overflow circular

Advantages	— Low weir overflow velocities.
	— Good flocculation of solid particles.
	— Ease of design and construction.
	— Standardization of sizes.
	— Hydraulic performance better than other types of circular clarifiers for large diameter (100') clarifiers.
Disadvantages	— Excessive short circuiting for small diameter (<20') clarifiers.
	— Sensitive to density currents.
	— Requires more land area than rectangular clarifiers for multiple units.

Peripheral feed peripheral overflow circular

Advantages	— Intermediate size (50 – 100' diameter) clarifiers exhibit good hydraulic performance.
	— Intermediate size clarifiers produce better solids removals than other types of clarifiers at higher overflow rates.
	— Minimizes density currents by introducing flow near the bottom of the clarifier.
	— Lower weir overflow velocities.

Table 6.3 Clarifier types — advantages and disadvantages (continued).⁷

Peripheral feed peripheral overflow circular (continued)	
Disadvantages	— Large diameter (100') clarifiers do not use the entire surface area of the clarifier for settling. — Requires large peripheral skirt for flow distribution. — Requires deep tanks so deposited sludge is not resuspended.
Peripheral feed center overflow circular	
Advantages	— Intermediate size clarifiers exhibit good hydraulic performance. — Minimizes density currents by introducing flow near the bottom of the clarifier.
Disadvantages	— High weir overflow velocities. — Requires large peripheral skirt for flow distribution. — Requires deep tank so deposited sludge is not resuspended.
Solids contact	
Advantages	— Better hydraulic performance than other types of circular or rectangular clarifiers. — Sludge blanket acts as a filter mat for capturing small particles. — Not upset by flow surges. — Good floc formation. — Reduced detention time for equivalent solids removal.
Disadvantages	— Long sludge detention time makes it impractical for wastewater treatment applications.
Tube settlers	
Advantages	— Provide greater surface area, thereby reducing clarifier size. — Provide laminar flow and quiescent settling conditions within the tubes.
Disadvantages	— Long sludge detention time and sludge deposits on tube surfaces may cause septic conditions. — Shorter life of plastic modules. — Short circuiting when influent warmer than basin temperature.
Parallel plate	
Advantages	— Low space requirements because of small size. — Not affected by wind currents. — Does not require sludge removal mechanisms in smaller units.
Disadvantages	— Sensitive to loading fluctuations. — Large units use chain- and flight-type of sludge removal mechanisms with their attendant maintenance problems. — Long sludge detention time and sludge deposits on plates may cause septic conditions. — Narrow flow distribution channels susceptible to clogging.

The horizontal-flow clarifier exhibits horizontal velocity gradients from the inlet to the outlet. Velocities are kept at a minimum to increase solids removal efficiency. Horizontal-flow clarifiers can be either circular or rectangular and can be made from carbon steel or concrete. They are generally used following biological treatment of hazardous waste.

Rectangular clarifiers are operated with the length parallel to the direction of flow. Length-to-width ratios are recommended to be greater than 2.75 : 1 to avoid streamlining along the walls. Sludge is removed by a rotating bottom scraper that pushes the sludge to one end into a hopper. Rectangular clarifiers can be fitted with oil removal mechanisms (such as belt type) to remove surface scum and oils.

Circular clarifiers are divided into two types according to their feed point—center- or peripheral-feed. Figure 6.2 illustrates center-feed and peripheral-feed clarifiers. The center-feed clarifier is characterized by the placement of the inlet structure at the center of the clarifier and the outlet weir along the periphery of the tank. The horizontal velocity decreases as the flow approaches the outer weir. Small diameter center-feed clarifiers are more susceptible to short-circuiting. Special inlet devices are required to prevent short-circuiting. Standardized center-feed circular clarifiers are available from most manufacturers in 5-m increments up to 50-m diameter.

Peripheral-feed circular clarifiers introduce influent at the subsurface around the periphery of the tank. Effluent exits at the outlet weir, located at the surface of the periphery of the tank. This design is intended to overcome short-circuiting.

Sludge removal in circular horizontal-flow clarifiers is accomplished two ways. A rotating scraper plows the sludge to a center hopper (a sloped floor is required) or the rotating scraper mechanism removes the sludge by suction, either induced by a pump or by a hydraulic head. Rapid removal of biological sludge is important to prevent anaerobic conditions that can lead to denitrification and gas formation.

Solids-contact clarifiers are equipped with a flocculation chamber and use an established sludge blanket to help filter product water. These clarifiers are built to provide for sludge recirculation to help promote better flocculation (Figure 6.3). These clarifiers are used to remove metal at the center where it is mixed with settled sludge and allowed to flocculate in the area inside the skirt. A rotating scraper is used to remove excess sludge. A minimum sludge blanket level is required for maximum solids removal. Long sludge ages are therefore a requirement and as a result, the solids-contact clarifier is not compatible with biological sludges. Effluent solids concentrations can be reduced to 10 mg/L using a solids-contact clarifier.

Inclined-surface clarifiers are either tube or inclined-plate settlers. Their design is based on the theory that shallow settling tanks require less detention time, hence are smaller in physical size. Shallow (closely spaced) passages, either tube or plate, shaped at an optimum angle of 50 – 60 degrees will

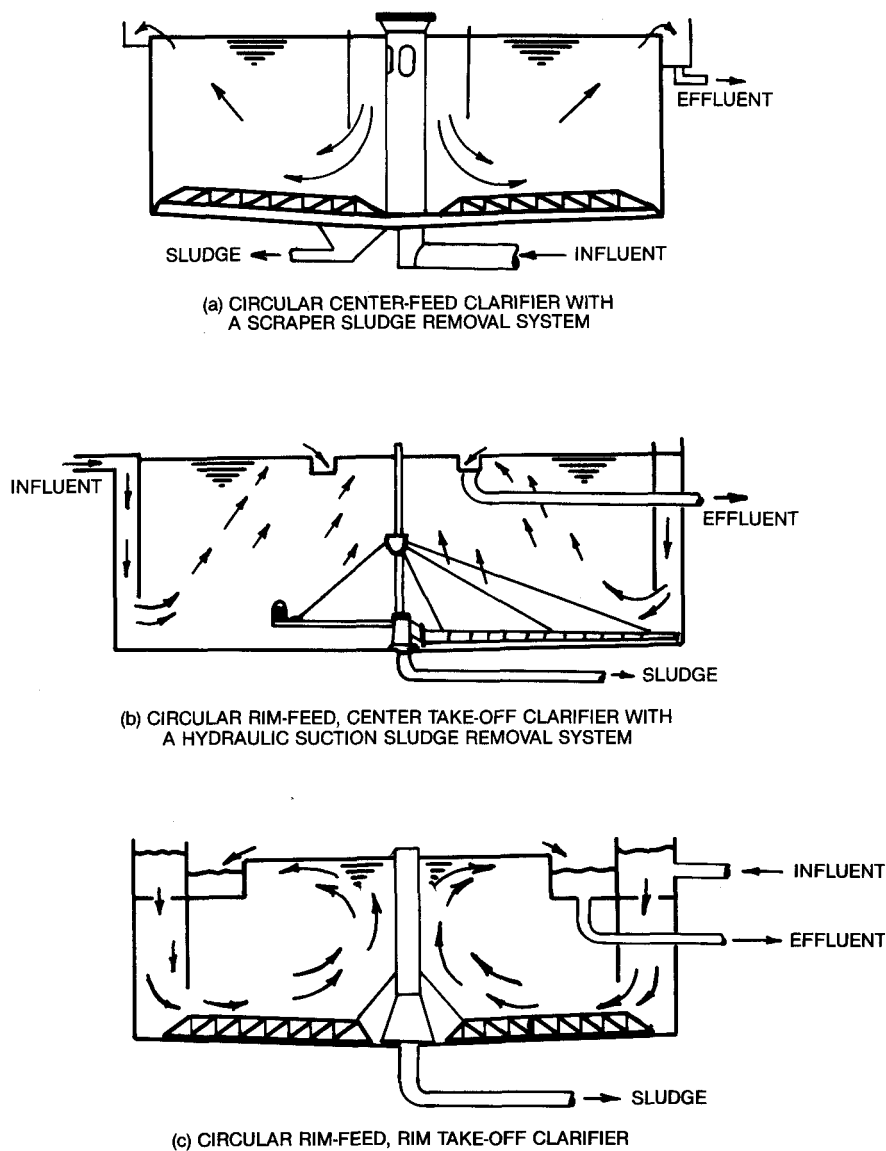


Figure 6.2 Typical clarifier configurations.

promote rapid settling and gravity drainage of the sludge into a bottom sludge hopper (Figure 6.4). Tube settlers can be either circular or square, with tube spacings available from 0.02 – 0.05 m. The tube geometry promotes laminar-flow conditions ideal for gravity sedimentation. Tube settlers can be installed in circular or rectangular, new or existing clarifiers.

Inclined-plate settlers are similar in design to tube settlers. Inclined plates are usually installed at a 50- to 60-deg incline, 0.02 – 0.05 m apart, depending on particle density. The major differences between inclined-plate

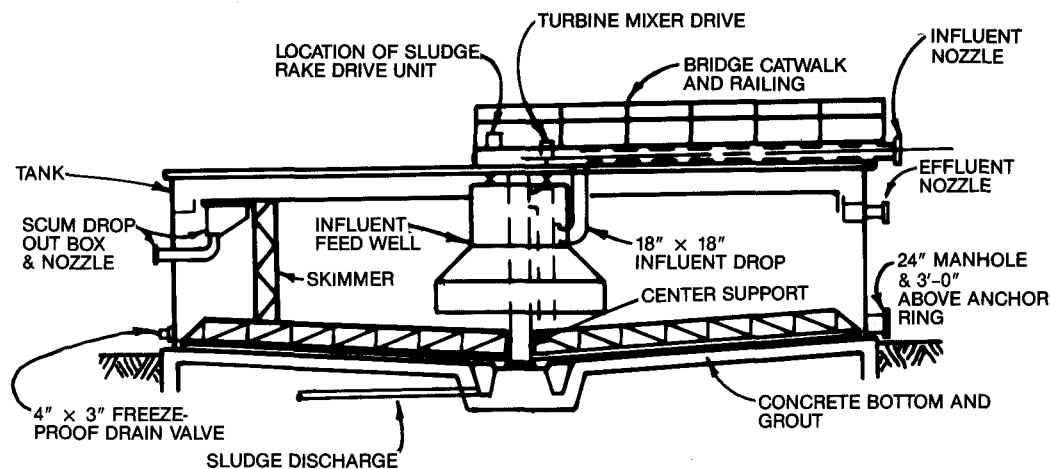


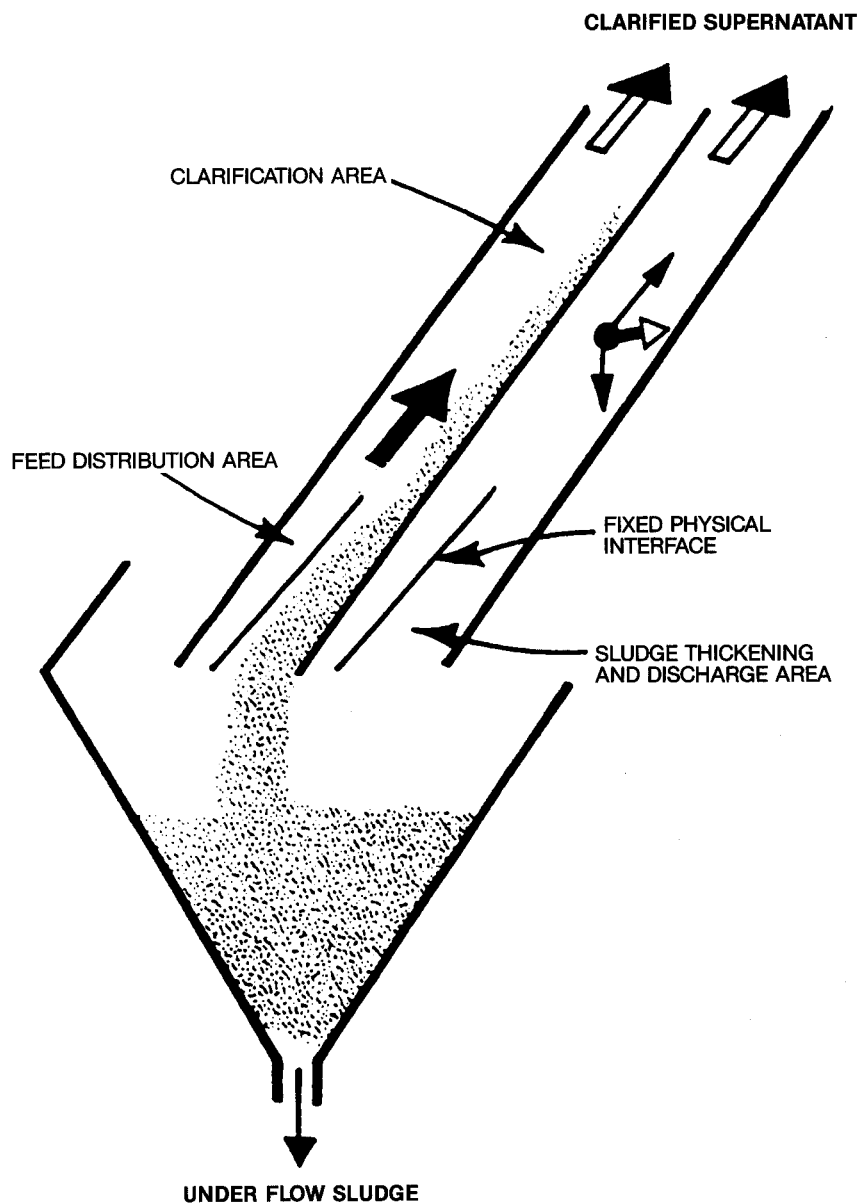
Figure 6.3 Solids contact clarifier.

clarifiers are the influent location relative to the plates and the mechanism for regulating flow, usually either weirs or orifices.

Inclined-surface clarifiers are compatible with most liquid inorganic hazardous wastes, however, any solids that exhibit a sticky characteristic should not be introduced to an inclined-surface clarifier. Plates or tubes can be made of FRP or polypropylene. Sludge settles to the bottom of a small or large hopper and does not require a scraper mechanism. Sludge can be removed by gravity, due to hydraulic head, or pumped to a sludge holding tank. Inclined-surface clarifiers can be supplied with rapid mix tanks and flocculation tanks that bolt onto the clarifier. Effluent suspended solids concentrations can range from 5 to 30 mg/L. Underflow solids concentrations range from 500 to 2000 mg/L. If influent solids concentrations are too low, sludge recirculation will be necessary.

Filtration. Filtration is employed to polish a clarifier effluent, act as a back-up to a clarifier, and/or pretreat hazardous wastes prior to granular activated carbon filters, ion exchange columns, or reverse osmosis units. The type of filter used depends on particle size and shape, particle characteristics, average- and peak-flow rates, regulatory limits, and residual disposal. Current hazardous waste treatment practice includes the use of multimedia granular filters and/or membrane filters to further reduce suspended solids concentrations of clarifier effluents. These clarifiers follow both biological and chemical treatment processes.

The number of cross-flow filters used to treat hazardous waste is still limited, but continuing studies have shown potential for their application. These filters may be used as polishing processes or stand-alone processes with their own unique function.



PRINCIPAL OF OPERATION

Figure 6.4 Inclined surface clarifier.

GRANULAR-MEDIA FILTERS/PROCESS DESCRIPTION. Granular-media filters can be used to remove hazardous constituents associated with solids down to a particle size of 0.1 m in diameter. Effluent solids concentrations

can be reduced to 1 mg/L from feed solids concentrations of 50 mg/L. Hydraulic head, induced either by gravity or a pump, drives the influent through the filtration media. The solids in the influent are then distributed on the media surface, within the media between the pores, or remain in the influent and pass through. During filtration, solids continuously deposit on the media surface until plugging of the filtration occurs. After plugging occurs, the filtration process is discontinued and the filter is backwashed to remove the trapped solids. The backwash wastewater must be treated and is usually recycled to the head of the hazardous waste treatment facility.

Granular-media filters can be classified according to the media used: single-media, dual-media, and multimedia. Single-media filters use either sand or anthracite coal. Dual-media filters use coarse anthracite on top of fine sand. A multimedia or mixed-media filter contains three layers of media: anthracite, fine sand, and a fine dense material called garnet.

Multimedia filters offer several advantages over a single-media filter. These advantages include filtration of hazardous wastes with high influent suspended solids, higher filtration rates ($\text{m}^3/\text{m}^2 \cdot \text{d}$), and longer filtration runs.

Multimedia filters are sometimes referred to as deep bed filters because particles can penetrate into the filter media. This is due to the media gradation that occurs due to different specific gravities of the different media; anthracite is the least dense, garnet the most, and fine sand in between. Backwashing of the media cleans the media of solids and maintains the gradation. As a result, more pore volume is available to store solids. Figure 6.5 illustrates the proper gradation for a multimedia filter.

DESIGN PARAMETERS. Design and selection of a granular-media filter involves carefully determining the following:

- Filter configuration (pressure or gravity),
- Filtration rate ($\text{L}/\text{m}^2 \cdot \text{s}$),
- Terminal head loss (m of water),
- Filter media (type, size, and depth),
- Backwashing requirements,
- Method of flow control.

The best method to select the best design and operating criteria is to perform bench-scale and pilot-plant tests—the first to determine filter configuration and media, the latter to determine the remaining design and operating criteria. Adams describes the studies necessary to determine design parameters.³

Filtration rates can vary from 1 – 7 $\text{L}/\text{m}^2 \cdot \text{s}$ depending on influent solids characteristics and concentration. Most single-media filters operate at 1.3 $\text{L}/\text{m}^2 \cdot \text{s}$, while multimedia filters can operate at higher levels depending on upstream treatment processes. Table 6.4 lists some of the media charac-

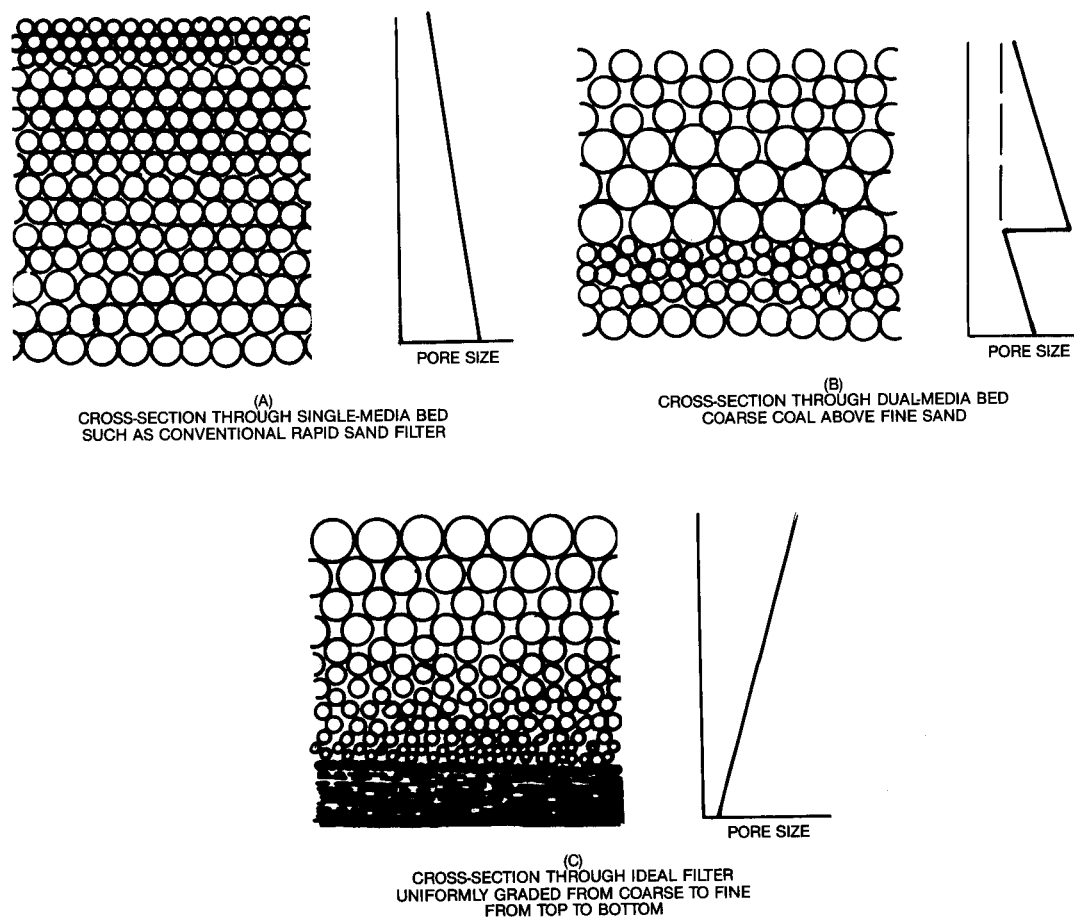


Figure 6.5 Various media designs.

Table 6.4 Typical design data for dual-media and multimedia filters.⁶

Characteristic	Value	
	Range	Typical
Dual-media		
Anthracite		
Depth, mm	300 – 600	450
Effective size, mm	0.8 – 2.0	1.2
Uniformity coefficient	1.3 – 1.8	1.6
Sand		
Depth, mm	150 – 300	300
Effective size, mm	0.4 – 0.8	0.55
Uniformity coefficient	1.2 – 1.6	1.5
Filtration rate, L/m ² •min	80 – 400	200
Multimedia		
Anthracite (top layer of quadmedia filter)		
Depth, mm	200 – 400	200

Table 6.4 Typical design data for dual-media and multimedia filters (continued).⁶

Characteristic	Value	
	Range	Typical
Multimedia (continued)		
Effective size, mm	1.3 – 2.0	1.6
Uniformity coefficient	1.5 – 1.8	1.6
Anthracite (second layer of quadmedia filter)		
Depth, mm	100 – 400	200
Effective size, mm	1.0 – 1.6	1.2
Uniformity coefficient	1.5 – 1.8	1.6
Anthracite (top layer of tri-media filter)		
Depth, mm	200 – 500	400
Effective size, mm	1.0 – 2.0	1.4
Uniformity coefficient	1.4 – 1.8	1.6
Sand		
Depth, mm	200 – 400	250
Effective size, mm	0.4 – 0.8	0.5
Uniformity coefficient	1.3 – 1.8	1.6
Garnet or ilmenite		
Depth, mm	50 – 150	100
Effective size, mm	0.2 – 0.6	0.3
Uniformity coefficient	1.5 – 1.8	1.6
Filtration rate, L/m ² •min	80 – 400	200

teristics and average filtration rates typically used. Biologically treated hazardous wastes are usually filtered closer to 1 L/m²•s. Biologically treated wastes with PAC are filtered on the average at 2 L/m²•s. Metal hydroxide solids can be filtered at 1 – 7 L/m²•s, with an average rate equal to 3 L/m²•s.

Backwashing requirements may include sand fluidization, air scour followed by sand fluidization, and surface washing before and after sand fluidization. Flow rates for sand fluidization range from 7 – 14 L/m²•s for a duration of 5 to 10 minutes. Air scour rates can range from 0.5 – 1 L/m²•s for a duration of up to 5 minutes.

The terminal head loss chosen for operation is based on effluent solids concentration, flow rate, and filter run length. Longer filter runs result in a less expensive system. Operating at high terminal head losses may result in a degradation of the effluent (higher solids). If a pressurized discharge is necessary to feed downstream process (granular activated carbon) equipment, low head loss operation will be required if subsequent repumping is to be avoided. Adding a filtration step to an existing system with limited head could also require a filter system that operates at a low terminal head loss.

The method of flow control to the filter can be accomplished using several methods. Most filters operated today use a rate-of-flow controller. The controller maintains a constant flow rate and water depth by varying the head

loss between the filter-media surface and downstream of the controller. Other methods can be evaluated during pilot testing.

TYPES OF EQUIPMENT. Pressure filters can be horizontal or vertical. Horizontal filters are used when flow rates exceed 1 to 1.5 mgd. Filter systems are usually sized such that with any one filter out of service, the remaining can treat at the design flow. Small filters can be permanently installed or skid mounted for transportation by a flat-bed truck. Filter vessels are usually made of coated carbon steel or stainless steel and usually rated at 5 – 7 kgf/cm². Automatic systems, completely piped and wired, initiate backwashing either by measuring head loss, elapsed time, or effluent total suspended solids or turbidity.

Recently, continuously backwashing sand filters, upflow or downflow, have been used to remove metal hydroxide solids from hazardous wastes. **Figure 6.6** illustrates a continuously backwashing sand filter. It is characterized by high loading rates (3 L/m²•s) and can be constructed of carbon steel or FRP for corrosion protection. Backwash rates range from 1 – 5 % of influent feed rates.

Another common type of sand filter used to remove suspended solids is the automatic backwashing sand filter. These units are rectangular and characterized by high loading rates and continuous operation. The sand bed is divided into compartments, each backwashed separately by a moving carriage containing level probes and a washwater pump. Backwashing is initiated by high water level or a timer. **Figure 6.7** illustrates an automatic backwashing filter. These filters are also used to remove metal hydroxide solids. Filtration rates range from 1 – 4 L/m²• s.

The use of diatomaceous earth as a filter media can be used for special purposes. This pressure filter employs filter elements precoated with diatomaceous earth. Both the deposited solids and the diatomaceous earth must be removed and disposed.

CROSS-FLOW OR MEMBRANE FILTERS/PROCESS DESCRIPTION. Cross-flow filtration uses pressurized flow of the hazardous waste stream through a membrane element. Part of the feed flows through the membrane and the remaining feed flows tangentially to the membrane surface. The tangential turbulent flow sweeps solids away from the membrane surface and prevents membrane fouling. Two streams result from the filter process—a product water or permeate and a concentrate. The concentrate may require further treatment or may be reused in some cases. **Figure 6.8** illustrates a cross-flow tubular filtration membrane.

The five general classes of membrane separation processes are

- Microfiltration (MF),
- Ultrafiltration (UF),

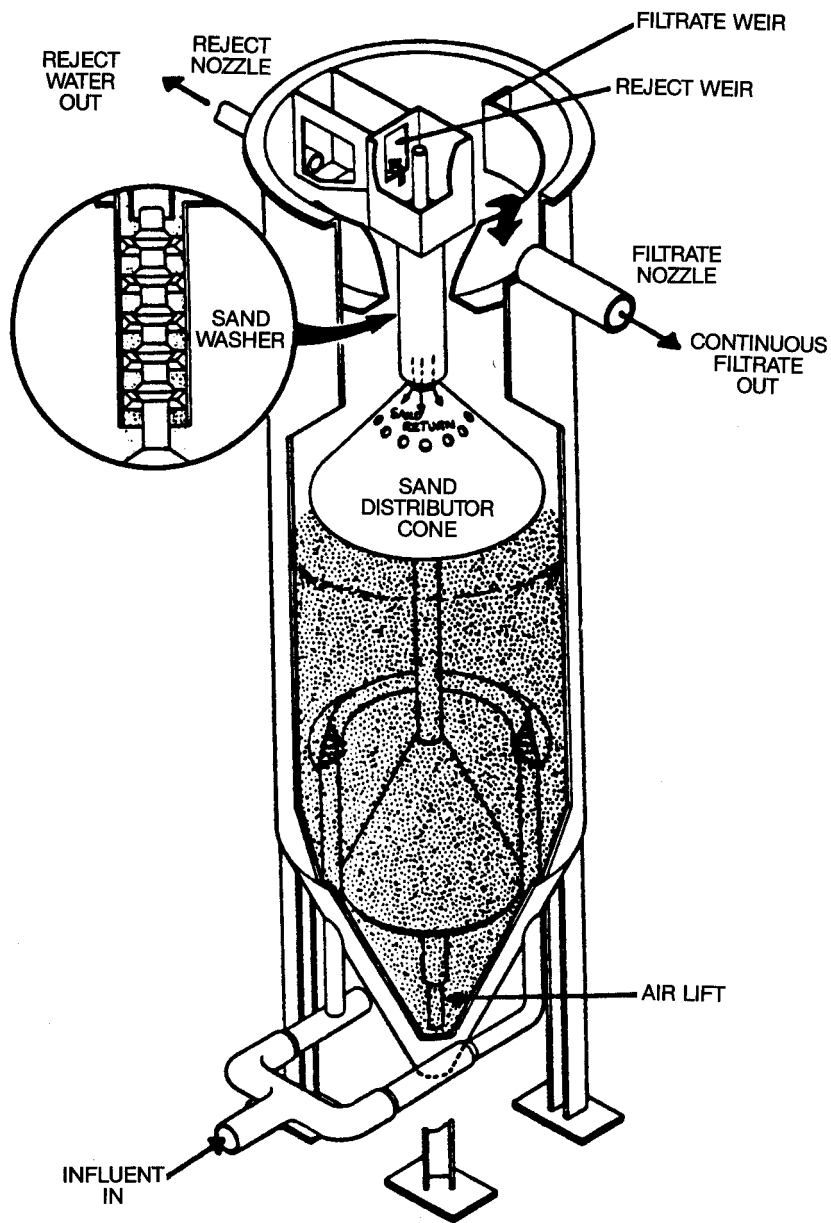


Figure 6.6 Continuously backwashing sand filter.

- Reverse osmosis (RO),
- Electrodialysis (ED), and
- Electrodialysis reversal (EDR).

Although each process uses membranes for separation, the removal mechanisms vary for each process. Figure 6.9 lists the principal removal

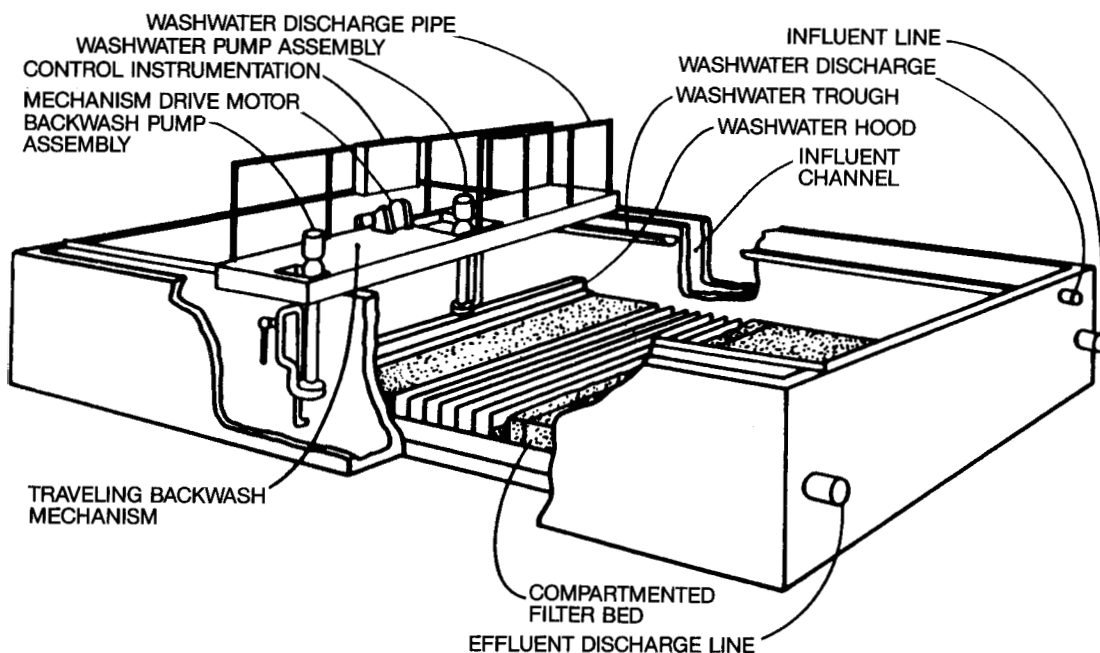


Figure 6.7 Automatic backwashing sand filter.

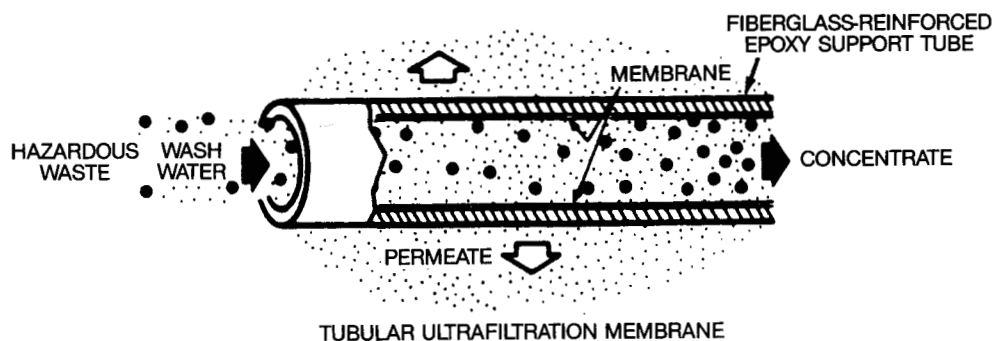


Figure 6.8 Cross flow tubular membrane.

mechanisms of several separation processes. MF and UF rely on pore size, RO on pore size and diffusion, and ED on diffusion. Each process can be used to remove hazardous waste solids of a minimum size, while RO and ED can separate out various molecules and dissolved salts (Table 6.5).

Microfiltration has been used to treat metal-bearing hazardous wastes. With its pore size in the range of 0.1 – 1.0 μ m, hard to settle (clarify) solids such as metal sulfide precipitates can be removed. It can be used as a polishing step following clarification or independently. It is less susceptible to upsets than conventional hazardous solids removal processes. Ultrafiltration

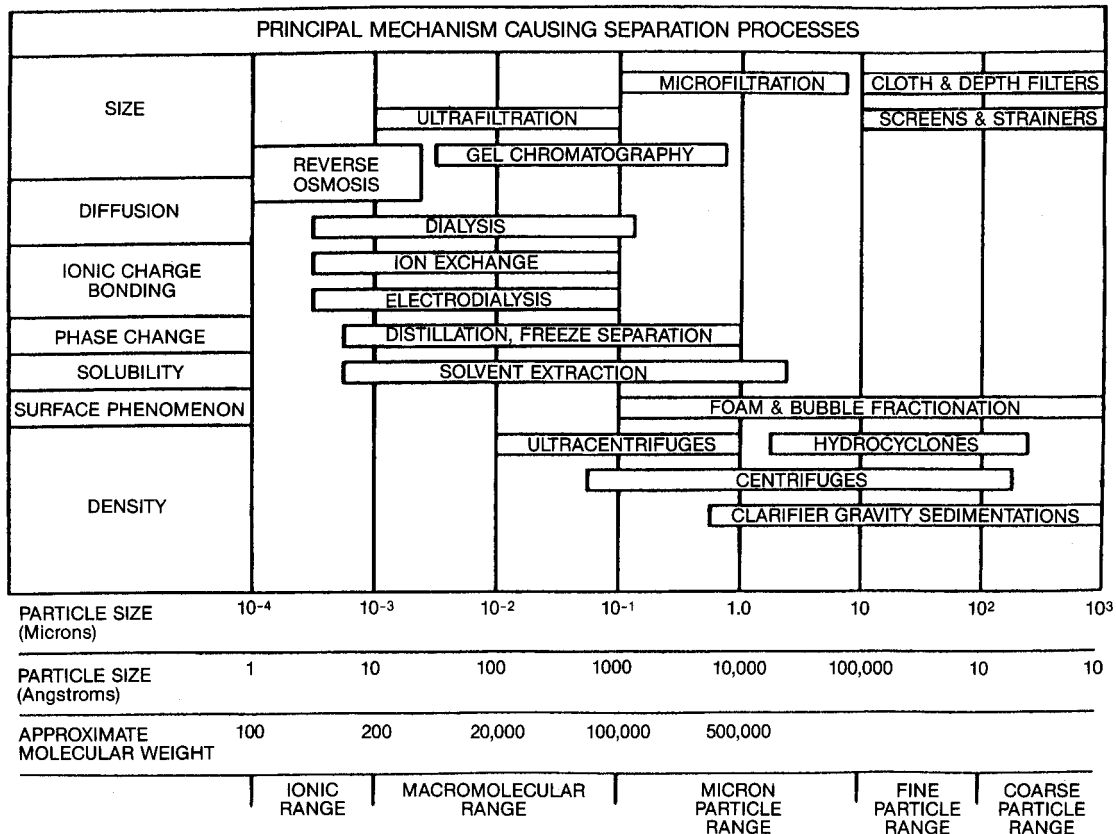


Figure 6.9 Separation processes and mechanisms.

Table 6.5 Summary of key cross-flow membrane separation processes.

Process	MF	UF	RO	ED/EDR
Pore size (Å)	1000	10	1	
	100 000	200	10	
Pressure (PSID)	10	10	100	
		100	1000	
Material separated				
Dissolved salts			Y	Y
TOC		Y	Y	
Colloids (0.2)	Y	Y	Y	
Dissolved silica			Y	
CO ₂ gas				
Bacteria	Y	Y	Y	
Viruses		Y	Y	
Pyrogens		Y	Y	
Oil Emulsions	Y	Y		

has been used to separate and concentrate oily hazardous wastes and large organic molecules. Its pore size range is from 0.002 – 0.1 μ m.

Reverse-osmosis membranes have pore sizes less than 0.002 μ m and have been used to remove dissolved solids and organic contaminants contained in landfill leachates. Slater *et al.* investigated, using RO following physical/chemical treatment and biological treatment on landfill leachates.^{8,9} One study resulted in TDS removals of 98%, COD removals of 68%, and TOC removals of 58%. Permeate flux averaged 0.17 m³/m²·d. The latter study resulted in TDS removals of 99% and TOC removals of 70.8% – 94.7%.

Whittaker *et al.* used a mobile RO system to treat hazardous wastes from landfills.¹⁰ Dilute organic leachates exhibited high removal rates for 1, 1-trichloroethane (85.3%), 1,2-dichloroethane (85.5%), diethylether (77.2%), and 1,4-dioxin (86.6%). Permeate recovery was in excess of 90%.

Membranes can be configured in four basic geometrics and be made of several materials. Table 6.6 illustrates the membrane process and available configuration and construction materials. Membrane material must be compatible with the quality of the feed flow. Figure 6.10 illustrates a spiral-wound UF membrane. Johnson and Michaels discuss the membrane types and materials of construction.^{11,12}

Table 6.6 Summary of key cross-flow membrane separation processes.

Process	MF	UF	RO	ED/EDR
Configurations				
Spiral wound		Y	Y	
Hollow fiber	Y	Y	Y	
Tubular	Y	Y	Y	
Plate and frame	Y	Y	Y	Y
Membrane material				
Cellulose acetate		Y	Y	
Polyamides			Y	
Acrylics		Y	Y	
Polysulfone	Y	Y	Y	
Polypropylene	Y			
Polystyrene				Y
Ceramic	Y	Y	Y	

DESIGN PARAMETERS. The design of a membrane filtration system will involve determining the following:

- Feed quality and volume,
- Fouling potential (SDI),
- Pretreatment requirements,
- System geometry and size,
- Permeate or product water quality,

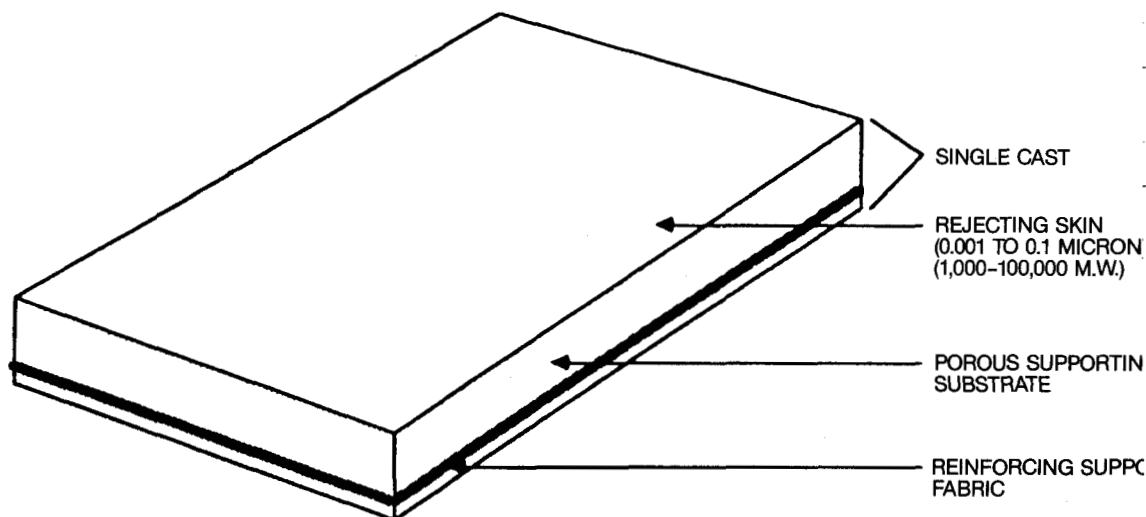


Figure 6.10 Spiral wound UF asymmetrical membrane in profile.

- Feed temperature and pressure,
- Membrane type, and
- Permeate rate ($\text{m}^3/\text{m}^2 \cdot \text{d}$) and rejection ratio.

The hazardous waste feed quality parameters of most importance are solids size, presence of colloids (silt density index SDI), and chlorine. Fouling can be caused by metal oxides, scaling salts, colloids (SDI), and biological growth. Pretreatment is important to prevent fouling of the membranes and increase removal efficiencies.

The system size is dependent on permeate flux rate ($\text{L}/\text{m}^2 \cdot \text{s}$), array (one-, two-, or three-stage), and recovery capability. The permeate quality must meet the regulatory requirements over a long-term period. The feed temperature and pressure affect the membrane selected and flux rate attainable. The type of liquid hazardous waste will help determine the membrane material of construction.

Pilot testing is required to determine the design parameters listed above. Skid-mounted units are available from several manufacturers. Manufacturers are usually willing to perform tests at a cost. Membrane-cleaning requirements may also be determined and may require several different agents. Typical cleaning agents include acids, alkalines, oxidizers, detergents, and organic solvents. The more corrosion-resistant a membrane, the easier it is to find a useable cleaning agent.

TYPES OF EQUIPMENT. An ultrafiltration membrane process and two RO membrane processes to treat hazardous waste are schematically shown in Figure 6.11 and Figures 6.12 and 6.13, respectively. The main components

include membrane elements, circulation pump, feed pump, controls, piping, and cleaning tank. Membrane filtration systems are usually manufactured for skid mounting. Process feed tanks and chemical feed systems are installed separately. RO systems can be one-stage or multi-stage, depending on the specific treatment and concentration requirements.

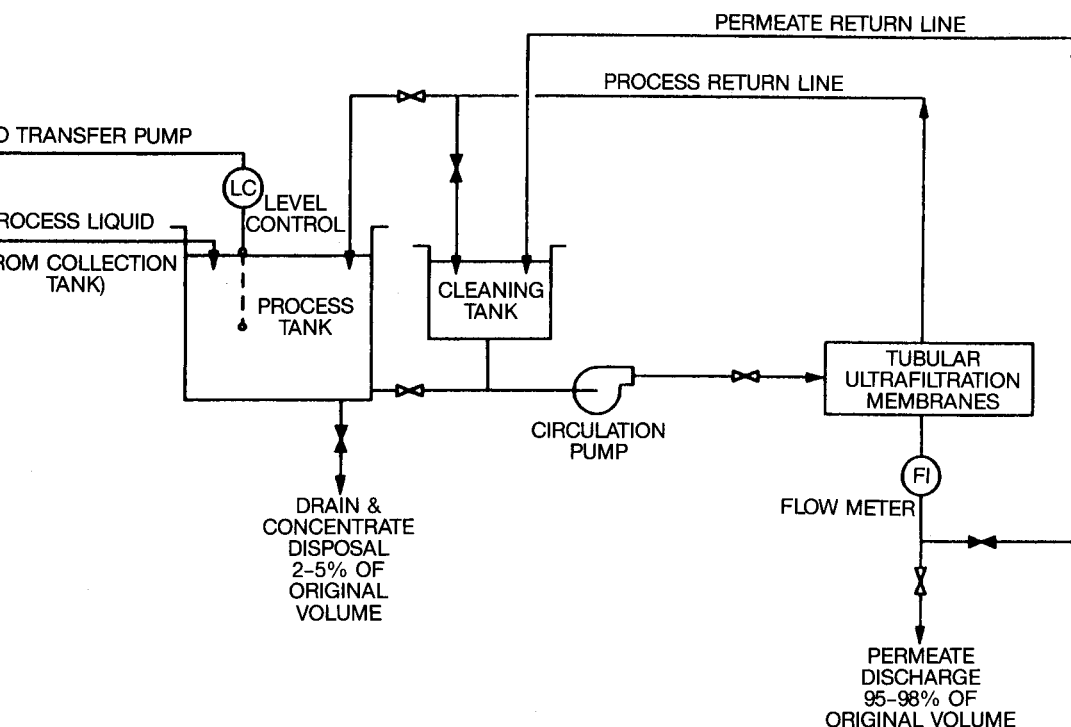


Figure 6.11 Ultrafiltration process diagram.

Spiral-wound microfiltration and UF membranes have been used mostly for the treatment of hazardous wastes. Spiral-wound pressure vessels have been used to remove metal hydroxides and bacteria. Figure 6.14 shows a typical cross section of a spiral-wound pressure vessel. Operating pressures for these systems can range from 7 – 172 kN/m².

UF tubular membrane systems have been used to treat oily hazardous wastes. Davies *et al.* demonstrated that a two-stage UF system could recover oil and produce an acceptable permeate.¹³ Permeate flux rates averaged 2 m³/m²·d, with a cleaning cycle only requiring permeate use.

Safety concerns include operating equipment at high pressures and the potential use of hazardous cleaning fluids.

Granular Activated Carbon (GAC) Adsorption. Granular activated carbon adsorption has been used extensively for the removal of organic com-

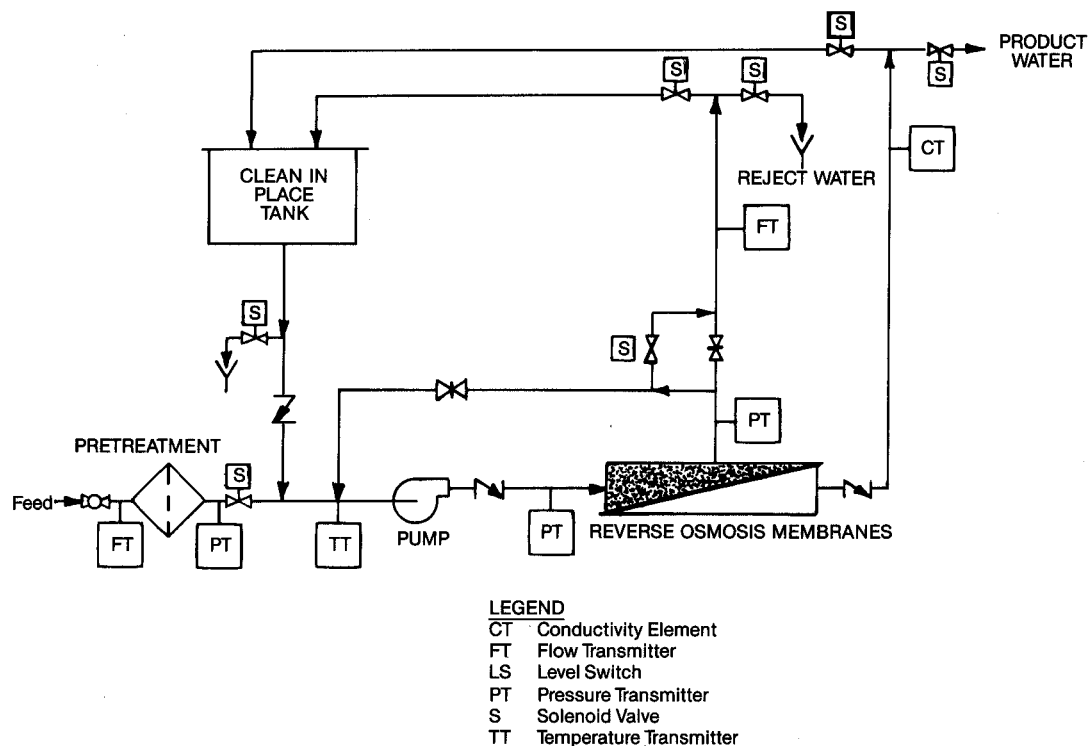


Figure 6.12 Single stage reverse osmosis system.

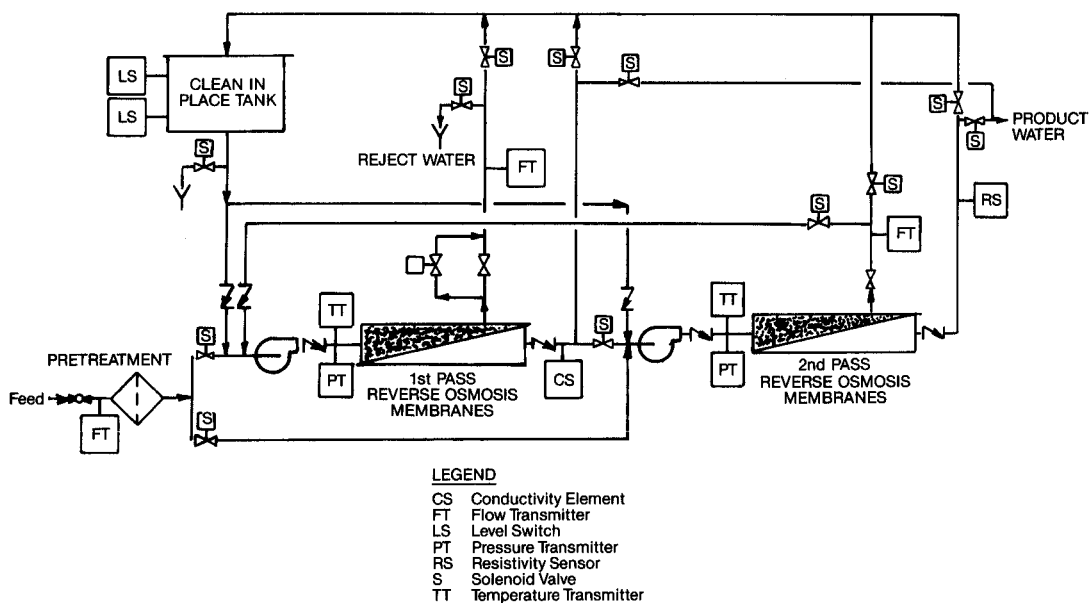


Figure 6.13 Two stage reverse osmosis system.

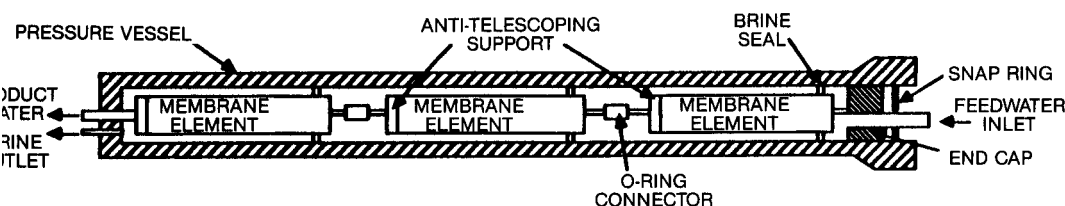


Figure 6.14 Cross section of spiral wound RO pressure vessel.

pounds from liquid hazardous wastes such as spent solvents and landfill leachates. There exists in the literature data on the quantitative adsorption capacity of activated carbon for most of the priority pollutant organic compounds found in hazardous wastes F001 – F005 (spent solvents) and additional hazardous wastes. U.S. Environmental Protection Agency (EPA) and Brenton *et al.* have presented data on the adsorption capacity of activated carbon for over 100 organic molecules.^{14,15} The choice to use activated carbon depends on the specific compounds involved and the result of bench and pilot tests to determine feasibility, design criteria, and cost. Activated carbon should be considered when organic concentrations are relatively high (up to 0.5%) and recovery is possible or as a polishing process when organic concentrations are in the mg/L range. Major considerations in the application of activated carbon to hazardous waste are the form of the activated carbon (granular or powder), carbon capacity, and rate of adsorption.

PROCESS DESCRIPTION. Adsorption is the collection and concentration of a molecule onto a solid surface from a liquid or a gas. The molecules are chemically attracted to the surfaces of the internal pores of the carbon granules but not destroyed or altered. The exact mechanism of attraction is effected by solute solubility, temperature, and pH. Adsorption kinetics of dissolved materials onto activated carbon involves three steps:

- Transport of the solute through a surface film to the exterior of the carbon,
- Diffusion of the solute to within the pores of the activated carbon, and
- Sorption of the solute onto the interior surface of the pores.

Granular activated carbon is used for adsorption of dissolved hazardous compounds because it is nonselective. Most organic and organo-metallic compounds adsorb; their percent removal depends on their chemical characteristics. Hence, one process can remove a wide range of hazardous substances.

The ability and extent of activated carbon to adsorb is a function of several factors. These include molecule weight, solubility, polarity, location

of functional groups, and the overall molecular configuration. Some general guidelines regarding the adsorption of molecules are

- Branch-chain compounds are more sorbable than straight-chain ones;
- Molecules low in polarity and solubility (less than 0.1 g/mL) are preferentially adsorbed;
- For molecules of similar chemical nature, large ones are more sorbable;
- Inorganic molecules offer a wide range of adsorption;
- Low pH promotes adsorption of organic acid; and
- High pH promotes adsorption of organic bases.

Tables 6.7 and 6.8 give some general guides as to the amenability of certain organics to carbon adsorption. Table 6.9 summarizes carbon adsorption capacities for several compounds. The adsorption capacity is reported in mg of compound adsorbed per gram of carbon.

Table 6.7 Classes of organic compounds adsorbed on carbon.

Organic chemical class	Examples of chemical class
Aromatic hydrocarbons	benzene, toluene, xylene
Polynuclear aromatics	naphthalene, anthracenes, biphenyls
Chlorinated aromatics	chlorobenzene, polychlorinated biphenyls, aldrin, endrin, toxaphene, DDT
Phenolics	phenol, cresol, resorcinol, and polyphenyls
Chlorinated phenolics	trichlorophenol, pentachlorophenol
High molecular weight aliphatic and branch chain hydrocarbons ^a	gasoline, kerosene
Chlorinated aliphatic hydrocarbon	1,1,1-trichloroethane, trichloroethylene, carbon tetrachloride, perchloroethylene
High molecular weight aliphatic acids and aromatic acids ^a	tar acids, benzoic acid
High molecular weight aliphatic amines and aromatic amines ^a	aniline, toluene diamine
High molecular weight ketones, esters, ethers, and alcohols ^a	hydroquinone, polyethylene glycol
Surfactants	alkyl benzene sulfonates
Soluble organic dyes	methylene blue, indigo carmine

^a High molecular weight includes compounds in the range of 4 – 20 carbon atoms.

Table 6.8 Amenability to adsorption of selected hydrocarbons.¹⁶

Compound	Molecular weight	Adsorbability g compound/ g carbon	Remarks
Alcohols			
Methanol	32.0	0.007	Compounds highly polar and highly soluble, resulting in low amenability of compounds to adsorption. Polarity decreases as molecular weight increases, resulting in increased adsorbability and with increasing molecular weight
Ethanol	46.1	0.020	
Propanol	60.1	0.038	
Butanol	74.1	0.107	
n-Amyl alcohol	88.2	0.155	
n-Hexanol	102.2	0.191	
Aldehydes			
Formaldehyde	30.0	0.018	Aldehydes, like alcohols, are highly polar compounds. Polarity decreases as molecular weight increases, resulting in increased amenability to adsorption.
Acetaldehyde	44.1	0.022	
Propionaldehyde	58.1	0.057	
Butyraldehyde	72.1	0.106	
Amines			
Di-N-Propylamine	101.2	0.174	Amenability to adsorption again limited by polarity and solubility.
Butylamine	73.1	0.103	
Di-N-Butylamine	129.3	0.174	
Allylamine	57.1	0.063	
Ethylenediamine	60.1	0.021	
Diethylenetriamine	103.2	0.062	
Aromatics			
Benzene	78.1	0.080	Low polarity and low solubility of compounds makes them relatively easy to remove by adsorption onto carbon. Removal is also enhanced by bonding between compound and carbon surface.
Toluene	92.1	0.050	
Ethyl benzene	106.2	0.019	
Phenol	94	0.161	
Hydroquinone	110.1	0.167	
Aniline	93.1	0.150	
Polycols			
Ethylene glycol	62.1	0.013 6	These compounds have multiple sites for hydrogen bonding, which gives them hydrophilic property makes compounds difficult to remove by adsorption.
Diethylene glycol	106.1	0.053	
Triethylene glycol	150.2	0.105	
Tetraethylene glycol	194.2	0.116	
Propylene glycol	76.1	0.024	

Table 6.9 Summary of carbon adsorption capacities.¹⁹

Compound	Adsorption ^a capacity (mg/g)	Compound	Adsorption ^a capacity (mg/g)
Di-(2-Ethylhexyl) phthalate	11 300	Phenanthrene	215
Di-tert-butylbenzyl phthalate	1520	Dimethylphenylcarbinol ^b	210
Di-tert-butylchlor	1220	4-Aminobiphenyl	200
Di-tert-butylchlor epoxide	1038	β-Naphthol ^b	200
Endosulfan sulfate	686	α-Endosulfan	194
		Acenaphthene	190

Table 6.9 Summary of carbon adsorption capacities (continued).¹⁹

Compound	Adsorption ^a capacity (mg/g)	Compound	Adsorption ^a capacity (mg/g)
Endrin	666	4,4' Methylene-bis-(2-chloroaniline)	190
Fluoranthene	664	Benzo(k)fluoranthene	181
Aldrin	651	Acridine orange	180
PCB-1232	630	α -Naphthol	180
β -Endosulfan	615		
Dieldrin	606	4,6-Dinitro- <i>o</i> -cresol	169
Hexachlorobenzene	450	α -Naphthylamine	160
Anthracene	376	2,4-Dichlorophenol	157
4-Nitrobiphenyl	370	1,2,4-Trichlorobenzene	157
		2,4,6-Trichlorophenol	155
Fluorene	330		
DDT	322	β -Naphthylamine	150
2-Acetylaminofluorene	318	Pentachlorophenol	150
α -BHC	303	2,4-Dinitrotoluene	146
Anethole ^b	300	2,6-Dinitrotoluene	145
		4-Bromophenyl phenyl ether	144
3,3-Dichlorobenzidine	300		
2-Chloronaphthalene	280	<i>p</i> -Nitroaniline ^b	140
Phenylmercuric acetate	270	1,1-Diphenylhydrazine	135
Hexachlorobutadiene	258	Naphthalene	132
α -BHC (lindane)	256	1-Chloro-2-nitrobenzene	130
		1,2-Dichlorobenzene	129
<i>p</i> -Nonylphenol	250		
4-Dimethylaminoazobenzene	249	<i>p</i> -Chlorometacresol	124
Chlordane	245	1,4-Dichlorobenzene	121
PCB-1221	242	Benzothiazole ^b	120
DDE	232	Diphenylamine	120
		Guanine ^b	120
Acridine yellow ^b			
Benzidine dihydrochloride	220	Styrene	120
β -BHC	220	1,3-Dichlorobenzene	118
<i>N</i> -Butylphthalate	220	Acenaphthylene	115
<i>N</i> -Nitrosodiphenylamine	220	4-Chlorophenyl phenyl ether	111
		Diethyl phthalate	110
2-Nitrophenol	99	Bromoform	20
Dimethyl phthalate	97	Carbon tetrachloride	11
Hexachloroethane	97	bis(2-Chloroethoxy)	
Chlorobenzene	91	methane	11
<i>p</i> -Xylene	85	Uracil ^b	11
		Benzo(ghi)perylene	11
2,4-Dimethylphenol	78		
4-Nitrophenol	76	1,1,2,2-Tetrachloroethane	11
Acetophenone	74	1,2-Dichloropropene	8.2

Table 6.9 Summary of carbon adsorption capacities (continued).¹⁹

Compound	Adsorption ^a capacity (mg/g)	Compound	Adsorption ^a capacity (mg/g)
2,3,4-Tetrahydro- phthalene	74	Dichlorobromomethane	7.9
adenine ^b	71	Cyclohexanone ^b	6.2
		1,2-Dichloropropane	5.9
ibenzo(a,h)anthracene	69	1,1,2-Trichloroethane	5.8
itrobenzene	68	Trichlorofluoromethane	5.6
4-Benzofluoranthene	57	5-Fluorouracil ^b	5.5
2-Dibromo-3-chloro- opane	53	1,1-Dichloroethylene	4.9
		Dibromochloromethane	4.8
hylbenzene	53	2-Chloroethyl vinyl ether	3.9
Chlorophenol	51	1,2-Dichloroethane	3.6
trachloroethene	51	1,2- <i>trans</i> -Dichloroethene	3.1
Anisidine ^b	50	Chloroform	2.6
Bromouracil	44	1,1,1-Trichloroethane	2.5
enzo(a)pyrene	34		
4-Dinitrophenol	33		
ophorone	32	1,1-Dichloroethane	1.8
ichloroethene	28	Acrylonitrile	1.4
ymine ^b	27	Methylene chloride	1.3
		Acrolein	1.2
		Cytosine ^b	1.1
oluene	26		
Chlorouracil ^b	25	Benzene	1.0
-Nitrosodi- <i>n</i> -propylamine	24	Ethylenediaminetetraacetic acid	0.86
s(2-Chloroisopropyl)		Benzoic acid	0.76
her	24	Chloroethane	0.59
enol	21	<i>N</i> -Dimethylnitrosamine	6.8 x 10 ⁻⁵
ot adsorbed			
cetone cyanohydrin		Adipic acid	
utylamine		Choline chloride	
yclohexylamine		Diethylene glycol	
ihanol		Hexamethylenediamine	
ydroquinone		Morpholine	
riethanolamine			

Adsorption capacities are calculated for an equilibrium concentration of 1.0 mg/L at neutral pH.
Compounds prepared in "mineralized" distilled water containing the following composition:

Ion	Conc. (mg/L)	Ion	Conc. (mg/L)
Na ⁺	92	PO ₄	10
K ⁺	12.6	SO ₄	100
Ca ⁺⁺	100	Cl ⁻	177
Mg ⁺⁺	25.3	Alkalinity	200

Adsorption of dissolved species by granular activated columns requires passing the waste stream through a carbon column either in the upflow or downflow mode. After the carbon has been exhausted, it is either regenerated on-site or off-site or disposed of in a hazardous waste landfill. During regeneration by one of several thermal techniques such as in a multiple-hearth or fluidized bed furnace, 10% or more of the carbon is lost and has to be replaced.

Activated carbon used to treat hazardous wastes can be made from lignite, bituminous coal, or petroleum residues. Table 6.10 lists some properties of carbon used to characterize its nature and predict performance. Table 6.11 gives some property values for two powdered carbons used in hazardous waste treatment.

Table 6.10 Selected properties of activated carbon.¹⁸

Property	Importance
Particle size distribution	Rate of adsorption increases as particle size decreases. Head loss through packed column increases as particle size decreases. Size distribution expressed as percentage passing various size sieves.
Surface area	A measure of the area available for adsorption. The larger the surface area, the greater the adsorptive capacity. Measured by determining the amount of nitrogen adsorbed by the carbon and reported as m ² /g.
Pore volume	Measure of total macropore and micropore volume within the carbon particles. Measured in cc/g.
Iodine number	Refers to milligrams of iodine adsorbed during standard test. Measures the volume present in pores from 10 – 28 Å in diameter. Carbons with a high percentage of pore sizes in this range would be suitable for adsorbing low molecular weight substances.
Molasses number	Refers to milligrams of molasses adsorbed during standard test and measures the volume in pores greater than 28 Å in diameter. Carbons with a high percentage of this size pores would be suitable for adsorbing high molecular weight substances.
Abrasion number	Measures ability of carbon to withstand handling and slurry transfer. This property is of limited value because measuring techniques are not reproducible.
Bulk density	Useful in determining the volume occupied by a given weight of carbon.

Table 6.11 Typical properties of two powdered carbons.

Property	Powdered carbon	
	HydroDarco H	HydroDarco C
Surface area (m ² /g)	475 (min)	550 (min)
pH	10.5	10.5
Tamped density (g/mL)	0.70	0.70
Molasses RF	40	95
kg/m ³ (lbs/cu ft)	704.9 (44)	704.9 (44)
Sieve analysis		
through 325 mesh (%)	70	70
Water solubles (%)	3.5	5.5

DESIGN PARAMETERS. A chemical analysis of the hazardous waste for specific organic compounds can give the design engineer indication whether GAC is applicable. However, removal of COD and TOC are not easily deduced from any published data and their removal would have to be determined by conducting bench-scale and pilot-scale adsorption tests.

A bench-scale batch test is used to construct an adsorption isotherm. The isotherm shows the relationship at a given temperature and pH between the amount of substance (compound X, COD, or TOC) adsorbed and its concentration in the surrounding solution. The adsorption isotherm provides information and is used to screen whether GAC is applicable and can reduce contaminant concentrations to the required levels at a reasonable carbon dosage. Different carbons are usually evaluated.

The Freundlich equation is the most widely used for constructing an adsorption isotherm from laboratory data. The equation and a representative plot are given in Figure 6.15. The constant, K , is a measure of the relative adsorption capacity. Larger values of K indicate higher adsorption capacities. The constant, n , indicates the effect of solution concentration on adsorption.

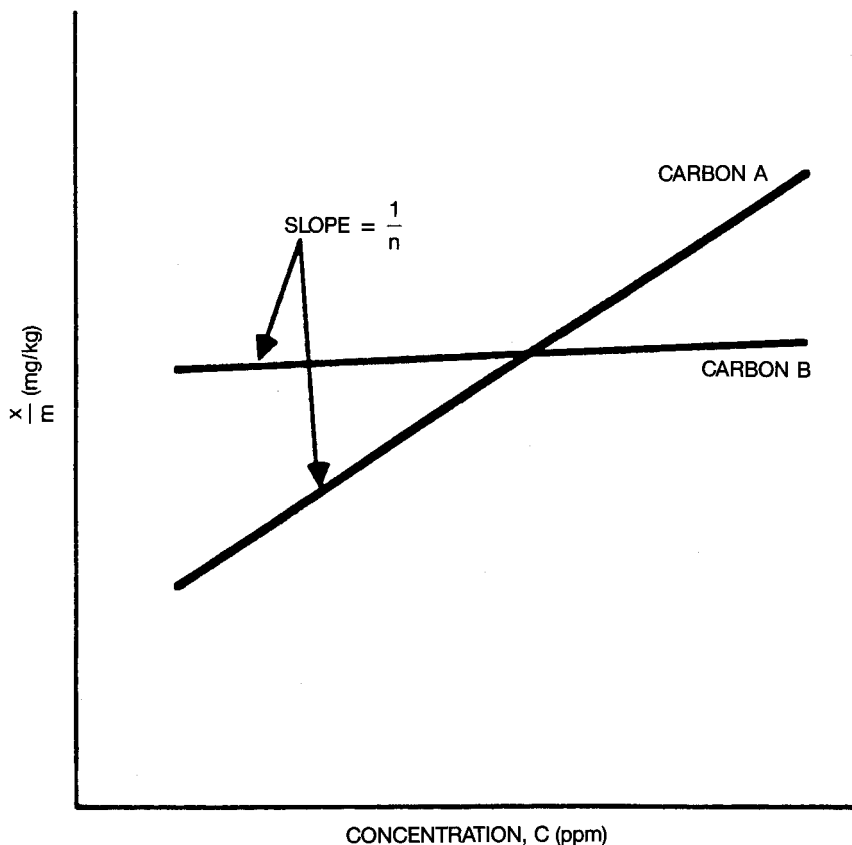
In most cases a dynamic column test will follow a successful batch isotherm test. The dynamic column test will determine the actual carbon usage and contact time required and therefore the costs of using the GAC process. Stenzel has used an accelerated column test (ACT) to evaluate dosages and contact times¹⁹

To obtain the required design and operating parameters for a full-scale system, pilot-scale carbon column tests are sometimes performed.

Table 6.12 lists the common design criteria necessary for design and some range of values for each used in the past to treat hazardous wastes. The most important ones include loading rates ($L/m^2 \cdot s$), bed depth, and contact time. The data obtained from a pilot test can be used to construct a breakthrough curve as shown in Figure 6.16. The curve indicates the time it will take to result in breakthrough at various flow rates. Column size and feed rates can be calculated from this curve.

Pretreatment requirements can also be determined from pilot-scale tests. These may include pH adjustment, solids removal, and treatment to control bacterial growth. Head loss characteristics can also be determined for sizing pumps and valves. Several GAC manufacturers use computer models to design GAC systems for the removal of many different organics in the same hazardous waste.

SYSTEM DESCRIPTION. GAC systems can be operated as downflow fixed-bed systems or expanded-bed upflow systems, also referred to as moving-bed systems. Downflow systems also remove suspended solids and therefore require pretreatment and backwashing to remove solids. Downflow systems require the ability to have one on-line filter while the other is being backwashed. Systems can be operated in series or parallel, depending on the



Key:

Freundlich Equation

$$x/m = KC \frac{1}{n}$$

x = Amount of Waste Constituent Adsorbed, mg

m = Weight of Carbon, kg

C = Concentration of Waste Constituent Left in Solution, ppm

K = Empirical Constant, Dimensionless

n = Empirical Constant, Dimensionless

Figure 6.15 Isotherms for carbon adsorption.

reliability and performance required. Systems designed for series operation can select different carbons for selective adsorption of different species.

Once exhausted, the carbon is removed for disposal or regeneration.

Downflow systems are often used to treat groundwater containing hazardous contaminants. Standard 3.0-m diameter vessels containing 9072 kg of GAC are used.

Table 6.12 Granular activated carbon column (GACC) design criteria.

Parameter	Value
Vessel diameter	0.6 – 3.7 m (2 – 12 ft)
Area loading	1.3 – 6.8 L/m ² •s (2 – 10 gpm/ft ²)
Organic loading	0.04 – 0.14 kg (0.1 – 0.3 lbs BOD or COD/lb-carbon)
Backwash	8.1 – 13.6 L/m ² •s (12 – 20 gpm/ft ²)
Air scour	8.1 – 13.6 l/m•s (3 – 5 ft ³ /min/ft)
Bed depth	1.5 – 9.1 m (5 – 30 ft)
Contact time	600 – 3000 s (10 – 50 min)
Land area	Minimal
Spent carbon	1.4 – 4.5 kg/kg (3 – 10 lb/lb COD removed)

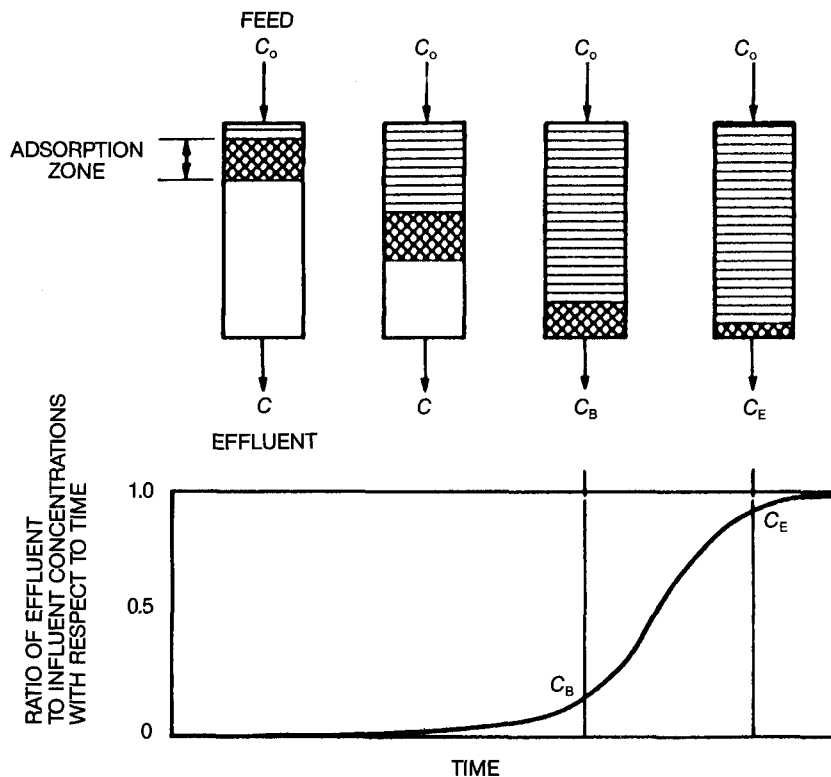


Figure 6.16 Plot of breakthrough curve.

Moving-bed GAC systems are designed to continuously replenish spent carbon. Feed flows upward through the expanded bed while the carbon moves downward for removal. Figure 6.17 illustrates an upflow moving bed GAC system. Makeup carbon enters at the top of the vessel. Void spaces between the carbon particles allow solids to travel through the column.

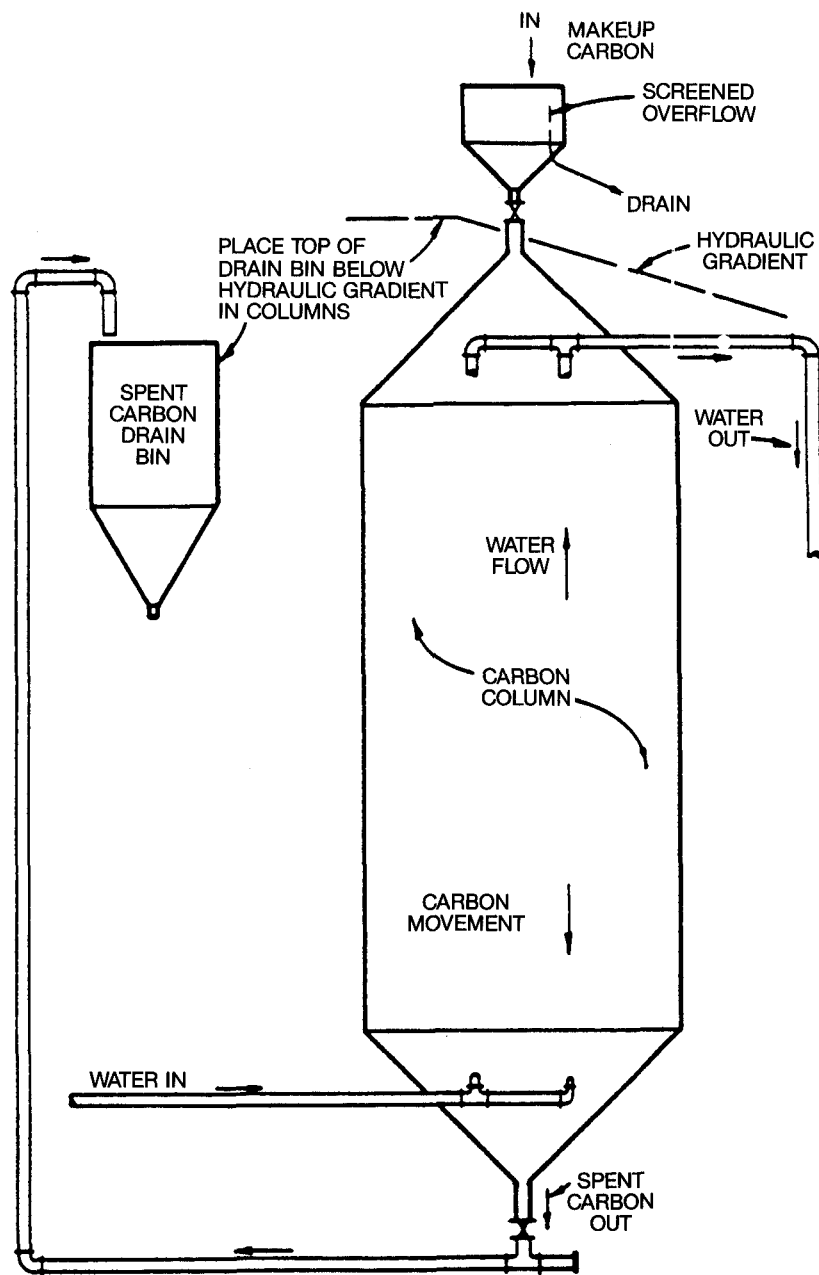


Figure 6.17 Upflow carbon column.

Because solids are not removed and pass through, pretreatment is required. Columns can be operated in series or parallel, similar to downflow systems.

Figure 6.18 illustrates an upflow GAC system with carbon regeneration. Regeneration losses depend on the system selected. Makeup carbon is washed prior to addition to the column.

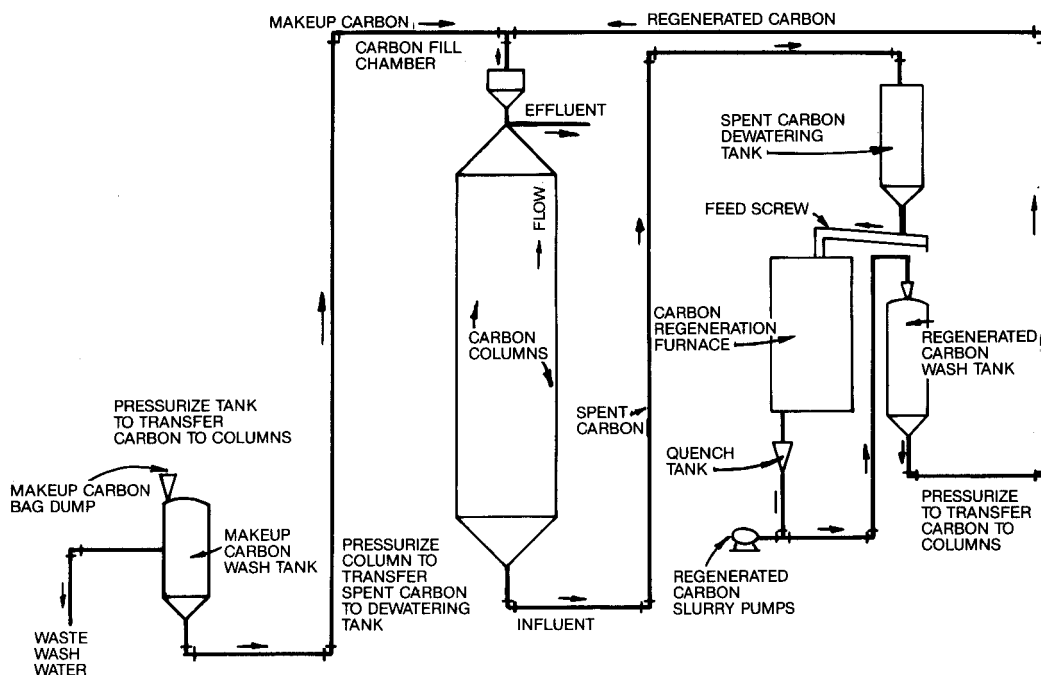


Figure 6.18 Carbon contacting and regeneration—process flow diagram with upflow contactors.

One important design consideration for a GAC system is to assure uniform flow distribution. Channeling and flooding, which can cause non-uniform flow distribution, result from improper column design and nonuniform column packing. Nozzles, plates, and rings are used to distribute the flow uniformly over the column. The carbon must be properly loaded into the column and a good bed support material must be used.

The selection of GAC as an economical treatment process of hazardous wastes may depend on the regenerationability of the activated carbon. For systems operating on long adsorption cycles, the carbon may be disposed of in an environmentally acceptable manner. However, if large quantities of carbon are to be disposed of, regeneration is necessary. The techniques available for regeneration include thermal, steam, acid and base, solvent, and biological; steam, thermal, and acid and base washing are the most common.

Air Stripping. This section presents an overview of air stripping as it applies to the removal of applicable hazardous waste constituents. Air stripping is a process whereby volatile chemicals are removed from a liquid to a gas phase. Intimate contact between the liquid and gas phases is achieved in a variety of equipment types. Air stripping has been applied to a variety of liquid phases containing volatile inorganic and organic constituents. For example, ammonia in wastewater can be removed from wastewater by air

stripping. The largest number of applications, however, pertain to removal of synthetic organic chemicals (SOCs) from groundwater, surface water, and wastewater. Typical SOCs include aromatic chemicals (such as benzene and toluene) associated with gasoline and other petroleum fuels, degreasing solvents (1,1,1-trichloroethane), and dry-cleaning fluids (tetrachloroethylene).

WASTE CHARACTERIZATION AND TREATABILITY STUDIES. The type of contaminants to be removed from the liquid phase must first be characterized to assess the applicability of air stripping to the waste stream in question. Analytical methods appropriate for the characterization include those found in "Standard Methods" or Environmental Protection Agency's published methods.^{19,20}

The need for conducting treatability studies, which include both bench-scale and pilot-scale equipment, must be determined before the process efficiency and applicability can be confirmed. Factors that should be considered in deciding to proceed with treatability studies include the following:

- Size of full-scale system—many air strippers for hazardous waste applications are small, 0.6 L/s, and a pilot unit may be as large as the full-scale system.
- Complexity of matrix—complex solutions of chemicals may cause unacceptable deviations of performance from published correlations.
- Availability of published data on similar systems and applications—the designer's experience in designing these systems will directly affect his or her confidence level. The designer's confidence level in applying empirical design criteria inversely affects the need for treatability studies.

PROCESS DESCRIPTION. Air stripping of volatile chemicals is a mass transfer operation in which a solute dissolved in the liquid phase is transferred from a liquid to a gas or air phase. In the environmental field, the liquid is usually water. The solute could be a volatile organic compound (VOC) or an inorganic such as ammonia or hydrogen sulfide. The principles of air stripping remain the same regardless of the solute.

The process is governed by the relative volatility of the solute compared to the solvent. If the solute is more volatile, it can be removed by air stripping; if it is less volatile than the solvent, it cannot be removed by air stripping. The relative volatility is a parameter that defines mathematically the ratio of the partial pressure of the chemical to that of water.

$$\alpha_{i,w} = M_{xi}/P_w \quad (1)$$

In this equation, M_{xi} is the "Henry's constant" for the chemical and P_w is the vapor pressure of water, both at the air-stripping system's operating temperature.

Henry's coefficient is a constant, unique to each chemical, defined as the ratio of the vapor phase concentration of the volatile chemical in equilibrium with an aqueous solution of the chemical:

$$M_{xi} = Y_i^* / X_i / X_i \quad (2)$$

Where

* = is the equilibrium point.

This coefficient is based on Henry's law, which states that for dilute solutions in equilibrium, the equilibrium partial pressure ($X_i \cdot (Y_i^*)$) is directly proportional to the liquid phase concentration, X_i .

Table 6.13 shows examples of Henry's coefficients and volatiles relative to water. Note should be taken of those chemicals with a relative volatility less than unity since they will not strip from water. Rather, a solution of these chemicals would become more concentrated if treated in an air stripper.

Table 6.13 Vapor-liquid equilibria of selected gases and liquids in water at 25°C.²¹

Component	Normal boiling point, °C	M_{xi}^a	i_w^a
1. Nitrogen	-195.8	86 500.0	2 768 000.0
2. Hydrogen sulfide (H ₂ S)	-59.6	54 500.0	1 744 000.0
3. Oxygen (O ₂)	-183.0	43 800.0	1 402 000.0
4. Ethane (C ₂ H ₆)	-88.6	30 200.0	966 400.0
5. Propylene (C ₃ H ₆)	-48.0	5690.0	182 100.0
6. Carbon dioxide (CO ₂)	-78.5	1650.0	52 480.0
7. Acetylene (C ₂ H ₂)	-84.0	1330.0	42 560.0
8. Bromine (Br ₂)	-58.8	73.7	2358.0
9. Ammonia (NH ₃)	-33.4	0.843	27.0
10. Acetaldehyde	20.2	5.88	188.0
11. Acetone	56.5	1.99	63.7
12. iso-propanol	82.5	1.19	38.1
13. n-propanol	97.8	0.471	15.1
14. Ethanol	78.4	0.363	11.6
15. Methanol	64.7	0.300	9.60
16. n-butanol	117.0	0.182	5.82
17. Acetic acid	118.1	0.062 7	2.01
18. Formic acid	100.8	0.024 7	0.790
19. Propionic acid	141.1	0.013 0	0.416
20. Phenol	181.3	0.010 2	0.326

^a Henry's Constant and relative volatility from equation 1.

A number of theories have been advanced to describe the mass transfer process in air stripping. The following discussion will use the mass transfer relationships to illustrate the principles of air strippers and the variables that affect stripper operation.

In general, mass transfer will depend on a concentration difference that describes a system's departure from equilibrium. The "mass transfer coefficient" is the parameter that indicates how much of a chemical is transported into the air per unit time, per unit volume of air stripper. The mass transfer coefficient is used in an equation of the following form:

$$J = k_y (Y_i - Y_i^*) \quad (3)$$

$$J = k_x (X_i^* - X_i) \quad (4)$$

In these equations, J is the mass flux of chemical defined as mass per unit time per unit surface area of exposed liquid. Y_i is the actual vapor concentration of chemical i at any point in the tower, and Y_i^* is the equilibrium vapor-phase composition at the same point in the tower corresponding to the liquid phase. At that point (from equation 2), k_y is the gas-phase mass transfer coefficient. Similar definitions apply to, X_i , X_i^* , and k_x , and k_x , the latter being the liquid-phase coefficient.

At steady state, when chemical i is not accumulating in gas or liquid pockets, the flux across the gas interface equals that across the liquid interface. Under this condition, and assuming no chemical reactions occur, equations 3 and 4 are equal. Standard texts can be consulted for the derivation of the following two equations:

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{M_x}{k_x} \quad (5)$$

and

$$\frac{1}{K_x} = \frac{1}{k_x} + \frac{1}{M_x k_y} \quad (6)$$

Equations 5 and 6 relate "overall" mass transfer coefficients, K_y and K_x , to the individual gas- and liquid-phase coefficients, k_y and k_x . These two equations show that the overall mass transfer coefficient is the sum of two "resistances" in series, the resistance presented by the gas phase ($1/k_y$) and that of

the liquid phase ($1/k_x$). Physically, these resistances to the transport of chemicals are analogous to electrical or hydraulic resistances in series.

A number of general correlations for mass transfer coefficients have been developed. Gossett showed, through careful experiments, that the correlations developed by Onda worked well in dilute solutions of five common VOCs.²² The Onda correlations are as follows:

$$k_1 \left\{ \frac{\rho_l}{\mu_x g} \right\}^{1/3} = 0.0051 \left\{ \frac{L_m}{a_w \mu_x} \right\}^{2/3} \left\{ \frac{\mu_x}{\rho_x D_x} \right\}^{-1/2} \{a_t d_p\}^{0.4} \quad (7)$$

$$\frac{k_y}{a_t D_g} = 5.23 \left\{ \frac{G_m}{a_t \mu_y} \right\}^{0.7} \left\{ \frac{\mu_y}{\rho_y D_y} \right\}^{1/3} \{a_t d_p\}^{-2.0} \quad (8)$$

Where

- ρ_x = liquid density,
- μ_x = liquid viscosity,
- g = acceleration due to gravity,
- L_m = liquid flow per unit area,
- a_w = wetted interfacial area per unit bed volume,
- D_x = liquid-phase diffusivity,
- a_t = total dry packing per unit bed volume,
- d_p = nominal diameter of a piece of packing,
- D_y = gas-phase diffusivity,
- G_m = gas flow per unit area,
- μ_y = gas viscosity, and
- ρ_y = gas density.

Onda further defined a_w and a_t as follows: (9)

$$a_w/a_t = 1 - \exp \left\{ -1.45 \left(\frac{\sigma_c}{\sigma} \right)^{0.75} \text{Re}^{0.1} \text{Fr}^{-0.05} \text{We}^{0.2} \right\}$$

Where

- σ_c = critical surface tension of the packing;
- σ = surface tension of the liquid;
- Re = Reynold's number, $L_m/(a_t \mu_x)$;
- Fr = Froude number, $L_m^2 a_t / (\rho_x^2 g)$; and
- We = Weber number, $L_m^2 a_t / (\rho_x \sigma a_t)$.

The above correlations for the mass transfer coefficients show them to be complex functions of the physical and chemical parameters of the chemical in the liquid and gas phases, the packing, and the tower. All of the parameters describing the system, except for L_m , g , d_p and G_m , are also functions of temperature.

Temperature will affect the stripping efficiency in a column. In general the higher the temperature, the higher the stripping rate will be. For example, Table 6.14 shows the temperature effects on a number of parameters in the Onda correlation and on the Henry's coefficient for trichloroethylene (TCE). One might conclude from Table 6.14 that liquid viscosity, diffusivity, and Henry's coefficient are the strongest functions of temperature and would thus affect mass transfer the most. This would only be true if transfer from the liquid phase were slower than that from the gas phase.

Table 6.14 Effects of temperature on system parameters.²²

Parameter	Value at 10°C	Value at 30°C	% Change
Gas viscosity ($10^{-5} \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$)	1.76	1.86	+5.7
Gas density ($\text{kg}\cdot\text{m}^{-3}$)	1.248	1.165	-6.7
Gas-phase diffusivity (example: TCE) ($10^{-6} \text{ m}^2\cdot\text{s}^{-1}$)	7.22	8.21	+13.7
Liquid viscosity ($10^{-3} \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$)	1.307	0.798	-38.9
Liquid density ($\text{kg}\cdot\text{m}^{-3}$)	999.7	995.7	-0.4
Liquid-phase diffusivity (example: TCE) ($10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$)	0.700	1.23	+75.7
Surface tension of water ($\text{kg}\cdot\text{s}^{-2}$)	0.074 2	0.071 2	-4.0
Henry's constant (example: TCE) (dimensionless)	0.173	0.440	+154

Under normal operating conditions in air strippers, one would expect the liquid-phase resistance to be the controlling transport factor for sparingly soluble compounds (most VOCs). This is because Henry's coefficient (equation 2) will be relatively large, and equation 6 will simplify to

$$\frac{1}{K_x} = \frac{1}{k_x} \quad (10)$$

At sufficiently high concentrations, other solutes may influence the stripability of the chemical in question. Gossett *et al.* studied the effect of mixtures of organic chemicals and ionic strength on both Henry's coefficient and the overall liquid-phase mass transfer coefficient. Their results of the Henry's coefficient studies were inconclusive, although their study showed mixture effects on the mass transfer coefficient to be insignificant.²²

Air stripping is a unit operation in which a liquid (usually wastewater or groundwater) containing volatile chemicals is brought into direct physical contact with a stream of air. Two types of basic contactors are possible, concurrent and countercurrent, the basic difference being the relative flow directions of the liquid and gas phases. Concurrent contactors are limited to one theoretical transfer unit or stage (defined later); they are seldom used in treating hazardous wastes.

Theoretically, aqueous or organic liquid wastes can be treated in air strippers although applications using the latter waste type are believed to be rare. Generally, the process is applicable for treatment of any aqueous waste that contains volatile organic and inorganic chemicals. For example, one of the first applications of air strippers was the removal of ammonia from domestic wastewater treatment plants.

DESIGN PARAMETERS. Two basic parameters require consideration in the design of packed air strippers, column diameter, and packing height.

Column Diameter. For a given liquid flow rate, which usually defines the design, the hydraulic problem is specifying a tower diameter that will provide adequate performance. In air strippers, the diameter is usually calculated using a correlation such as the following, developed by Sherwood *et al.*²³:

$$\frac{U_t^2 a_p}{g \epsilon^3} \frac{\rho_g}{\rho_l} \mu_l^{0.2} = \text{function} \frac{L_m}{G_m} \sqrt{\frac{\rho_g}{\rho_l}} \quad (11)$$

Where

- U_t = superficial gas velocity, m/s;
- a_p = total area of packing, m^2/m^3 bed;
- ϵ = fractional voids in dry packing;
- g = gravitational constant, 9.8 m;
- ρ_g and ρ_l = gas and liquid densities, kg/m^3 ;
- L_m = liquid-mass rate, $\text{gm}^{-2}\text{s}^{-1}$;
- G_m = gas-mass rate, $\text{gm}^{-2}\text{s}^{-1}$; and
- μ = liquid viscosity, centipoise.

An example of this relationship is shown in Figure 6.19.

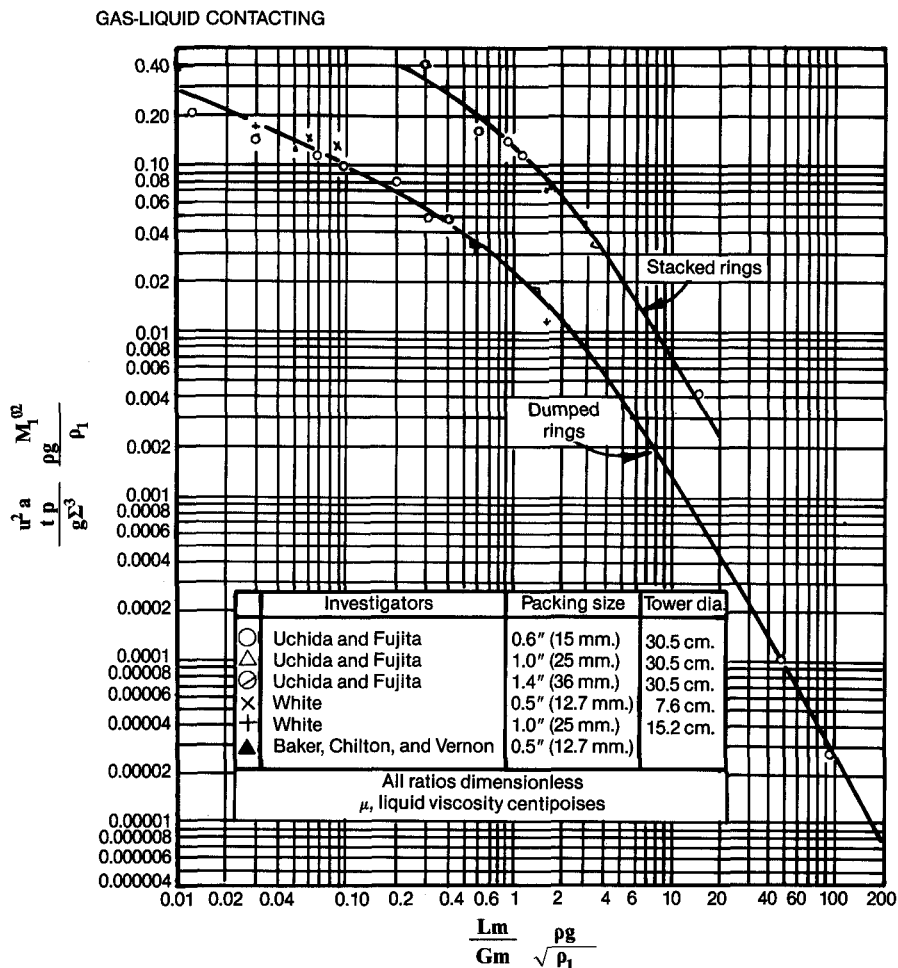


Figure 6.19 Generalized correlations of flood points (packed columns).

The limiting factor in tower design is the "flooding point," which is reached when the gas-to-liquid ratio (L_m/G_m) reaches a point where liquid cannot flow down the tower or is blown out of the tower.

Packing Height. The packing height is calculated by using mathematical relationships describing vapor/liquid equilibria between the liquid and gas phases and by considering the mass transfer relationships. The height of packing is selected to ensure that the required liquid effluent concentration is achieved given the liquid influent flow rate and concentration. This is done using a differential form of equation 3 or 4 and integrating over the tower height. In the limiting case of dilute solutions without chemical reactions and solutes that have low solubilities (thus the liquid phase controls), the equation for tower height reduces to a form such as

$$K_x Z \frac{L}{(x - x^*)} = L (x_a - x_b) \quad (12)$$

Where

- K_x = overall liquid phase coefficient,
- Z = packing height,
- L = liquid flow,
- x_a = inlet liquid concentration,
- x_b = effluent liquid concentration, and
- $*$ = equilibrium point.

$$(x - x^*) = \frac{(x_a - x_a^*) - (x_b - x_b^*)}{\ln \left\{ \frac{x_a - x_a^*}{x_b - x_b^*} \right\}}$$

which equals the logarithmic mean overall concentration difference.

TYPES OF EQUIPMENT. Air-stripper types can consist of spray chambers, packed towers, and tray towers.

Spray Chambers. A spray chamber is simply a device where the large liquid surface area required for efficient stripping is supplied by spraying the liquid phase into a chamber in which air flows countercurrent to the sprayed liquid.

Tray Towers. These are similar in design to traditional bubble cap or sieve tray distillation towers. Each tray represents a transient reservoir for liquid as it cascades from tray to tray in its journey from the top to the bottom of the column. Air typically flows countercurrent to the liquid.

Packed Towers. Packed towers generate large liquid surface areas by allowing the liquid to flow from top to bottom in the tower in a thin film on the surface of "dumped," "stacked," or "structured" packings. Dumped packings take on a variety of unusual "snowflake structures." Stacked packings are individual packings, placed in a tower in an organized manner. Structured packings are modular, self-supporting media that are placed in the tower in large units.

Air strippers, packing, and auxiliary equipment are fabricated out of standard materials. Packings are of stainless steel, polyethylene, PVC, and ceramic. Tower shells have been fabricated from carbon and stainless steel, aluminum, and fiberglass reinforced plastic (FRP). The latter seems to be found more on small-diameter columns for which FRP is well-suited. Large diameter and/or tall columns could require use of metal shells.

RESIDUALS MANAGEMENT. There are three residuals from air-stripping towers that may require management: liquid effluent, air emissions, and biological growth and/or chemical scaling that can develop on the packing.

The liquid effluent can be discharged to a local sewer, to a surface water body, through land application, or through an infiltration basin. The specific disposal method will depend on a number of factors such as local and state regulations, ability or desire of the wastewater treatment facility to accept the liquid effluent, and/or site-specific factors such as permeabilities of on-site soils.

The air phase may require further treatment to remove stripped chemicals prior to discharge to the ambient air. Treatment for removal of VOCs could include activated carbon, catalytic oxidation, or a combination of both.

Biological growth or chemical scale removed from the packing should be disposed off-site in most cases. "Environmentally safe" water additives are also now available that inhibit biological growth.

ENVIRONMENTAL CONCERNS. The main environmental concern about the operation of air strippers is air emissions. As discussed earlier, the air discharge may require treatment to reduce VOCs in the discharge to a point where ambient air concentrations will not be a concern.

REGULATORY REQUIREMENTS. A number of permits may be required, including local building permits, air pollution construction and/or operating permits, sanitary wastewater discharge permits, and NPDES or on-site disposal permits. Frequently, consideration of these permits during design will guide system development.

SAFETY ASPECTS. Perhaps the most important safety concern is explosivity. Because many applications will involve chemicals that can create explosive mixtures in air, consideration should be given to the approach to the lower explosive limit (LEL) in the gas phase. This can be calculated during system design. If a potential problem exists, an explosive-vapor meter can be incorporated into the design.

OPERATING RESULTS. The performance of specific systems will vary depending on the actual design used, variation in system parameters, and operation and maintenance. A recent review by Byers showed the data included in Table 6.15.^{24,25}

Dissolved Air Flotation. WASTE CHARACTERIZATION AND TREATABILITY STUDIES. Bench-scale and/or pilot-scale tests can be used to estimate flotation characteristics for waste. Eckenfelder²⁶ suggests using the flotation cell shown in Figure 6.20 and the following procedure:

Table 6.15 Air stripping sizing and performance histories.²⁵

Case	Hydraulic loading (L/m ² ·s)	Packing type ^a	Packed depth (m)	Air water ratio	Influent contaminant concentration (g/L) ^b	Observed removal efficiency (%)
Port Malabar	8.3	structured poly-propylene	3.6	70	TCE/50 <i>trans</i> /50 total/113	99
Tacoma Well 12A	4.2	0.02 m (1") plastic saddle	6.1	300	1,1,2,2 TCA/350	95
Verona wellfield	17.3	0.09 m (3.5") plastic	12.2	20	CHC/40	90
Wurtsmith AFB	5.2	0.01 m (5/8") plastic	8.2	10	TCE/500	86
Schofield Barracks	10.4	p.r.	25	25		98
Sydney Mine	8.4	0.09 m (3.5") plastic	5.3	60	TCE/29 – 47	98.9
	9.4	t.p.				
		0.09 m (3.5") plastic	7.3	200	aromatics/31 MeCL/503 other CHCs/41	99.8
					TCFM/71	98.6
Savannah River	12.7	0.02 M (1") plastic p.r.	5.5	80	CHC/150 000	99.99
	15.5	0.02 m (1") plastic p.r.	8.5	50	CHC/150 000	99.99
	14.0	0.02 m (1") plastic p.r.	10.3	45	CHC/150 000	99.99
Confidential Site 1	7.7	0.02 m (1") Nor-Pac	4.6	100	TCE/138	98.9
Confidential Site 2	8.1	structured poly-propylene	4.1	420	aromatics/700	99.9
Confidential Site 3	5.2	0.09 m (3.5") plastic	6.1	200	CHC/549 230 benzene/34 000	99.6
Confidential Site 4	13.5	t.p.			PCE/59 – 90	98.6
		0.09 m (3.5") plastic	6.1	50		98.3
		t.p.			TCE/2.5 – 18 <i>trans</i> /10	96 – 98.3
Confidential Site 5	19.0	0.09 m (3.5") plastic	6.1	45	TCE/11 – 77 PCE/50 – 89	91 – 98.2 98 – 99.2
		t.p.				

^a t.p. = tripacks; p.r. = pall-type rings.

^b Key to contaminant abbreviations:

TCE = Trichloroethylene	<i>trans</i> = <i>trans</i> -1,2-dichloroethylene
PCE = Tetrachloroethylene	TCA = Trichloroethane
MeCl = Methylene chloride	CHC = Chlorinated hydrocarbons
TCFM = Trichlorofluoromethane	aromatics = Benzene, toluene, xylenes, ethylbenzene

- Partially fill the calibrated cylinder with waste or flocculated sludge mixture and the pressure chamber with clarified effluent or water.
- Apply compressed air to the pressure chamber to attain the desired pressure.

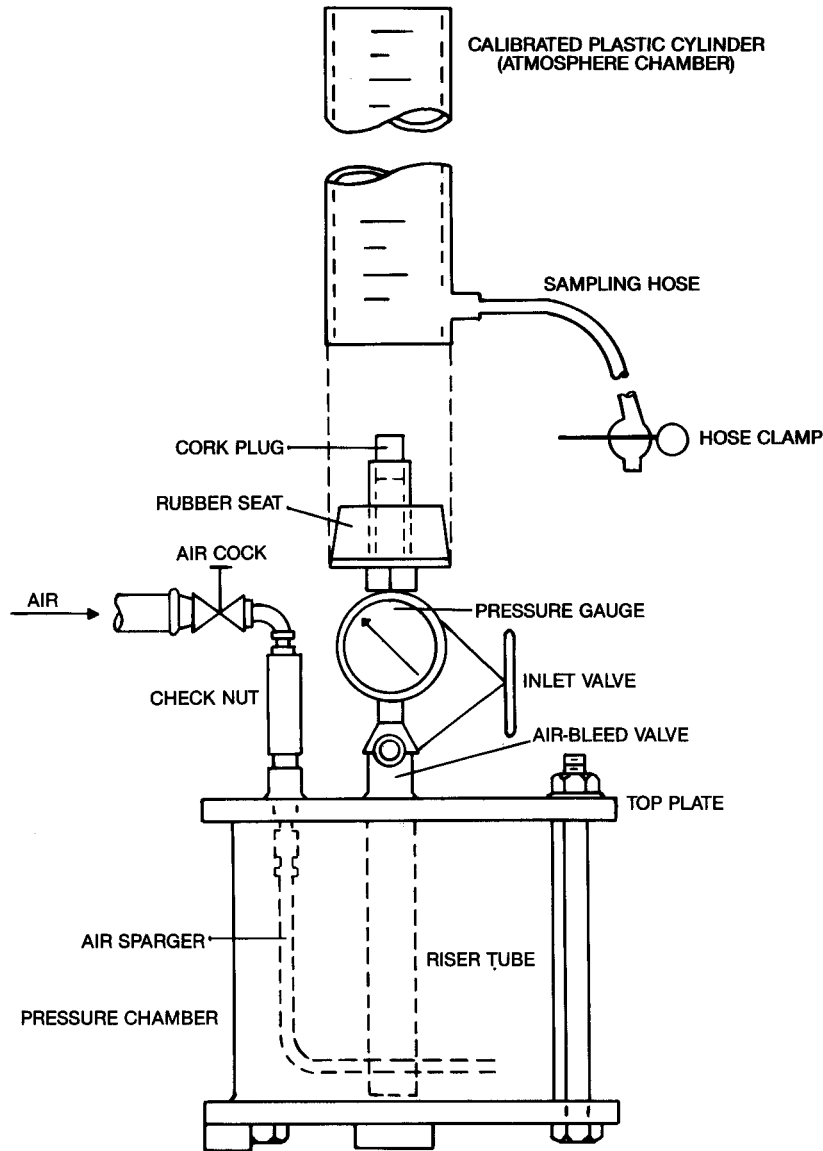


Figure 6.20 Laboratory flotation cell.

- Shake the air-liquid mixture in the pressure chamber for 1 minute and allow it to stand for 3 minutes to attain saturation. Maintain the pressure on the chamber for this period.
- Release a volume of pressurized effluent to the cylinder and mix with the waste sludge. The volume to be released is computed from the desired recycle ratio. The velocity of release through the inlet nozzle should be of such a magnitude as not to shear the suspended solids in the feed mixture but should achieve adequate mixing.

- Measure the rise of the sludge interface with time. Correction must be applied to scale up the height of rise in the test cylinder to the depth of the prototype unit. Determine the rise rate from the data and convert to surface loading rate units.
- After a detention time of 20 minutes, the clarified effluent and the floated sludge are drawn off through a valve in the bottom of the cylinder.
- Relate the effluent quality to the air-to-solids ratio and surface loading rate as shown in Figure 6.21. For sludge thickening applications, relate the float solids concentration to the air-to-solids ratio.

PROCESS DESCRIPTION. Dissolved air flotation (DAF) is a separation process used for removal of suspended solids, oil and grease, and fibrous matter from wastewater and for the thickening of sludges. Materials are removed by floating them to the surface by virtue of a specific gravity differential, the particles being lighter than water. In this process, the waste flow or a portion of the DAF effluent is pressurized to 3.5 – 4.9 kgf/cm² in the presence of sufficient air to approach the saturation concentration of air in water. Either the pressurized liquid mixed with the forward waste flow or the pressurized waste flow is released to atmospheric pressure in the flotation tank, in which microscopic air bubbles (30 – 120 μ m in diameter) are liberated. Suspended solids, oil globules, or sludge flocs are floated by these minute air bubbles, rising to the surface of the flotation unit where they may be skimmed off. Clarified liquid effluent is removed from near the bottom of the flotation tank; a portion of the effluent may be recycled back to the pressurization system. Pressurized recycling is usually used when flocculant sludges are to be clarified.

Foam or froth flotation is a related process in which a significant portion of the separation phenomenon is provided by a difference in surface activities between the liquid and suspended or dissolved materials. Surface-active materials have a tendency to preferentially attach to the air-liquid interfaces of the foams or froths. As the bubbles rise through the column of liquid, the attached material is removed. Wilson and Clarke provide a thorough overview of waste treatment applications.²⁷ Cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc have been removed from solution to appreciable degrees via foam flotation. Surfactants are often added to facilitate the process.

Dispersed- or induced-air flotation is similar to DAF except that the air bubbles are formed by mechanical agitation or by forcing air through porous media. Vacuum flotation is another process variant in which a partial vacuum is applied to the flotation tank to force the dissolved gases to be released from solution as bubbles.

The principal design parameters and variables for DAF systems are the air-to-solids ratio, hydraulic loading rate, recycle flow or ratio, influent con-

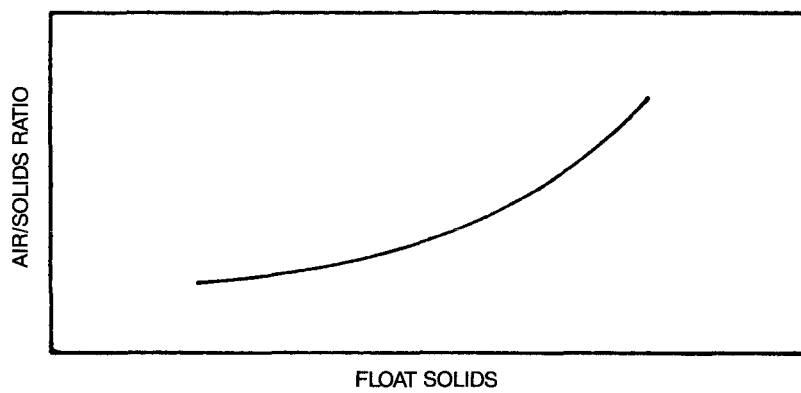
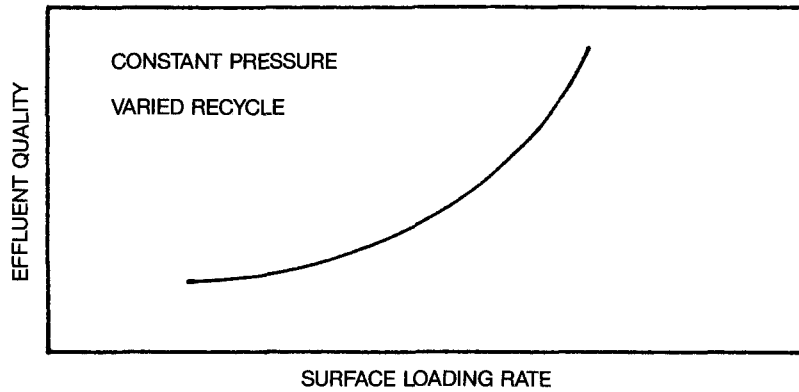
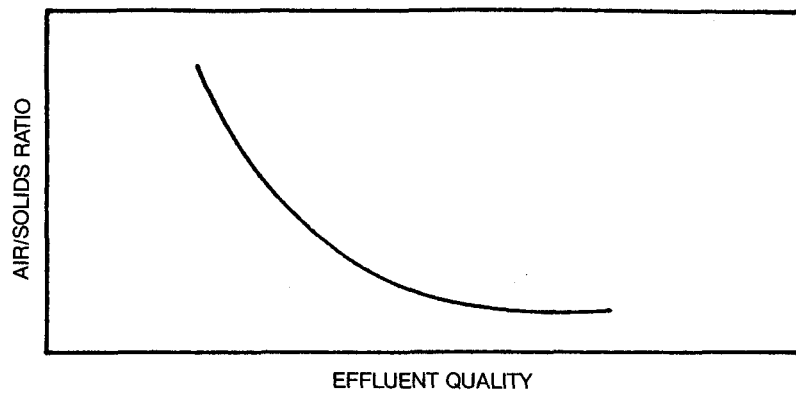


Figure 6.21 Treatability study data interpretation.

centration of suspended matter and/or oil, and waste flow rate. When used for sludge thickening, the solids loading rate is also considered. The flotation process is most successful when light, low density materials are to be removed. Chemical coagulants (usually alum) and polyelectrolytes are often added upstream of the DAF unit to facilitate the removal of collected or emulsified constituents.

Figure 6.22 depicts flotation systems with and without effluent recycling. The principal equipment components in a DAF system are the pressurizing pump, air injector, retention tank, pressure regulating device, and the flotation tank. Air may be added on the suction side of the pump or directly to the retention tank. The hydraulic residence time in the retention tank is typically on the order of 1 to 3 minutes. Flotation tanks are constructed in rectangular and circular shapes, with a skimmer to remove float solids.

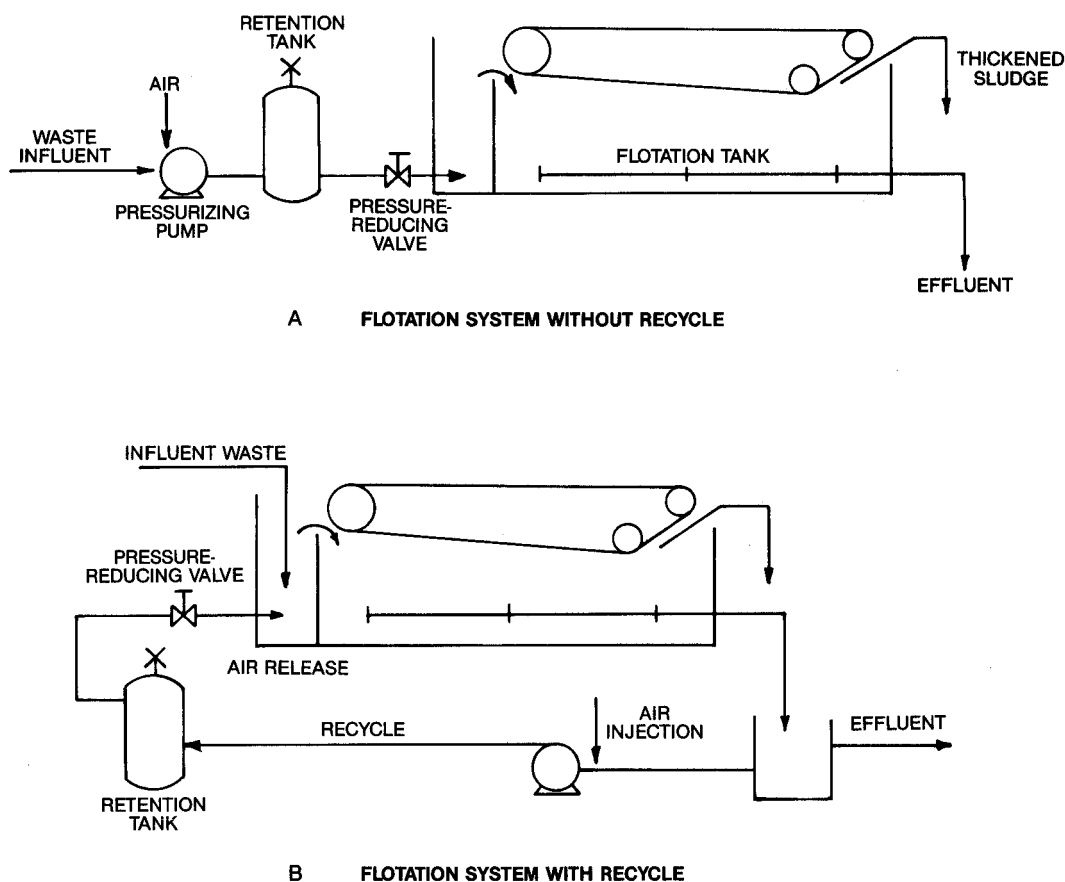


Figure 6.22 Flotation systems.

Pertinent design parameters must be determined on a waste-specific basis. In full-scale systems, successful performance has been obtained by pressuriz-

ing the retention tank to 275.8 – 413.7 kPa, air-to-solids ratios of 0.1 (mass per mass) or less, 10 – 50% recycle, and hydraulic loading rates of 0.7 – 2.7 L/m²•s. Hydraulic retention times in such systems are in the range of 20 to 40 minutes. Float solids concentrations of 1 – 3% by weight are common. For sludge thickening applications, float solids in the 3 – 6% range are attainable, with lower hydraulic loading rates (0.33 – 0.68 L/m²•s) and solids loading rates of 116 – 580 kg/m²•d. Eckenfelder summarized DAF performance for oil removal and suspended solids removal, as shown in Tables 6.16 and 6.17, respectively.

Table 6.16 DAF oil removal performance.²⁶

Influent oil (mg/L)	Effluent oil (mg/L)	Removal (%)	Chemical	Configuration
1930	128	93	Yes	Circular
580	68	88	Yes	Circular
105	26	78	Yes	Rectangular
68	15	75	Yes	Rectangular
170	52	70	No	Circular
125	30	71	Yes	Circular
100	10	90	Yes	Circular
133	15	89	Yes	Circular
94	13	86	Yes	Circular
638	60	91	Yes	Rectangular
153	25	83	Yes	Rectangular
75	13	82	Yes	Rectangular
61	15	75	Yes	Rectangular
360	45	87	Yes	Rectangular

Table 6.17 DAF suspended solids removal performance.²⁶

Type of application	Influent TSS (mg/L)	Effluent TSS (mg/L)	Removal (%)
Domestic wastewater	180	63	65
Domestic wastewater	145	70	52
Domestic wastewater	130	59	55
Domestic wastewater	158	93	41
Domestic wastewater	171	65	62
Domestic wastewater	142	66	53
Domestic wastewater	148	54	64
Domestic wastewater	103	44	57
Domestic wastewater	128	54	58
Domestic wastewater	185	80	57
Domestic wastewater	177	40	74
Domestic wastewater	183	82	56

Table 6.17 DAF suspended solids removal performance (continued).²⁶

Type of application	Influent TSS (mg/L)	Effluent TSS (mg/L)	Removal (%)
Refinery	58	14	76
Refinery	59	32	46
Paper mill	5700	400	93
Aircraft mfg.	70	25	65
Meat packing	4360	170	96
Meat packing	3830	270	93

DESIGN PARAMETERS. The saturation concentration of air in water is directly related to pressure and inversely related to temperature. Considering air solubility and release, the theoretical quantity of air that will be released from solution when the pressure is reduced to 1 atm may be expressed as:

$$C = C_a P_a - C_a \text{ or } C_a (P_a - 1) \quad (14)$$

Where

C = air released at atmospheric pressure at 100% saturation, mg/L;

C_a = air saturation concentration in water at atmospheric pressure, mg/L;

and

P_a = absolute pressure, atm.

The actual quantity of air released will depend on the effectiveness of the retention tank, the mass transfer characteristics of the wastewater, the turbulence at the point of release, and the air solubility in the wastewater. Therefore, a correction is usually applied to determine the actual quantity of air released (f), which is generally in the range of 50 – 90% ($f = 0.50 - 0.90$). Thus, the equation above is modified to

$$C = C_a (f P_a - 1) \quad (15)$$

The absolute pressure, P_a , is related to the gauge pressure, P , as follows:

$$P_a = \frac{P}{14.7} + 1 \quad (16)$$

Where

P_a = absolute pressure, atm; and

P = gauge pressure, kPa.

Therefore, by substituting,

$$C = C_a [f ([P / 14.7] + 1) - 1] \quad (17)$$

There must be sufficient air to float all of the suspended solids and/or oil globules. The air-to-solids ratio may be expressed as

$$A/S = \frac{C}{X_o} \quad (18)$$

Where

A/S = air to solids ratio, kg/kg;

C = air released, mg/L; and

X_o = influent suspended solids or oil, mg/L.

For a system without recycle, the A/S value may be calculated by

$$A/S = (C_a / X_o) [f ([P / 14.7] + 1) - 1] \quad (19)$$

For a system with pressurized recycling, the A/S value is calculated as

$$A/S = (R/Q)(C_a / X_o) [f ([P / 14.7] + 1) - 1] \quad (20)$$

Where

R = pressurized recycle flow, and

Q = influent flow.

Ion Exchange. INTRODUCTION. Ion exchange is the process of removing undesired ions from solution in an equivalent exchange for preferred ions with the aid of a natural or synthetic material called "zeolite". The zeolite is periodically recharged with the preferred ions while flushing previously accumulated undesired ions. A typical example may be the removal of calcium ions (hardness) by sodium zeolite, a common process shown by the reaction



Clays are found to have ion exchange properties although synthetic organic materials have been used for specific applications.

Modern ion exchange resins are primarily synthetic organic materials that contain ionic functional groups to which exchangeable ions are attached. These synthetic resins are structurally stable (they can tolerate a range of temperature and pH conditions), exhibit a high exchange capacity, and can be tailored to show selectivity toward specifications. The exchange reaction is reversible and concentration-dependent, and it is possible to regenerate the exchange resins for reuse. Sorptive (macroporous) resins are also available for removal of organics, and the removal mechanism is one of sorption rather than ion exchange.²⁸

WASTE CHARACTERIZATION AND TREATABILITY STUDIES. The establishment of promotional programs by EPA and the trend towards developing new applications and innovative technologies to hazardous waste treatment have evolved in bench- and full-scale treatability studies to establish certain design guidelines of an existing process. Recent trends and advancements in ion exchange have found applications in the analysis of drinking water, metal concentration, removal from process waters, and radioactive isotope removal from groundwater.

Analytical applications of ion exchange processes have shown development in assessing low level concentrations of organic substances known to have caused mutation. Amerlite XAD resins have proven successful in concentrating and testing the water samples. The resins are simple to use and enable sampling of large quantities of water.

The design and operation of a full-scale ion exchange system were successfully used for the removal of uranium from well water at a radioactively contaminated area.²⁹ Regeneration studies were also conducted by EPA with three different resins. A combination solution consisting of 4% sodium hydroxide and 1 N hydrochloric acid was more effective than a 10% solution of sodium chloride (NaCl), although neither regenerative solution was effective in removing the uranium on the resin.

In considering the applications of an ion-exchange resin for the treatment of a hazardous waste, the process should be reviewed to find the most advantageous process stage to obtain the desired result. Generally, the most favorable stage is that during which the ionic component to be removed is present at its lowest concentration or the desired dilution of the process stream is least objectionable. The following factors are to be considered prior to further design considerations:

- Determine the composition of the process stream to the fullest extent;
- Analyze the process stream, carefully segregating the ionic and non-ionic compounds. Ionic compounds identified should have concentrations determined in milliequivalents per liter;
- Aggressive conditions such as oxidizing and reducing agents should be checked;
- Physical parameters such as temperature, pH, density, and clarity should be noted;
- Flow rates and volumes should be determined in terms of the requirements and consistently expressed in specific units (volume per day, or day);
- Anticipated changes in the waste stream should be specified. This change may be in terms of purity obtained, percent of the component recovered, or maximum volumes; and

- The source of the regenerant chemicals, capital limitations, and space requirements for the installation of the system should also be stipulated.

Chemical differences between the components of the system are then examined to determine the basis for practical ion-exchange separation. Major bases for separation may be summarized as follows:

- Segregation of ionized and non-ionized solutes as one is subject to change and the other is not;
- Cationic components in the system are subject to exchange, without affecting the composition of the anionic components and vice versa; and
- It should be remembered that the separation process in either of the above cases is dependent on the nature of the ion-exchange reaction.

Estimating process limitations is possible when proposed processes involve common ions. An ion-exchange reaction can be written from equilibrium calculations. The data needed are the compositions of the influent and/or regenerant solutions and some knowledge of the selectivity coefficient in the system. An estimate of the order of magnitude is sufficient in many cases to give useful solutions. If these limits fail, the process may be discarded from further evaluation.

Three types of equilibrium-controlled process limits may be estimated if approximate selectivity coefficients are available:

- Maximum capacity,
- Maximum degree of regeneration, and
- Initial leakage.

Breakthrough curves are generally constructed for exchanges. The equilibrium capacity is the maximum number of equivalents of the desired ion that can be removed from solution for a specified volume of the resin. When the influent contains only one species of an ion, the resin could be converted to that form. In such a situation the equilibrium capacity is equal to the total capacity.

The presence of two or more species of ions in the solution, passing through the resin until the composition of the effluent is the same as the influent, will then be equal to the influent. The estimated equilibrium concentration, in this case, can be calculated from the solution composition when an estimation of the selectivity coefficient is available. The equilibrium capacity for the more tightly held counter ion will be the product of the fraction of the resin sites occupied at equilibrium by the total capacity of the resin.

In practice, the equilibrium capacity can generally be realized. Influent ions will appear in the effluent before equilibrium is reached and the run will normally be stopped. Also, if the equilibrium capacity is unfavorable, it may be impractical to approach the equilibrium value due to the inherent inefficiency of a nonsharpening front. Because the use of an equilibrium expression requires estimation of a separation factor for the exchange process, this indicates the nature of the exchange front, providing a clear estimate of the occurrence of the exchange front.

When design considerations and system sizing are incorporated, equipment design should consider

- The structural material that should be used for the design of the tank;
- Material considerations for ancillary equipment and piping; and
- Regulatory considerations related to the design, installation, and operation procedures.

Equipment design consists of a steel shell holding the ion exchange bed, provided with piping and valves to permit the essential operation of softening, back-washing, brining, and rinsing. Instrumentation may be provided to help the operator determine resin exhaustion of the bed and removal for regeneration. Care should be taken to detect exhaustion in the earlier stages to avoid complete reduction in effluent quality beyond the acceptable guidelines and limitations.

Generally, sodium zeolite systems use a meter for measuring water flow by the installation of an alarm so that when the volume, measured in liters corresponding to the bed has been reached, the system operator is forewarned of the need to regenerate.

PROCESS DESCRIPTION. Generally, exchangers or resins (zeolites) find applications mostly in water conditioning. These are skeletonlike structures having many exchange sites. The skeleton, usually made of synthetic material, is electrically charged to adsorb ions of opposite charge.

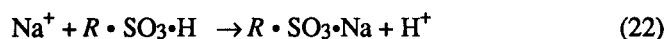
Two types of exchangers are generally available, cation exchangers and anion exchangers. Resins that carry negatively charged sites are “positive” and are called cation-exchange resins. Resins carrying positively charged sites are “negative” and are called anion-exchange resins.

Resins are in the form of beads, having an approximate size of 20 – 40 mesh. The material is porous, permeable, and capable of accommodating the exchange process to take place entirely within the resin. The capacity of the resin is expressed in normality, milliequivalents per milliliter (meq/ml), or milliequivalents per dry gram.

Most commercially used resins are synthetic plastic materials such as copolymers of styrene and divinyl benzene.³⁰ In order to produce cation-

exchange resins, the plastic or resin material is reacted with sulfuric acid, sulfonic groups attaching to each of the sites to produce a strong exchange site.

The following is a typical reaction in a cation exchange process:



in which R is the resin structure. It is also conventional to express the above equation by replacing the active group ($-\text{SO}_3\text{H}$) and the total exchange molecule by the letter Z for zeolite. The above equation may be rewritten as



where Z is considered the divalent cation exchange unit. As shown in the above equations, the sodium ions are replaced by hydrogen and the process is called the hydrogen cycle operation. Once the resin is depleted or exhausted, it may be regenerated by an acid wash using HCl as shown below.



Cation exchange resins, used in water purification, remove hardness with a Na^+ exchanger, iron removal, and nickel recovery from plating wastes.

Selectivity differs with increased concentrations. For example, in the sodium cycle, the exchanger has preference for Ca^{+2} over Na^+ at 1000 mg/L, but its preference is Na^+ over Ca^{+2} for concentrations greater than 100 000 mg/L.²⁸

Cation-exchange resins are the most widely used in the chemical processing industry and have found their applications in water purification processes during the past decade. In the recent past, synthetic resins replaced natural zeolites in most processing operations. Attention had also focused on the development of synthetic resins, more towards the alumino-phosphate chemistry than the alumino-silicate chemistry, for applications in catalysis, separation, purification, and ion exchange in the petroleum and petrochemical industries.³¹

The ion-exchange process is proven to recover chromates and chromate-laden wastewaters through the use of anion-exchange resins at acidic pH ranges.³ In the recent past, a great deal of attention has been focused on XAD-2, XAD-4, XAD-7, and XAD-8 resins. These resins have been used to concentrate organics of mutagenic potential for drinking water.³² Potential uses and applications of these and other resins have not been extensively applied to the treatment of hazardous wastes in the United States, although applications have been found in foreign industries.

Ion exchange in wastewater treatment involves removing a broad range of ionic species from water, including

- All metallic elements when present as soluble species, either anionic or cationic;
- Inorganic anions such as halides, sulfates, nitrates, and cyanides;
- Organic acids such as carboxylics, sulfonics, and some phenols at a pH sufficiently alkaline to form the ions; and
- Organic amines when the solution acidity is sufficiently acid to form the corresponding acid salt.³³

Sorptive resins can remove a wide range of polar and nonpolar organics. A practical upper concentration limit is about 2500 – 4000 mg/L. A highly concentrated waste stream results in rapid exhaustion of the resin and high regeneration costs. Hence, suspended solids in the feed stream should have a concentration less than 50 mg/L in order to prevent plugging of the resins. Also waste streams must be free of oxidants.³³

Applications of ion-exchange resins have also included full-scale design and operation of an ion-exchange system, used for the removal of uranium from groundwater.²⁹ This was followed by the regeneration of exchange resins that was conducted during a U.S. EPA study, using three different resins. Combination solutions used consisted of 4% sodium hydroxide and 1 N hydrochloric acid, which proved to be more effective than a 10% solution of sodium chloride (NaCl), although neither regenerative solution was effective in removing the uranium on the resin.

DESIGN PARAMETERS. Specific ion-exchange and sorptive resin systems must be designed on a case-by-case basis. The following are the three major operating models:

- Fixed-bed concurrent systems,
- Fixed-bed countercurrent systems, and
- Continuous countercurrent systems.

Fixed-bed countercurrent systems are the most widely used. Continuous countercurrent systems are suitable for high flows. Demineralization, which is the complete removal of cations and anions, can be accomplished by using the hydrogen form of a cation-exchange resin and the hydroxide form of an anion-exchange resin. For the removal of organics and inorganics, a combination adsorptive/demineralization system can be used. In this system, lead beds carry sorptive resins that serve as organic scavengers, with the end beds containing anion- and cation-exchange resins. The use of different types of adsorptive resins (polar and nonpolar) permits removal of a broad spectrum of organics.

Ion exchange is an established technology applied to the removal of heavy metals and hazardous anions from dilute solutions. Also, when the feed waste characteristics vary in composition, the technology is expected to perform

well for these applications, provided the system's effluent is continually monitored in order to determine when the resin bed exhaustion has occurred. As mentioned previously, the reliability of ion exchange depends heavily on the presence of suspended solids. The use of sorptive resins is relatively new, and reliability under various conditions is not well known.

Ion exchange systems are commercially available from several vendors. The units are relatively compact and are considerably efficient. Startup and shutdown operations of most systems available can be accomplished easily and quickly.³⁴ These features allow for the convenient use of ion-exchange and sorptive resin systems in mobile treatment systems.

Exchange columns can be operated manually or automatically. However, manual operation is preferred and better-suited for applications at hazardous waste sites because of the diverse characteristics of the wastes encountered. In a manually operated system, a skilled operator can decide when to control the system, (stop the service cycle and begin the backwash cycle).³⁴ A change in operating procedures for most hazardous waste treatment processes is foreseen in light of the revolutionary introduction of expert systems for environmental applications.

The use of several ion-exchange columns at a site can provide considerable flexibility in operating procedures and cycles. As described previously, various resin types can be used to remove anions, cations, and organics. Columns can be arranged in series to increase service life between regeneration of the exchange bed or in parallel for maximum hydraulic capacity. The piping arrangement designed generally allows for one or more beds to be taken out of regeneration while the other columns remain in service.³⁴

Consideration must be given to the disposal of the contaminated ion-exchange regeneration solution. Another important operational consideration involves the selection of regeneration chemicals to ensure the compatibility of the regenerating chemical with the groundwater being treated. For example, the use of nitric acid to regenerate an ion-exchange column containing ammonium ions would result in the formation of ammonium nitrate, a potentially explosive compound.

Other Treatment Processes. OIL/WATER SEPARATION. Oil/water separation is possible when the force of gravity is used to separate two or more substances with different densities (oil and water). Liquid/liquid separation occurs when the liquid mix is allowed to settle. Thus, flow rates in continuous processes must be kept low. The waste flows into a chamber where it is kept quiescent and permitted to settle. The floating oil is skimmed off the top with an oil skimmer while the water or effluent flows out of the lower portion of the chamber. Acids may be used to break an oil/water emulsion and enhance the removal of the oil.

The effectiveness of the separation process can be influenced by the flow rate, pH, and temperature of the waste stream. Separation constitutes a

pretreatment process step in a unit such as an oil/water separator in situations where the oil skimmings require further treatment.

CENTRIFUGATION. Centrifugation is a physical separation process in which the components of an aqueous mixture are separated, based on their relative density, by rapidly rotating the mixture in a vessel. Solid particles that are denser than the fluid medium are deposited farthest from the axis of rotation, while the liquid supernatant is deposited near the axis. Centripetal forces, similar to gravitational forces, are created during centrifugation, creating rotational forces that are much greater. The magnitude of these forces depends on the diameter and rotational speed of the centrifuge.

This treatment in the wastewater process is limited to the physical separation of suspended solids from the waste stream, as in dewatering sludges (including metal-bearing sludges), separating oils from water, and clarification of viscous gums and resins. The use of centrifuges is more suitable than vacuum filters for wastestreams with the sludge types mentioned above.

Disc-type centrifuges can be used to separate three-component mixtures (oil, water, and solids). Centrifuges often cannot be used for clarification because they may fail to remove less dense solids and those which are small enough to remain in suspension. Recovery and removal efficiencies of this process are generally enhanced by a paper or cloth filter installed in a centrifuge.

HEAVY MEDIA SEPARATION. Heavy media separation is a process applied to separating two solid materials that have significantly different absolute densities. The mixed solids to be separated are placed into a fluid whose specific gravity is chosen (or adjusted) so that the lighter solid floats, while the heavier solid sinks. Usually the separating fluid, a heavier media, is a suspension of magnetite in water. The specific gravity of the fluid is thus adjustable by varying the amount of magnetite powder used. Magnetite may then be recovered magnetically from rinsewaters and spills. The heavy media may then be reused.

This type of separation is readily used for separating two insoluble solids having different densities. Limitations of this process are

- The possibility of dissolving solids and deterioration of the heavy media,
- The presence of solids of similar density to those whose separation is desired, and
- The inability to cost-effectively separate magnetic materials (because of the need to recover magnetite).

This process is commonly used in the mining industry to separate ores from tailings.

EVAPORATION. Evaporation is the physical separation of a liquid from a dissolved or suspended solid by the application of energy to volatilize the liquid. In hazardous waste treatment, evaporation may be used to isolate the hazardous material in one of the two phases, simplifying subsequent treatment. If the hazardous material is in the volatilized phase, the process is usually called "stripping." (See the Air Stripping section.)

Evaporation can be applied to any mixture of liquids and nonvolatile solids, provided the liquid is volatile enough to evaporate under reasonable heating or vacuum conditions (both the liquid and the solid should be stable under those conditions). If the liquid is water, evaporation can be carried out in a large pond provided with solar energy. Evaporation of aqueous wastes can also be performed in a closed unit in which energy is supplied by steam and the resulting water vapor condensed for possible reuse. Energy requirements are usually minimized by applying techniques such as vapor recompression or multiple-effect evaporators. Evaporation is applied in cases where the waste solvent is contaminated with nonvolatile impurities such as oil, grease, paint solids, or polymeric resins. Mechanically agitated evaporators or wiped-thin film evaporators are used. The solvent is evaporated and recovered for reuse. The residue is the bottom stream, typically containing 30 – 50% solids.

Steam stripping uses steam to evaporate volatile organics from aqueous wastes. Steam stripping is essentially a continuous fractional distillation process carried out in a packed or tray tower. Clean steam, rather than reboiled bottoms, provides direct heat to the column in which gas flows from the bottom to the top of the tower. The resulting residuals are contaminated steam condensates, recovered solvents, and stripped effluents. The organic vapors and the raffinate are sent through a condenser in preparation for further purification. The bottoms will require further consideration as well. Possible posttreatments may include incineration, carbon adsorption, and land disposal.

Steam stripping is used to treat aqueous wastes contaminated with chlorinated hydrocarbons, aromatics such as xylenes, ketones such as acetone or MEK, alcohols such as methanol, and high boiling point chlorinated aromatics such as pentachlorophenol. Steam stripping will treat less volatile and more soluble wastes than will air stripping and can handle a wide concentration range (from less than 100 mg/L to about 10% organics). The steam-stripping process requires some type of air pollution control mechanism in order to eliminate toxic emissions resulting from stripping operations.

DISTILLATION. Distillation is a process of evaporation, followed by condensation, whereby separation of volatile compounds can be optimized by controlling temperatures and pressures of both the evaporation chamber and the condenser chamber.

Distillation separates miscible organic liquids for solvent reclamation and applicable organic liquids for waste volume reduction. The resulting residuals are generally still-bottoms (often containing toxic metals from ink and paint pigments) and intermediate distillate cuts.

Two major types of distillation processes are currently used are batch distillation and continuous fractional distillation.

Distillation is used to separate liquid organic wastes, primarily spent solvents, for full or partial recovery and reuse. Both halogenated and nonhalogenated solvents can be recovered via distillation. Liquids to be separated must have different volatilization limits or volatilities. Distillation for recovery can be limited by the presence of either volatile or thermally reactive suspended solids. If constituents in the input waste streams can form an "azeotrope" (a specific mixture of liquids exhibiting a maximum or minimum boiling point with the individual constituents), the energy cost of breaking this azeotrope can limit the application of this process.

Batch distillation in a heated still pot with condensation of the overhead vapors is easily controlled and flexible but cannot achieve the high-product purity typical of continuous fractional distillation. Small packaged batch stills, treating one drum per day or less, are becoming popular for on-site recovery of solvents. Continuous fractional distillation is accomplished in tray columns or packed towers ranging up to 12.2 m in diameter and 61 m high. Each distiller is equipped with a reboiler, a condenser, and an accumulator. The capacity of a distillation unit is a direct function of the waste being processed, purity requirements, reflux ratio, and heat input.

Fractional distillation is not applicable for liquids with high viscosity at high temperature, liquids with a high-solids concentration, and polyurethanes and inorganics.

SOIL WASHING. Soil washing is an *in situ* extraction process whereby inorganic or organic compounds are flushed/removed from soils by passing extractant solvents through the soils, using an injection/recirculation process. These solvents include water, water surfactant mixtures, acids or bases (for inorganics), chelating agents, and oxidizing and/or reducing agents. Soil washing consists of similar treatments, but the soil is excavated and treated at the surface in a soil washer.

At the present time, soil washing is a widely used process in the *in situ* treatment of contaminated hazardous waste soils. Soil washing fluids must have good extraction coefficients, low volatility and toxicity, be safe and easy to handle, and be recoverable/recyclable. This technology is promising for extraction of heavy metals from soils, although problems are likely in dry or organic-rich soils.

Surfactants can be used to extract hydrophobic organisms. Soil characteristics such as type and uniformity are important. Certain surfactants, when tested for *in situ* extraction, clogged soil pores and precluded further washing.

CHELATION. A chelating molecule contains atoms that can form ligands with metal ions. If the number of such atoms in the molecule are sufficient and if the final molecular shape is such that the metal atom is essentially surrounded, then the metal will not be able to form ionic salts that can precipitate out. Thus, chelation is used to keep metals in solution and aid in dissolution for subsequent transport and removal using soil-washing technology. Chelating chemicals can be chosen for their affinity to particular metals (EDTA and calcium). The presence of fats and oils can interfere with the chelation process.

LIQUID/LIQUID EXTRACTION. Two liquids that are well-mixed or are mutually soluble may be separated by liquid/liquid extraction. The process requires that a third liquid be added to the original mix. This third liquid must be a solvent for one of the original components but must be insoluble in and immiscible with the other. The final solvent stream can be subsequently separated by distillation or by chemically extracting the solvent captured for reuse.

Complete separation is rarely achieved, so that some form of posttreatment is required for each separated stream. To effectively recover solvent and solute from the process, other treatment processes are needed (distillation or stripping).

SUPERCRITICAL EXTRACTION. At certain combinations of temperature and pressure, fluids reach their critical point beyond which their solvent properties are greatly enhanced. For instance, supercritical water is an excellent nonpolar solvent in which most organics are readily soluble. These properties make extraction rapid and efficient by using a distillation process or any conventional solvent extraction method. Supercritical carbon dioxide, applied to the extraction of hazardous organics from aqueous streams, is being investigated.

This technology, demonstrated on a laboratory scale, is potentially useful to extract hazardous waste from aqueous streams. Specific applicability and limitations of this technology have to be determined.

ELECTRODIALYSIS. Electrodialysis concentrates or separates ionic species contained in a water solution. In electrodialysis, a water solution is passed through alternately placed cation- and anion-permeable membranes. Electrical potential is applied across the membrane to provide the motive force for ion migration. These ion-selective membranes are thin sheets of ion-exchange resins, reinforced by a synthetic fiber backing.

The process is well-established for purifying saline water and recovering metal salts from plating rinse operations. Electrodialysis units are being marketed to reclaim metals of value from rinse streams. Such units are

mobile when skid-mounted and are equipped with flexible piping and electrical connections.

Although the processes described above provide the basis for removal and treatment, situations may generally result in using a combination of the above processes to form a treatment process train for the desired conditions and effective removal of specific hazardous constituents from the waste stream.

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Chapter 7

Chemical Treatment of Hazardous Wastes

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*I*NTRODUCTION

The application of chemicals for hazardous waste treatment remains the backbone of the applicable treatment processes. In many cases, the application of appropriate chemicals is essential for successful biological and physical treatment. The use of chemicals to adjust pH or enhance precipitation are examples of simple chemical treatment.

Chemical treatment can be applied at the generator's site; at an off-site treatment, storage, and disposal facility (TSDF); or at the point of disposal. Generally, chemical treatment should be performed at the generator's site so that any necessary transportation can be performed with minimum risk to human health and the environment. An example of this would be neutralization of a waste stream so that strong acids or caustics need not be transported

on public roads. Frequently, however, economics or other situations preclude high levels of treatment to a waste stream prior to its receipt at a TSDF or disposal site.

WASTE CHARACTERIZATION AND TREATABILITY STUDIES

Characterization of the waste stream is essential for protection of workers, treatment facilities, and the environment from an inappropriate combination of chemical compounds. Formation of explosive or toxic mixtures is always a potential result of most chemical reactions. This is particularly true of waste streams that can no longer be counted on to react in the predictable manner of virgin chemicals of definite constituents and concentration. Care must be taken to ensure that representative samples are obtained and that a wide range of analyses are performed to provide a true picture of the waste constituents.

Many chemical treatment process selections are clear cut, and the end result of treatment is identifiable within a short period of time. However, more time may be required to evaluate complete chemical treatment processes such as solvent extraction. Also, many processes can be tested and demonstrated by bench-scale study. Some chemical reactions must be tested at larger, pilot-scale studies so that sufficient quantities of product and byproduct (including off-gases) can be evaluated to establish that they are of less environmental risk than the original waste.

Factors to be considered in designing the bench-scale study include the following:

- The general state-of-the-art knowledge of the proposed treatment process. Well-established treatment processes need not be demonstrated on a large scale.
- The perceived hazards of the proposed treatment process including explosiveness and toxic byproducts.
- The estimated unit cost of the proposed treatment. Alternative chemicals or even other waste products can be readily and economically evaluated at bench or pilot scale.

TREATMENT TECHNOLOGY

Chemical treatment processes identified in this chapter include the following:

- pH adjustment,

- Oxidation,
- Chemical precipitation, and
- Stabilization and solidification.

A wide range of chemicals are applied in these processes, ranging from common material such as lime and portland cement to less commonly applied chemicals such as hydrogen peroxide and ozone. Generally, more than one chemical will serve the intended purpose. Consequently, other factors will be involved in selection of a chemical. These factors include

- Initial cost of chemical procurement,
- Safety of chemical handling and storage, and
- Quantity and characteristics of process byproducts.

Chemical treatment requires adequate mixing to bring sufficient chemical into intimate contact with the waste stream constituents for a sufficient time to enable completion of the chemical reactions. The required chemicals must be capable of being safely transported to and stored on the site. Any residual treatment chemicals must be capable of being safely disposed of at a reasonable cost.

Mixing of the chemicals and the waste streams may take many forms, based on the phase of the treatment chemical and the waste stream. Aspirators may be appropriate for mixing a gaseous treatment chemical with a liquid waste, while a pug mill may be an appropriate device for mixing a stabilizing liquid or dry chemical with a granular waste.

Sufficient real time must be provided for completion of the chemical reaction. Loss of reaction time by short circuiting in most mixing devices must be provided for in design considerations. Once the chemical and waste have been adequately mixed together, it is likely that another vessel will be required to more economically provide the necessary reaction time.

Key design factors include

- Control and monitoring,
- Selection of materials for construction,
- Personnel safety, and
- Environmental protection.

Assurance that the chemical reaction has gone to completion is essential. The methods and equipment by which this is determined should be part of the design. Difficulty in monitoring the process may require that a treatment process be carried out on a batch basis rather than continuous flow. Also, the need for reprocessing must be taken into account.

Control and monitoring equipment, testing, and procedures must be appropriate for the reaction environment. Analytical procedures or truly surrogate

analyses, appropriate for the reaction site, must be performed regularly to ensure appropriate treatment. Preferably the test should be to confirm that the reaction has been completed (closed loop) rather than predicting that the dosage will be adequate (feed forward).

Many of the waste streams and chemicals will have damaging effects on common materials of construction such as concrete, carbon steel, and polyvinyl chloride. Careful selection of materials for construction of storage, reaction, and transport vessels, as well as piping, is necessary for the longevity of the units, and for operator safety. This selection must be chemical specific. For example certain types of stainless steel would be appropriate for ozonized gas but inappropriate for wastes with high chloride levels. Complicating factors in material selection include multicontaminant waste streams, temperature, and the effect of erosion.

Personnel involved in treatment activities must be protected from the unique features of the chemical treatment processes. Guidance can be taken from the chemical industry. However, many of the situations are unique to the hazardous waste management industry. Site remediation activities would likely make use of mobile treatment units erected on-site on a temporary basis. In these situations, there may be a temptation to proceed without safety facilities or equipment which would only be used for a short time or which had not yet been delivered to the site. At TSDFs, receipt of unfamiliar waste streams may require additional worker training and modified monitoring programs. In all cases, comprehensive safety plans must be aggressively applied by trained professionals.

Chemical treatment of an environmental pollutant should not result in the escape of pollutants to the environment. Spills, leaks, overflows, and other results causing displacement of chemical or waste streams should be provided for during site preparation, containment construction, and provision of emergency equipment. Handling of waste material such as dust, vapors, and fumes should be provided for by hoods, recovery systems, or treatment units such as scrubbers.

pH ADJUSTMENT. Adjustment of the pH of a waste stream is a process that is common to many other treatment processes sensitive to pH levels. pH adjustment may be the only treatment required to eliminate the hazardous nature of the waste stream.

Chemical treatment to adjust pH involves the application of acidic chemicals to lower the pH of caustic streams and caustic chemicals to raise the pH of acidic waste streams. A carefully designed and operated system is capable of achieving any desired pH level. However, the range of pH required should be realistically established in the interest of economic facility construction, practical operation, and maintenance.

Either virgin chemicals or another waste stream may be used for pH adjustment depending on the specific requirements of the reaction. Chemi-

cals commonly used to increase pH are pebble lime, hydrated lime, and sodium hydroxide. Chemicals used to lower pH include hydrochloric acid and sulfuric acid. Table 7.1 provides information on chemicals commonly used for pH adjustment. Examples of waste products used in pH adjustment include carbide lime from the manufacture of acetylene gas and pickle liquor from steel processing.

Table 7.1 Acid and alkali costs for neutralization.

Chemical	Specification	Cost ^a ¢/kg	Equiv. cost ^b \$/kg equiv.
Sulfuric acid (H ₂ SO ₄ [oil of vitriol])	66° Be' – 93%	1.13 ^c	.59
Hydrochloric acid (HCl [muriatic acid])	20° Be' – 32%	.81 ^c	.96
Limestone (CO ₃)	200 mesh; 93%	.18 ^c	.10
Quicklime (CaO)	Lump, 90%	1.11 ^d	.34
		.79 ^c	.25
Hydrated lime (Ca(OH) ₂)	Pulverized, 93%	1.04 ^d	.42
Soda ash (Na ₂ CO ₃)	Light, 50% Na ₂ O	2.42 ^d	1.41
		1.58 ^e	.92
Caustic soda (NaOH)	Dry	7.03 ^d	2.81
	Dry	6.57 ^e	2.63
	50% liquid	3.62 ^a	1.45
Ammonia (NH ₃)	Liquid	4.08 ^c	.69

^a Cost is given in ¢/kg of product as shipped, not including freight, except for 50% liquid caustic, where cost is ¢/kg NaOH.

^b Cost per kg-equivalent is ¢/kg × kg/kg equivalent; kg-mole/valence.

^c Bulk cost in tank cars, tank trucks, or hopper cars.

^d Cost in bags.

^e Cost in drums.

The wastes requiring pH adjustment are most frequently in the liquid phase. Chemicals for pH adjustment may be in the gaseous, liquid, or solid (granular) phase. Carbon dioxide for pH reduction may be generated on site by submerged combustion processes or transported to the site and stored as a liquified gas. Gases are dissolved in the wastewater by applications of static mixers, venturi sections in pipelines, submerged diffusers, and submerged turbines.

Solid material requiring pH adjustment normally must be processed to bring it to a granular form for treatment. Processing may include a wide range of materials handling equipment such as grinders, shredders, and crushers designed to bring the material to a size and condition that it can be brought into intimate contact with liquid or dry treatment chemicals. Hazard-

ous waste gases can be treated with chemicals in liquid form or dissolved in a carrier liquid in scrubbers.

Design considerations for waste treatment by pH adjustment include the following:

- Phase of the waste—gas, liquid, or solid;
- Proposed treatment site—remediation site, TSDF, or disposal site;
- Quantity of waste; and
- Material status—finite quantity or continuing production.

OXIDATION. Chemical oxidation of organic compounds may be attributed to the following reactions:

- Addition of oxygen,
- Withdrawal of hydrogen, and
- Withdrawal of electrons with or without withdrawal of protons.

The following chemicals are commonly used in oxidation reactions:

- Oxygen or air (O_2),
- Ozone (O_3),
- Hydrogen peroxide (H_2O_2),
- Potassium permanganate ($KMnO_4$),
- Chlorine (Cl_2),
- Hypochlorates, and
- Chlorine dioxide (ClO_2).

The choice of chemical is based primarily on economics and materials' handling.

Factors controlling the rate of reaction and the required reaction time include the following:

- Concentration of the reaction,
- Temperature conditions and changes due to the reaction,
- Variations in the composition of the system,
- Role of impurities, and
- pH.

The nonhomogeneity of the waste streams frequently requires that bench-scale testing be performed before full-scale treatment is attempted. The presence of other contaminants in the waste stream must also be addressed in the interest of personnel safety and overall process economics.

The oxidation process is similar to pH adjustment in chemical management and mixing requirements. Reaction times are based on bench-scale testing. Process control is frequently possible in the closed loop mode by redox

measurements or by a sensor measuring the primary contaminant under treatment.

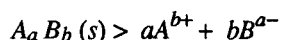
Waste streams frequently treated by oxidation reactions include compounds of the following:

- Iron,
- Manganese,
- Organic matter,
- Cyanide,
- Sulfides,
- Phenol, and
- Benzene.

CHEMICAL PRECIPITATION. Precipitation is applicable to the treatment of aqueous wastes and slurries containing heavy metals. The metals that most commonly require treatment include cadmium, copper, chromium, lead, mercury, nickel, and zinc. Precipitation is based on altering the chemical equilibria of the system by exceeding the solubility product for the species. The water-insoluble precipitate is then removed by standard solids separation processes. Because metals are conservative, precipitation serves as a concentration process rather than a method of destruction. The product formed during the process must therefore be disposed of as a hazardous waste.

Both equilibrium and kinetic considerations are important in precipitation treatment. Equilibrium relationships provide the theoretical basis for calculating the concentration of the metal at equilibrium and the mass of precipitant (sludge) formed as the result of treatment.

The theoretical concentration of heavy metal in solution after precipitation is described by the solubility product, in which a precipitate dissolves in water to form its corresponding ions:



The solubility product is defined as

$$K_{sp} = (A^{b+})^a (B^{a-})^b$$

Where () denotes the activity of the species in solution. Common solubility products are listed in Table 7.2. The solubility product is influenced by solution ionic strength. In general, the solubility of metals increases with ionic strength, hence the use of activity in the K_{sp} equation. In dilute solutions, concentrations can be used in place of activities.

Although equilibrium calculations describe treatment if the reaction proceeds to completion, in most cases kinetics describe the extent of reaction because insufficient time is available to achieve equilibrium. Precipitation

Table 7.2 Solubility product constants.

Substance	Formula	K_{sp}
Aluminum hydroxide	$Al(OH)_3$	5×10^{-32}
Barium carbonate	$BaCO_3$	4.9×10^{-9}
Barium iodate	$Ba(IO_3)_2$	1.57×10^{-9}
Barium oxalate	BaC_2O_4	1.6×10^{-7}
Barium sulfate	$BaSO_4$	1.0×10^{-10}
Cadmium carbonate	$CdCO_3$	2.5×10^{-14}
Cadmium sulfide	CdS	1×10^{-28}
Calcium carbonate	$CaCO_3$	4.8×10^{-9}
Calcium oxalate	CaC_2O_4	1.9×10^{-9}
Calcium sulfate	$CaSO_4$	6.1×10^{-5}
Copper (II) hydroxide	$Cu(OH)_2$	1.5×10^{-19}
Copper (II) sulfide	CuS	8.5×10^{-45}
Copper (I) bromide	$CuBr$	5.9×10^{-9}
Copper (I) chloride	$CuCl$	3.2×10^{-7}
Copper (I) iodide	CuI	1.1×10^{-12}
Copper (I) thiocyanate	$CuSCN$	4×10^{-14}
Iron (III) hydroxide	$Fe(OH)_2$	1.5×10^{-36}
Lanthanum iodate	$La(IO_3)_3$	6×10^{-10}
Lead carbonate	$PbCO_3$	1.6×10^{-13}
Lead chloride	$PbCl_2$	1×10^{-4}
Lead chromate	$PbCrO_4$	1.8×10^{-14}
Lead hydroxide	$Pb(OH)_2$	2.5×10^{-16}
Lead oxalate	PbC_2O_4	3.0×10^{-11}
Lead sulfate	$PbSO_4$	1.9×10^{-6}
Lead sulfide	PbS	7×10^{-26}
Magnesium ammonium phosphate	$MgNH_4PO_4$	2.5×10^{-13}
Magnesium carbonate	$MgCO_3$	1×10^{-13}
Magnesium hydroxide	$Mg(OH)_2$	5.9×10^{-12}
Magnesium oxalate	MgC_2O_4	8.6×10^{-5}
Manganese (II) hydroxide	$Mn(OH)_2$	4×10^{-14}
Manganese (II) sulfide	MnS	1.4×10^{-15}
Silver arsenate	Ag_3AsO_4	1.0×10^{-22}
Silver bromide	$AgBr$	7.7×10^{-13}
Silver carbonate	Ag_2CO_3	8.2×10^{-12}
Silver chloride	$AgCl$	1.82×10^{-10}
Silver chromate	Ag_2CrO_4	1.1×10^{-12}
Silver cyanide	$AgCN$	2×10^{-12}
Silver iodate	$AgIO_3$	3.1×10^{-8}
Silver iodide	AgI	8.3×10^{-17}
Silver oxalate	$Ag_2C_2O_4$	1.1×10^{-11}
Silver sulfide	Ag_2S	1.6×10^{-49}
Silver thiocyanate	$AgSCN$	1.1×10^{-12}
Strontium oxalate	SrC_2O_4	5.6×10^{-8}
Strontium sulfate	$SrSO_4$	2.8×10^{-7}
Thallium (I) chloride	$TlCl$	2×10^{-4}
Thallium (I) sulfide	Tl_2S	1×10^{-22}
Zinc hydroxide	$Zn(OH)_2$	2×10^{-14}
Zinc hydroxide	ZnC_2O_4	7.5×10^{-8}
Zinc sulfide	ZnS	4.5×10^{-24}

occurs in three steps: nucleation, crystal growth, and agglomeration and ripening of the solids.

Precipitation sometimes does not occur in supersaturated solutions, not because of slow rates, but because of the lack of nucleation sites. In such situations, precipitation can be induced by increasing the degree of supersaturation or the addition of a seed of fine particles to the solution.

The effectiveness of precipitation treatment is determined by the factors that affect chemical equilibrium. These include ionic strength, the common ion effect, pH, complexation, and temperature. Ionic strength lowers the activity of the metal in solution thereby increasing its solubility. The common ion effect, i.e., the presence of the same ion in the solution as the precipitant, increases the metal's solubility after precipitation treatment. Complexation may also inhibit precipitation treatment. The presence of some organic ligands binds metals and interferes with their precipitation. Cyanide, an inorganic ligand, is common to many metal waste streams and is highly effective in keeping metals in solution. Temperature is also a variable. Except for the precipitation of metal carbonates, metal solubility increases as a function of temperature.

The practical treatment of metal wastes usually relies on site-specific treatability tests rather than specific solubility product calculations. Although a number of anions can be used to precipitate metals, hydroxide and sulfide are the most common. Both of these anions react with metals producing low metal concentrations after precipitation. Because of the common ion effect, complexation, and kinetic limitations, approximately three times more precipitant is needed. Precipitation reactions are also nonspecific for multivalent cations. Therefore, these are removed from solution with the toxic metal. Suspended and colloidal materials may also be removed by precipitation treatment. As a result, large quantities of sludge are often produced. The sludge volume is also usually greater than what is expected based on theoretical calculations.

Jar tests are the most common method for determining the optimum precipitant and chemical dosages. Design parameters that are determined by jar tests include optimum pH, mixing requirements, settling characteristics, and sludge production. Some materials, especially sulfide precipitates, settle as fine colloidal particles. Settling properties of these precipitates can be improved by the addition of flocculents such as alum or polyelectrolytes.

Precipitation is a relatively simple and well-established technology. The process requires only chemical pumps, meters, mixing tanks, and settling tanks; this equipment is readily available from process equipment manufacturers. The performance and reliability of precipitation depends on the variability and characteristics of the waste being treated.

STABILIZATION AND SOLIDIFICATION. Hazardous waste disposal on land, even in "secure chemical landfills," may lead to serious groundwater

pollution problems. The interest in the development of processes to render these wastes less dangerous before disposal has greatly increased. One process that has received a great deal of attention, primarily because of the Solid and Hazardous Waste Act amendments which bans disposals of liquids on land, is the stabilization and solidification of wastes. In this process, waste sludges are combined with various additives that both chemically bind and physically solidify the hazardous materials, making them less susceptible to leaching. Stabilized and solidified wastes may still leach, but the rate of contaminant leaching should be very low so that the pollutants will disperse harmlessly into the environment.¹

The terms “stabilization” and “solidification” are used here as defined by EPA.² Both stabilization and solidification refer to treatment processes that are designed to accomplish one or more of the following results:

- Improve the handling and physical characteristics of the waste, as in the sorption of free liquids;
- Decrease the surface area of the waste mass across which transfer or loss of contaminants can occur; and
- Limit the solubility of any hazardous constituents of the waste, such as by pH adjustment or sorption phenomena.

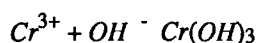
Stabilization techniques are those which limit the solubility or mobility of the contaminants with or without change or improvement in the physical characteristics of the waste. Examples include the addition of lime or sulfide to a metal hydroxide waste to precipitate the metal ions or the addition of a sorbent to an organic waste. Stabilization usually involves adding materials which ensure that the hazardous constituents are maintained in their least mobile or toxic form.

Solidification implies that the beneficial results of treatment are obtained primarily through the production of a solid block of waste material which has high structural integrity—a product often referred to as a “monolith.” The monolith can encompass the entire waste disposal site—called a “monofill”—or be as small as the contents of a steel drum. The contaminants do not necessarily interact chemically with reagents, but are mechanically locked within the solidified matrix. This is called “microencapsulation.” Contaminant loss is limited largely by decreasing the surface area exposed to the environment, thereby minimizing moisture contact and leaching, or isolating the contaminants from environmental influences by microencapsulating the waste particles. Wastes can also be “macroencapsulated,” that is, bonded to or surrounded by an impervious covering.³

Processes. Many stabilization and solidification processes have been developed, including cement-based, lime-based, thermoplastic, organic polymer, encapsulation, glassification and self-cementing techniques.⁴ These

processes vary widely in their applicability to certain waste types, but most are suitable only for primarily inorganic wastes. The more commonly used fixation processes use cement, fly ash or silicates, or combinations of these, to produce pozzolanic reactions resulting in heavy metal binding and conversion of liquids and sludges into solid waste forms.

Cement-based stabilization and solidification is a process in which waste sludges or contaminated soils are mixed with Portland cement. Water in the waste, or additional water added, causes hydration reactions which solidify the waste-cement matrix. Heavy metals in the waste typically react with cement constituents to form hydroxides, silicates, and other relatively insoluble products.



Small amounts of other additives, such as fly ash, clay, sodium silicate or sulfides, may be added to improve the final product. Depending on the amount of cement and other additives used, the final product may vary from a granular, soil-like material to a solid monolith resembling hardened cement. The cement-stabilized mass generally has a high free lime content, buffering it against attack by acidic groundwater. This process is commonly used for stabilization and solidification of plating wastes.

Lime-based processes involve pozzolanic reaction of lime with siliceous and aluminosilicate materials to cementaceous substances. Commonly used pozzolans are fly ash, lime kiln dusts, and blast furnace slag, all of which contain significant amounts of silicates. The resulting reactions are similar to those for cement hydration, although generally slower. The final product is similar to that from cement-based processes.

Thermoplastic stabilization and solidification utilizes a thermoplastic material, such as asphalt or polyethylene, to bind the waste constituents into a solidified mass. Contaminants are physically entrapped (microencapsulated) within the mass, minimizing their potential to leach. These processes have been used for oil- or gasoline-contaminated soils, and may have applications for some electroplating and refinery sludges. Organic polymers have been used in a few cases to complex the waste into a solidified mass. Urea formaldehyde is the most commonly used organic polymer for stabilization and solidification.

Glassification, in which the waste is mixed with molten glass and then allowed to solidify, has been used for radioactive wastes. Recently, *in situ* vitrification processes have been developed, primarily by Battelle Pacific Northwest, for use at hazardous waste sites. *In situ* vitrification consists of inserting electrodes into soils, along with flaked graphite and glass, and applying an electric current. The soil is heated above its melting point and then cooled into a solid, vitrified mass incorporating inorganic contaminants. Organic contaminants are either destroyed by pyrolysis at the elevated

temperatures, or are vaporized and collected by a collection hood and scrubbers.

Macroencapsulation is used to stabilize and solidify wastes in overpack drums. The wastes are typically agglomerated with lime, cement or a polybutadiene binder and then encapsulated with a polyethylene resin overpack drum.

Waste Characterization and Treatability Studies. Wastes to be stabilized and solidified must be characterized before and after treatment. Pretreatment testing is performed to determine basic information on treatability of the waste material. Poststabilization and solidification characterization is needed to ensure that the process has been successful.

Both physical and chemical tests are used to evaluate waste stabilization and solidification processes.³ Physical tests used to evaluate waste stabilization and solidification processes include:

- Index property tests, which provide data that are used to relate general physical characteristics of a material (for example, suspended solids) to process operational parameters (for example, pumpability);
- Density tests, which are used to determine weight to volume relationships of materials;
- Permeability tests, which measure the relative ease with which fluids (water) will pass through a material;
- Strength tests, which provide a means for judging the effectiveness of a stabilization and solidification process under mechanical stresses; and
- Durability tests, which determine how well a material withstands repeated wetting and drying or freezing and thawing cycles.

Specific tests associated with each of these are shown in Table 7.3.

Chemical tests used with stabilization and solidification processes include those for pH, alkalinity, oxidation-reduction potential, total organic carbon,

Table 7.3 Physical testing methods or stabilization solidification.

Test procedure	Reference	Purpose
Index property tests		
Particle size analysis	ASTM D 422-63	To determine the particle size distribution of a material.
Atterberg limits		
Liquid limit	ASTM D4318-84	To define the physical characteristics of a material as a function of its water content.
Plastic limit	ASTM D4318-84	
Plasticity index	ASTM D4318-84	
Moisture content	ASTM D2216-80	To determine the percentage of free water in a material.

Table 7.3 Physical testing methods or stabilization solidification (continued).

Test procedure	Reference	Purpose
Suspended solids	EPA method 209C	To determine the amount of solids that do not settle from a column of liquids.
Paint filter test	EPA method 9095-SW846	To determine the presence of free liquids in a representative sample of bulk or noncontainerized waste.
Density testing		
Bulk density Drive cylinder method	ASTM D2937	To determine the in-place density of soils or soil-like materials.
Bulk density Sand-cone method	ASTM D15556-82	To determine the in-place density of soils or soil-like materials.
Bulk density nuclear methods	ASTM D2022-81	To determine the in-place density of soils or soil-like materials.
Compaction testing		
Moisture density relations of soil- cement mixtures	ASTM D558-82 ASTM D1557	To determine the relation between moisture content and density of a material.
Permeability testing		
Falling head permeability	EPA method 9100-SW846	To measure the rate at which water will pass through a soil-like material.
Strength testing		
Unconfined compressive strength of cohesive soils	ASTM D2166-85	To evaluate how cohesive, soil-like materials behave under mechanical stress.
Unconfined compressive strength of cylindrical concrete specimens	ASTM D1633-84	To evaluate how cement-like materials behave under mechanical stress.
Compressive strength of hydraulic cement mortars	ASTM C109-86 ASTM C109-86	To measure the compressive strength of hydraulic cement.
Flexural strength	ASTM D1635-87	To evaluate a material's ability to withstand loads over a large area.
Cone index	ASTM D3441-79	To evaluate a material's stability and bearing capacity.

Table 7.3 Physical Testing Methods or Stabilization Solidification (continued).

Test procedure	Reference	Purpose
Durability testing		
Freeze-thaw durability	ASTM D560-82	To determine how materials behave or degrade after repeated freeze-thaw cycles.
Wet-dry durability	ASTM D559-57	To determine how materials behave or degrade after repeated wet-dry cycles.

oil and grease, elemental analysis for metals, and analyses for specific organic compounds.⁵

The most important characterization procedure is for contaminant leaching potential. Numerous leaching tests have been developed to test solid wastes, including specific tests for those wastes which have been stabilized and solidified. Table 7.4 lists some of the more common leaching tests. Each of these has its advantages and disadvantages; normally, more than one test is needed to determine the leaching properties of a specific waste.

Table 7.4 Leaching test methods for stabilized/solidified wastes.

Test method	Leaching medium	Number of extraction
EP Tox	0.04 M acetic acid (pH=5.0)	1
TCLP	Acetic acid	1
Cal WET	0.2 M sodium citrate (pH=5.0)	9 or more
MEP	Same as EP Tox, then with synthetic acid rain	9 or more
MWEP	Deionized water	4
Equilibrium leach test	Distilled water	4
Acid neutralization capacity	HNO ₃ solutions of increasing strength	1
Sequential extraction test	0.04 M acetic acid	15
AMS-16.1	Deionized water	12
Dynamic leach test	Deionized water	Varies

The extraction procedure toxicity test (EP Tox) is mandated by EPA as the procedure to classify wastes as hazardous or nonhazardous. It does have limitations though, and can't be used to determine leaching rates or leaching of volatile organics. The toxicity characteristics leaching procedure (TCLP) was later proposed by EPA to replace EP Tox as the criterion for defining hazardous and nonhazardous wastes. It has the advantage of being capable of evaluating leaching of volatile and semivolatile organic compounds. The Cal

WET procedure is used in the state of California. It is similar to TCLP, except that it uses sodium citrate as the leachant, and therefore is a more stringent leach test for some metals. All three of these test procedures use a single extraction of the waste and consequently do not provide leaching rate data.

Many of the remaining leach tests listed in Table 7.4 are dynamic leach tests, in that the leaching solution is periodically replaced with new solution. These tests simulate leaching of a monolithic waste form under nonequilibrium conditions and can often be used to predict flux or leaching rates from the waste. None of the leaching tests will produce results that are directly applicable to leaching behavior in the field. Nevertheless, results from several leach tests or from leach tests combined with physical tests can be used as indicators of field performance.^{3,7} Bench-scale testing is needed to determine proper waste:binder ratios and to evaluate the durability of the finished material.

Processing. The stabilization and solidification process can be used to process newly created wastes for disposal as well as for contaminated soils at hazardous waste sites. Mixing of the waste and binder can be done in a drum or plant process or *in situ* for contaminated soils. It is usually easier, though, to provide proper mixing in a reactor than when solidifying a pit, pond, or lagoon.⁸

To date, very little specialized equipment has been developed for the application of stabilization and solidification processes. Equipment in use today has been adapted from either the building construction or chemical processing industries.⁹ Mixing units similar to those used for mixing concrete are commonly used. Others include pug mills, ribbon blenders, mixers, extruders and screw conveyors. Many of the stabilization and solidification activities at hazardous waste sites have used area mixing. The reagents are mixed directly into the soil or waste using backhoes or screw augers. This method has the benefits of not requiring removal of the waste from the site and of low cost, but mixing is often incomplete and inadequate.

Placement of the stabilized and solidified waste depends on its form. The majority of the waste stabilized and solidified to date has been stabilized and solidified *in situ* and replacement is of no consequence.³ Soil-like materials should be placed in lifts using earth-moving equipment and then compacted. Monolithic materials must be placed before setting occurs.

Proposed Processes. *In situ* vitrification is a process which has recently been developed by Battelle Pacific Northwest.¹⁰ This process uses electrodes placed into contaminated soil and an electrical current that produces temperatures sufficient to melt the soil and pyrolyze most organics present. On cooling, the soil is converted to a monolithic glassy mass.

A number of companies are proposing stabilization and solidification processes that use proprietary reagents which enhance the stabilization of

both organic and inorganic wastes. Other companies are investigating the use of organophilic clays along with cementaceous materials to truly bond organic wastes.¹¹ This technology looks very promising and may extend the use of stabilization and solidification beyond its current primary use as a treatment method for inorganic wastes.

Applications. Stabilization and solidification processes, although in the developmental stage, are already widely used. Stabilization and solidification processes have seen significant use for treating industrial wastes. A 1986 TSDF survey found 107 stabilization and solidification units in operation in the U.S., of which 50 were cement-based and 37 were pozzolanic processes. Approximately 658 000 tons of wastes were being processed annually. These processes are also being used to treat contaminated soils and other wastes at Superfund sites. Approximately 25% of all Superfund sites were using some form of stabilization and solidification in 1988. The EPA SITE program has evaluated six stabilization and solidification processes to date for use at Superfund sites.

Costs. Costs for treatment and disposal using stabilization and solidification processes depend on waste-specific and site-specific conditions. Important factors are the waste's characteristics, type of process, disposal requirements, and other special factors. Table 7.5 gives estimated ranges for stabilization and solidification processing costs for Superfund sites.¹²

Table 7.5 Cost of solidification/stabilization of contaminated soils.

Item	Estimated cost
Mobilization	\$100 000 – 200 000/site
Excavation	\$8 – 38m ³
Processing	\$38 – 76m ³
Disposal	\$76 – 191m ³

Stabilization and solidification technology has been used for over 20 years to treat industrial and radioactive waste. Most recently the technology has received greater interest as a treatment approach for a variety of RCRA hazardous waste, contaminated soils, sludges, and municipal combustion residuals. Examples of EPA RCRA hazardous waste for which stabilization and solidification is being evaluated as a treatment technology include

- Dissolved air flotation (DAF);
- Float from the petroleum refinery industry—K04852 (chromium and lead);
- Wastewater treatment sludges from manufacturing formulation and loading of lead-based initiating compounds—K046 (lead);

- Metal finishing waste—F006 (cadmium, chromium, lead, nickel, and silver); and
- Distillation tar—K022 (chromium and nickel).

Stabilization was applied at a Superfund site in New Jersey with about 2200 cu yd (1682 m³) of contaminated landfill created by the dumping of glazing waste and degreasing agents. After the majority of the degreasing wastes were removed and incinerated, the residual material containing high concentrations of lead were treated by a stabilization process consisting of spreading the wastes in uniform layers, introducing stabilizing agents, homogenizing the waste-additive mixture by mechanical equipment and disposing of the treated material in a second landfill. Tables 7.6 and 7.7 show the typical results of the process.

Table 7.6 EP—toxicity results for lead.

Characteristics	Composite sample					
	I	II	III	IV	V	VI
Untreated						
Total Pb, mg/kg	2400	8000	5600	5800	680	16 000
Leachable Pb, mg/L	11.5	16.5	15.2	16.8	4.9	16.5
Stabilized						
Leachable Pb, mg/L	0.01	0.02	0.02	0.02	0.06	0.03
Standard						
Leachable Pb, mg/L	5.0	5.0	5.0	5.0	5.0	5.0

Table 7.7 Glazing wastes—TCLP results for trichloroethylene (TCE).

Characteristics	Sample	
	I	II
Highest level found on site		
Total TCE, mg/kg	2.7	2.7
Lab samples, spiked, untreated		
Total TCE, mg/kg	10.5	21.7
Leachable TCE, mg/L	0.19	0.91
Lab samples, stabilized		
Leachable TCE, mg/L	0.001	0.001
Standard proposed		
Leachable TCE, mg/L	0.070	0.070

A stabilization and solidification process developed by Hazcon Inc. was recently demonstrated at a former oil reprocessing plant in Douglassville, Pa. Soils at the site were contaminated with both organic and inorganic contaminants including oil and grease, volatile and semivolatile organics, PCBs,

and heavy metals (particularly lead). After excavation, the contaminated soil is screened and fed to a mobile field blending unit consisting of soil and cement holding bins, a chloronan (proprietary nontoxic additives that encapsulate organic molecules, rendering them ineffective in interfering with the solidification process), and blending. Here the waste and pozzolanic material (cement, fly ash, and kiln dust) are added along with chloronan and water to produce a slurry. The slurry is then allowed to harden into a concrete-like mass before disposal. Results of the project are summarized below and in Tables 7.8 and 7.9:

Table 7.8 Chemical properties.

Sample	Leachate concentrations, mg/L					
	Untreated soil			28-day cores		
	VOC ^a	BNA ^b	Lead	VOC ^a	BNA ^b	Lead
1	0.92	ND ^c	1.5	0.38	ND ^c	0.007
2	0.02	1.02	31.8	0.06	1.45	0.005
3	1.03	2.81	17.9	0.72	2.79	0.400
4	5.10	0.01	27.7	0.37	0.10	0.050
5	1.10	0.01	22.4	0.84	0.11	0.011
6	0.06	0.01	52.6	0.11	0.73	0.051

^a VOC — Volatile organic carbon

^b BNA — Base neutral/acid extractable

^c ND — Not determined

Table 7.9 Physical properties.

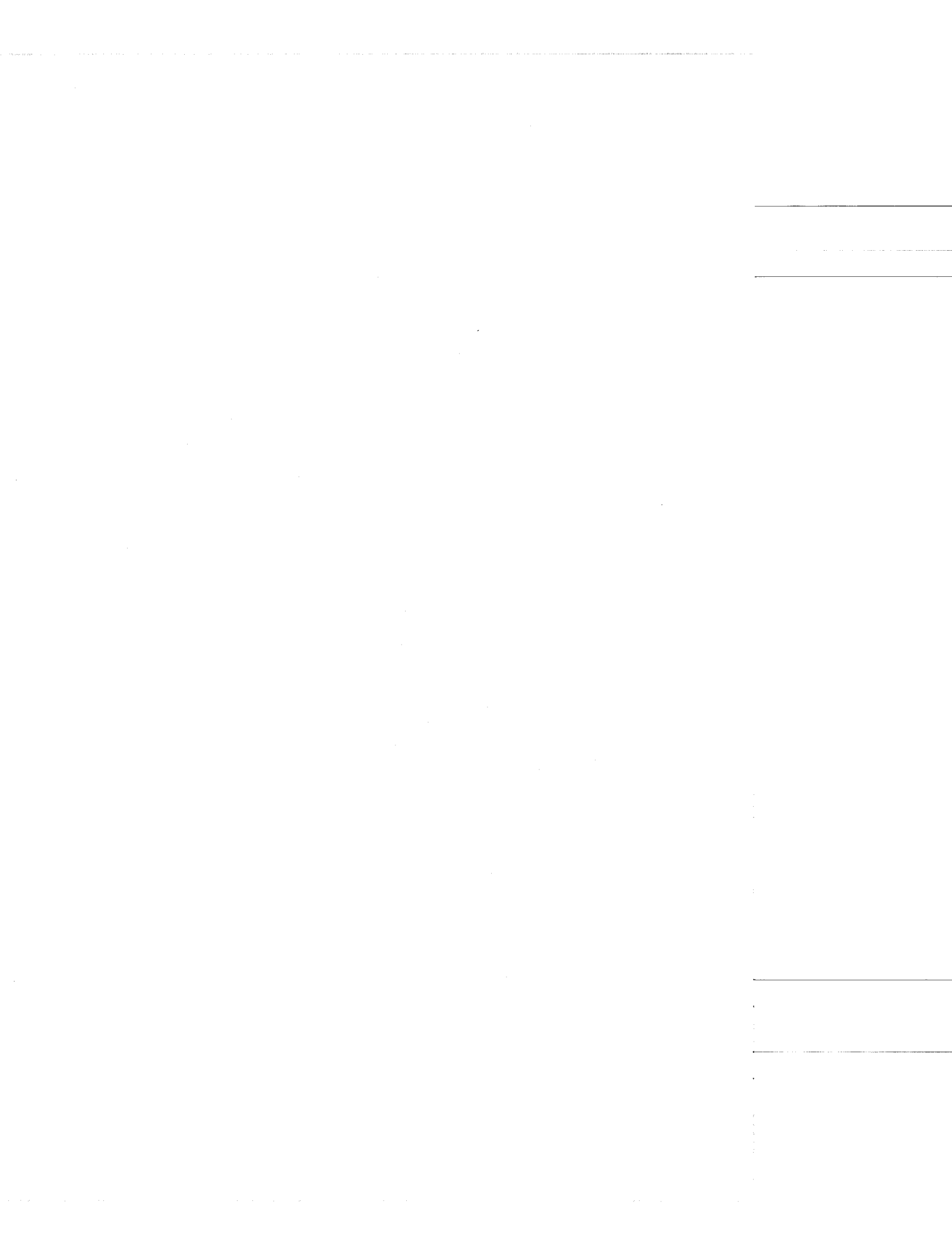
Sample	Untreated soil			28-day cores		
	Oil and grease, percent	Bulk density, g/mL	Permeability, cm/s	Bulk density, g/mL	Permeability, cm/s	UCS, psi
1	1.0	1.23	5.7×10^{-1}	1.95	1.8×10^{-9}	1110
2	16.5	1.40	1.8×10^{-3}	1.61	4.0×10^{-9}	520
3	25.3	1.60	Impermeable	1.51	8.4×10^{-9}	220
4	4.3	1.68	2.0×10^{-2}	1.84	4.5×10^{-9}	940
5	4.5	1.73	7.7×10^{-2}	2.07	5.0×10^{-10}	1570
6	7.8	1.59	1.5×10^{-5}	1.70	2.2×10^{-9}	890

- Volume of the solidified mass was more than double the undisturbed soil.
- Permeabilities after 28 days curing were 10^{-8} to 10^{-9} cm/s.
- Unconfined compressive strength ranged from about 220 to 1570 psi.
- Wet-dry and freeze-thaw weathering tests showed small weight losses (0.5 to 1.5% after 12 cycles).
- Volatile organics found in leachate appeared to be approximately the same in both the untreated and treated soils (less than 1 mg/L).

- Leachate from the solidified soils showed metal levels at or near detection limits, with lead the predominant metal lower by a factor of 500 (from 20 to 50 mg/L in untreated soil to 0.1 mg/L in the treated soil).

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Chapter 8

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INTRODUCTION

Historically only a small percentage of the hazardous waste generated has been disposed of by thermal destruction processes, specifically incineration. However, over the last few years concern over improper disposal practices of the past has resulted in the passage of numerous federal and state laws that closely regulate hazardous waste disposal. These laws combined with the high cost of cleaning sites has greatly increased the interest in thermal disposal.

The more notable and previously lower cost disposal methods of landfill, storage in surface impoundments, and deep well injection are being replaced by waste minimization at the source of generation, recycling, and treatment. Hazardous waste treatment includes physical, chemical, biological treatment, chemical stabilization and solidification, and thermal treatment.

Of the final treatment and disposal technologies properly designed incineration systems are capable of the highest overall degree of destruction and control for the broadest range of hazardous waste streams.¹ Another way of stating this is "Destroy a waste and you are done with it forever. Bury the waste and it may come back to haunt you."²

Research by the U.S. Environmental Protection Agency (EPA) indicates that there is a significant amount of experience with both the design and operation of thermal treatment systems. A large number of commercial systems are already available.

While thermal destruction is recognized by many as providing the highest overall degree of destruction, the EPA has recognized that there is a large amount of public opposition to this type of treatment. In 1985 the EPA determined that the major public concerns about thermal destruction were¹

- Hazardous material spills in storage, treatment, and handling;
- Environmental and health impacts of land-based and ocean facilities;
- Poor site selection processes;
- Distrust of incinerator owners and operators; and
- Inability of government agencies to enforce compliance.

The above study helped the EPA to develop a national strategy for the permitting of thermal destruction facilities.

REGULATIONS GOVERNING THERMAL TREATMENT

PROCESSES Important regulations governing thermal treatment are

- The Resource Conservation and Recovery Act of 1976 (RCRA). This act provided "cradle to grave" provisions for controlling the storage, transport, treatment, and disposal of hazardous waste.

- The Toxic Substances Control Act (TSCA), Section 6(e), in 1979 prohibited the further manufacture of polychlorinated biphenyls (PCBs), established limits on PCB use in commerce, and established regulations for proper disposal.
- The cleanup of uncontrolled waste sites created by the poor disposal practices of the past was provided for in the Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA). This act established a national fund (Superfund) to assist in remedial actions.
- The 1986 Superfund Amendments and Reauthorization Act (SARA) expanded the provisions and funding of the initial CERCLA act.
- The Hazardous and Solid Waste Act of 1984 (HSWA) significantly amended and reauthorized RCRA. The amendments established a strict timeline for restricting untreated hazardous waste from land disposal. By 1990 most wastes will be restricted and pretreatment levels achievable by the best demonstrated available technology (BDAT).

CANDIDATES FOR THERMAL DESTRUCTION A thermal destruction process is defined as “an engineered process using high temperature to thermally destroy organic waste and to reduce the volume of the waste, sometimes with heat recovery to recover some of the energy in the waste.”¹ Even in cases where volume reduction is not significant, the thermal process can be used to eliminate the hazardous or toxic constituent in the waste rendering the waste nonhazardous.

The most appropriate candidate for thermal treatment is a waste with high organic content, which experiences a large volume reduction during treatment, and a high heat of combustion so that little additional fuel is required. Common examples of wastes that are incinerated are

- Fumes from process or other treatment steps. The organic contents of the fumes are destroyed before discharge to the air.
- Liquids generated in processes or other treatment steps.
- Wastewater sludges, normally after dewatering to reduce fuel requirements. The sludges can come from the wastewater treatment system, from other treatment steps, or from impoundments previously used for the storage of the sludges.
- Process sludges high in organic content such as sludges from impoundments.
- Municipal waste which can also include plant trash and solid waste that is not hazardous such as wooden pallets and empty boxes.

Any waste with an organic constituent is a candidate. Totally inorganic wastes are not candidates because there is no organic component that can be destroyed by combustion. Examples of wastes with small organic contents are

- Contaminated water which is incinerated to destroy trace quantities of toxic or hazardous compounds. The hazardous materials are destroyed and the water evaporated to reduce volume. Only salts and scrubber water are left for disposal.
- Contaminated soil which is incinerated to remove organic contaminants, leaving sterile soil that can be reused as fill material.

The most difficult organic wastes for thermal treatment are wastes containing large quantities of toxic metals. The metals tend to be discharged with the combustion gases requiring very efficient air pollution control. Even so, metal emissions can still be excessive making thermal treatment impractical.

COMMON THERMAL TREATMENT TECHNOLOGIES. The most common thermal treatment technologies available include

- Liquid or vapor incinerator (single-chamber unit),
- Catalytic (primarily used for fume and vapor incineration),
- Fluidized bed,
- Rotary kiln with an afterburner,
- Multiple hearth with an afterburner,
- Fixed hearth, and
- Wet air oxidation.

The advantages and disadvantages of the most common types are discussed in Table 8.1. Table 8.2 lists the applicability of available incineration processes to the types of hazardous waste.

In general, the approach is to try and use the treatment process that is the most economical for the waste. For example, the single-chamber liquid or vapor incinerator is normally the most economical as long as no large solids are present. A solids kiln would not be used to treat only liquids. Similarly, a fluidized bed unit is normally more economical than a rotary kiln and would be used if all the solids are small enough or were shredded small enough for feed to the bed. Rotary kilns are frequently used if flexibility is required, even though they are not the least expensive. A rotary kiln unit will burn almost anything.

THERMAL TREATMENT SYSTEMS. Thermal treatment systems are made up of a number of subsystems (unit operations). The major subsystems are

- Waste preparation, pretreatment, and feeding;
- Thermal treatment (incineration or combustion);
- Air pollution control; and
- Residue and ash handling.

Table 8.1 Thermal treatment technologies.

Technology	Advantages	Disadvantages
Liquid injection	• Lowest investment, operating, and maintenance cost. • Capable of a high turndown ratio.	• Can only burn waste that can be atomized in a burner. • Cannot handle large particles, slurries, or solids.
Fluidized bed	• Lower cost than other solids handling incinerators. • Low gas temperature and low excess air reduce fuel requirements for low-Btu wastes and wet sludges. • Acid gases can be trapped in the bed reducing air emission control requirements. • Retains heat during shutdown, thus, does not need to operate continuously.	• Cannot handle large solids without extensive shredding. • Maximum temperature may be limited by melting of the bed or ash.
Rotary kiln	• Will incinerate a wide range of liquids, sludges, and solid wastes. • Can be fed drums and bulk containers. • Can operate at temperatures in excess of 1400°C for destruction of difficult compounds.	• High capital cost. • Thermal shock and refractory damage is an operating concern. • Requires high excess air.
Fixed hearth	• Handles bulk solid wastes.	• Low capacity. • Low thermal efficiency.
Multiple hearth	• High solids retention time. • High thermal efficiency, especially if an afterburner is not required. • Can handle wet sludges.	• Poor temperature response. • High maintenance costs.

Figure 8.1 shows the common subsystems in the order they commonly occur. Figure 8.1 also lists the unit operations that are often a part of each subsystem. The selection of the appropriate unit operations is a function of the physical and chemical properties of the feed along with the type of incineration system used.

Table 8.2 Applicability of thermal treatment to various wastes.

Waste type	Liquid injection	Fluidized bed	Rotary kiln	Fixed hearth	Multiple hearth
Gases	■ ^a	■	■	■	■
Liquids					
Low enough viscosity for atomization	■ ^a	■	■	■	■
Viscous liquids		■ ^a	■	■	■
Slurries					
Organic		■ ^a	■	■	■
Wet		■ ^a	■	■	■
Solids					
Shredded		■ ^a	■	■	■
Bulk			■ ^a	■	
Drums			■ ^a		

^a Generally the most economical for the waste.

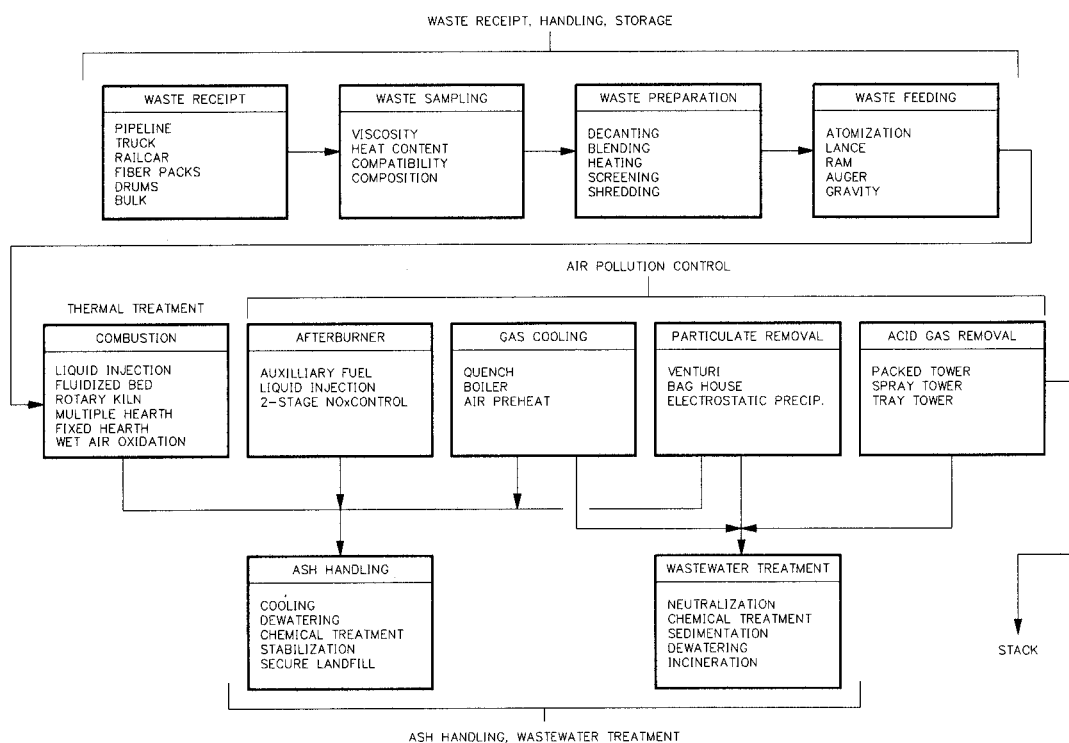


Figure 8.1 Components of a thermal treatment system.

***A*PPPLICATIONS OF THE COMMON THERMAL TREATMENT TECHNOLOGIES**

There are five main ways that thermal treatment systems are used:

- Fixed units at commercial disposal sites. Historically this was the most common method.
- Centralized units serving multiple sites by the same company. Companies that installed units in the 1970s and early 1980s frequently installed centralized units to take advantage of the economy of scale.
- Units at the site of generation. This type of unit is becoming more popular because of public opposition to the transportation of wastes and because industry has recognized the potentially high financial liability associated with the transportation of wastes.
- Mobile units. The use of mobile units that can be moved to contaminated sites to eliminate the cost and hazard of transporting waste on the highway was spawned by CERCLA. The mobile units are normally rotary kiln or fluidized bed units small enough to be loaded on a truck bed or designed to be broken down into modules for transport. Studies by EPA¹ indicate that the performance of these mobile units are equivalent to the performance of stationary units, although the mobile units are more expensive.
- Ocean incineration. Once common in Europe, this type of incineration has not been popular in the U.S. because of public opposition.

WASTES MOST COMMONLY DISPOSED OF BY INCINERATION.

The wastes that are frequently disposed of by incineration include

- Vapors or fumes from processes or other treatment steps. This is the most common application of thermal treatment.
- Sludges generated in a process or another treatment step and sludges obtained from cleaning out ponds.
- Wastewater treatment sludges.
- Municipal waste.
- Plant solid wastes (drums, paper bags, and so on).
- Soil contaminated by spills or previous land disposal.
- Contaminated water.
- Medical wastes.

PERMITTING. Permitting is the most critical factor in the development of any thermal treatment project. As mentioned earlier, even though thermal treatment provides the most complete destruction of hazardous waste, there is still a large amount of public opposition to any thermal treatment process.

Public opposition can effectively slow the permitting process by requiring the developer to increase the amount of information submitted for obtaining the permit.

The goal of most regulatory agencies is to review and approve thermal treatment permits within 18 months of the date the first draft of the permit is filed. But in reality, many permits take years of review before final approval is granted.

A large amount of information is required to obtain these permits. Between 30% and 40% of the total engineering required for a project must be completed during the permitting phase in order to provide the data for the permit.

Once the regulatory agencies agree on the design and operating conditions in the permit, an interim permit is prepared. This interim permit allows the facility to be constructed and sets out the guidelines for a test burn which is used to demonstrate that the destruction and emissions limitations listed in the permit can be achieved. After a successful test burn, the final permit can be issued.

EMISSION CONTROL. The equipment used to control the emissions from thermal treatment facilities is very critical. Past EPA studies have indicated that thermal treatment systems almost always achieved the desired destruction of organic compounds. But, a number of systems have had to upgrade their air pollution control devices to meet the requirements for particulate removal. This requires that strong emphasis be placed on the design of particulate removal equipment.

The five types of emissions that need to be controlled are

- Organic pollutants, which are normally controlled by providing adequate residence time, temperature, turbulence, and excess oxygen in the primary combustion area. For systems where organic vapors are vaporized out of the primary device without complete destruction (rotary kilns and multiple hearths) an afterburner is used to complete the destruction.
- Particulates. These are normally removed in venturi scrubbers electrostatic precipitators, or in bag houses. Particulate removal can be particularly critical if there are organic phosphates in the waste. Phosphates tend to vaporize in the combustion chamber and recondense in the emission control equipment.
- Acid gases and halogens such as sulfur dioxide, hydrochloric acid, and chlorine. These are normally removed by scrubbing the gases in packed towers.
- Metals, particularly heavy metals, which are normally removed with the particulates. The critical applications are metals such as lead that tend to vaporize in the combustion chamber and condense as a fine

mist in the emission control equipment. The particulate removal equipment must be designed to handle the fine metal particles.

- Nitrogen Oxides. These are commonly controlled by using low temperature burners for waste streams and any supplemental fuel streams. If the wastes contain significant amounts of organically bound nitrogen a two-stage incineration system may be required. The first stage burns the organics in the reducing (oxygen deficient) atmosphere and the second stage completes the combustion with excess air.

Table 8.3 lists the common emission control equipment used along with a brief description of their advantages and disadvantages. A common emission control system would be an afterburner followed by either a waste heat boiler or a quench to cool combustion gas, followed by a venturi scrubber for particulate removal, and a packed tower to remove acid gases. If very fine particulates are present, the packed tower may be followed by an electrostatic precipitator or a baghouse.

Table 8.3 Emission control equipment.

Technology	Advantages	Disadvantages
Afterburner	• Final destruction of organic vapors, if required.	
Venturi scrubber	• High particulate removal efficiency down to 1-μm particulates. • Can provide partial absorption of acid gases.	• High pressure drop. • Cannot achieve a high removal of acid gases. • Dust is collected wet.
Packed bed scrubber	• High acid gas removal. • Can remove large particles. • Low to moderate pressure drop.	• Low removal efficiency for less than 10-μm particles. • Dust is collected wet.
Electrostatic precipitator	• Wet type can provide partial absorption of acid gases. • Can remove fine particles with a low pressure drop. • Can be economical for large units particularly downstream of other emission control equipment.	• High capital cost.

Table 8.3 Emission control equipment (continued).

Technology	Advantages	Disadvantages
Bag house	• Can remove fine particles with a low pressure drop. • Dust is collected dry. • Can be economical for large units.	• High capital cost. • Temperature sensitive. • Susceptible to plugging with hydrosupic dusts.

PERMITTING

REGULATORY BASIS. Any facility that incinerates or otherwise treats, stores, or disposes of hazardous waste must apply for and receive a permit before construction of the incineration facility may begin. This permit is required by the Resource Conservation and Recovery Act (RCRA) of 1976 as amended in 1984. Specific incinerator regulations were promulgated on June 24, 1982. The owners and operators must maintain a permit during the active life of the facility, and the permit application must be submitted every 5 years for repermitting.

Incinerator permits will generally create significant public comment. This is especially true in the case of commercial facilities. Sensitive issues such as location near environmentally sensitive areas, incineration of extremely hazardous wastes, and special local concerns should be thoroughly understood. In some areas there is a misconception about what incineration actually does. Some people still view incinerators as the same type of units that were once used behind grocery stores to burn boxes. The public relations aspects of the application should be well understood and addressed as a part of the overall permit process.

For the most part, the federal government has delegated permitting responsibilities to the individual states. The states are free to adopt a more stringent interpretation of the federal regulations. The application required by the regulator is commonly referred to as a Part B application.

The incinerator requirements are just one portion of RCRA permit application. RCRA regulations cover all aspects of hazardous waste activities from generation and transportation to disposal. The regulations are arranged into unit specific sections addressing landfills, land treatment, tank systems, surface impoundments, waste piles, and incinerators. Numerous general facility requirements are also specified.

STRUCTURE OF THE RCRA REGULATIONS. RCRA regulations are codified in the Code of Federal Regulations (CFR), Parts 260-271. The code is updated annually. New and proposed regulations appear in the *Federal Register (FR)*. A list of 40 CFR 260-271 reads as follows:

- 260—Hazardous Waste Management System: General;
- 261—Identification and Listing of Hazardous Waste;
- 262—Standards Applicable to Generators of Hazardous Waste;
- 263—Standards Applicable to Transporters of Hazardous Waste;
- 264—Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities;
- 265—Interim Status Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities;
- 266—Standards for the Management of Specific Hazardous Wastes and Specific Types of Hazardous Waste Management Facilities;
- 267—Interim Standards for Owners and Operators of New Hazardous Waste Land Disposal Facilities;
- 268—Land Disposal Restrictions;
- 270—EPA Administered Permit Programs: Hazardous Waste Permit Program.

Sections of RCRA regulations that specifically address incineration are:

- Part 264, Subpart O—Incinerators;
- Part 270.19, Subpart B—Specific Part B Information; and
- Part 270.62, Subpart F—Specific Permits (Trial Burn Plan).

OTHER APPLICABLE REGULATIONS. RCRA permit application is in itself a major undertaking. However, there are additional permits and approvals that must also be obtained separately. Various other federal, state, and local laws and regulations must also be followed.

A new air emission permit or permit modification will be required to construct an incinerator. The federal regulatory basis for this permit is the Clean Air Act (CAA), as amended in 1979, 42 U.S.C. Applications will generally be required at the Federal and State level. In some areas local air pollution districts also have authority. The source can be reviewed under any of the following programs:

- New source performance standards (NSPS),
- National emission standards for hazardous air pollutants,
- Prevention of significant deterioration,
- Nonattainment area regulations,
- Air toxics regulations,
- General state regulations, and
- General local regulations.

RCRA regulations focus primarily on the hazardous waste aspects of the incinerator, whereas the agency regulating air will be concerned about fugitive and point source emissions of compounds such as nitrogen oxides,

sulfur oxides, volatile organic constituents, metals, carbon monoxide, air toxics, and others.

A new water discharge permit or permit modification will be required for a new discharge source, or if new constituents are introduced into an existing wastewater stream. A federal permit is required under the National Pollutant Emission Discharge and Elimination System (NPDES). State and local permitting may also be required.

An environmental impact study may be required at federal, state, and local levels if the facility is determined to have a significant impact on the quality of the human environment. The applicable federal standard is the National Environmental Policy Act of 1969 (NEPA). Information necessary for a proper environmental review is generally provided by the applicant in an environmental information document or report. These reports can be exhaustive. Therefore, the EPA and state and local agencies should be contacted at the preliminary stages of the project to determine requirements pertaining to environmental impact.

Under RCRA regulations, the agency must evaluate certain laws before issuing a permit. These laws are:

- The Wild and Scenic Rivers Act. 16 U.S.C. 1273 *et seq.* Section 7 of the act prohibits the issuance of a permit if it has a direct, adverse effect on the values for which a national wild and scenic river program was established.
- The Endangered Species Act. 16 U.S.C. 1531 *et seq.* Section 7 of the act and subsequent regulations (50 CFR Part 402) require the EPA Regional Administrator to ensure that issuance of a permit is not likely to jeopardize the continued existence of any endangered or threatened species or adversely affect its critical habitat.
- The National Historic Preservation Act of 1966. 16 U.S.C. 470 *et seq.* Section 106 of the act and subsequent regulations (36 CFR Part 800) require the adoption of measures, when feasible, to mitigate potential adverse effects of the facility and properties listed or eligible for listing in the National Register of Historic Places.
- The Coastal Zone Management Act. 16 U.S.C. 1451 *et seq.* Section 307(c) of the act and subsequent regulations (15 CFR Part 930) prohibit the issuance of a permit affecting land or water use in the coastal zone until the applicant certifies proposed activity complies with the state coastal zone management program.
- The Fish and Wildlife Coordination Act. 16 U.S.C. 661 *et seq.* Requires that the permitting agency consult with the state wildlife agency to conserve those resources if the permit application proposes the impoundment, diversion, control, or modification of any body of water.

All permit and approval requirements should be determined early in the project. As discussed above, water discharge permitting, air emission permitting, and environmental impact requirements are key initial considerations. It should also be noted that incineration of PCBs are regulated under the Toxic Substance Control Act (TSCA) and any incineration of PCBs regulated under this act must be permitted accordingly.

PERMIT APPLICATION CONTENT. Regulations applicable to incineration facilities include requirements for design, waste analysis, designation of principal organic hazardous constituents (POHCs) in the waste material, and specific requirements for operation, inspection, and monitoring. Applicants are required to keep records of all data used to complete permit applications and any supplemental information submitted for 3 years.

Exposure information may be required under RCRA Section 3019 if the incineration facility also stores, treats, or disposes of hazardous waste in an impoundment or a landfill. This information can be used in the includes determination of the reasonable potential to emit hazardous waste from the site and during transport, and considers both normal and accidental events. Pathways and effect are also be addressed. Several states require that this information be developed for incinerators also.

The primary requirements of permit application content are listed in Part A and B of 40 CFR 270. Part A requirements are general and are satisfied by filling out a standard form. The Part B requirements are extensive and can amount to several volumes of data and narrative. There is no standard form for Part B of the application. Part B information must be submitted in narrative form and contain the information set forth in the applicable sections of 270.14 through 270.29 of the regulations. Owners or operators of new hazardous waste management facilities must submit Parts A and B of the permit applications at least 180 days before physical construction is scheduled to begin. This is the minimum permit application review period. The RCRA requires a permit for the "treatment, storage, or disposal (TSD) of any hazardous waste" as identified or listed in 40 CFR Part 261.

Other hazardous waste TSD units on the facility should be listed on the permit application also. For instance a landfill, treatment unit, or storage unit may be a part of the facility. The regulatory agency may issue or deny a permit for one or more units without simultaneously issuing or denying a permit to all of the units existing at a facility.

Detailed design information is required to satisfy regulatory requirements. The permitting does not, however, require full detailed design of the facility. The following list summarizes the information generally required:

- Detailed engineering description of the incinerator;
- Incinerator specifications;
- Description of monitoring, control, and interlocks;

- Piping and instrumentation diagrams (P&IDs); and
- Detailed drawings of secondary containment areas.

Three major performance standards have been developed to ensure incinerator performance. The primary requirement is that the principal organic hazardous constituents (POHCs) designated in each separate waste feed stream must be destroyed or removed to an efficiency of 99.99%. The selection of POHCs is based on a chemical's concentration and destruction difficulty. The POHCs should be designated by the applicant, but the agency will make the final determination. The second requirement is that particulate emissions not exceed 180 mg/m³ (dry standard), corrected to 7% oxygen. The third requirement is that hydrochloric acid (HCL) emissions, produced by wastes containing chlorine, not exceed 1.8 kg/h or achieve a removal efficiency of 99%.

The application must also include general facility information to satisfy general facility standards. These standards require detailed descriptions of equipment, plans, and implementation procedures addressing the following:

- Security;
- Facility inspections;
- Personnel training;
- Procedures for reactive, ignitable, and incompatible wastes;
- Floodplain standard;
- Seismic standard;
- Emergency preparedness and prevention;
- Equipment for emergency preparedness and prevention;
- Contingency plan;
- Recordkeeping and reporting;
- Facility closure and postclosure care;
- Waste analysis and waste analysis plan;
- Financial requirements; and
- Use and management of containers.

A facility can be exempt from the specific incineration requirements if the wastes are classified as hazardous only because they are ignitable, corrosive, or reactive. A facility exempted from incineration standards will still be required to submit an application to permit storage tanks and other hazardous waste operations, and must include a waste analysis plan.

Trial Burn Plan. The trial burn plan is an important element of a RCRA Part B application. The regulations require either a trial burn or data from a trial burn conducted for a similar facility. Generally, the regulatory agency will consider a similar trial burn if the parameters of the test burn such as feed rate and incinerator size are within approximately 10% of the proposed

facility design and operational criteria. The trial burn plan is submitted with the Part B application as a separate document. It consists of the following information:

- Detailed waste stream analysis,
- Waste analysis plan,
- Facility description including incinerator specifications,
- Description of fuels to be used,
- Controls and stack monitoring,
- Test schedule,
- Description of operating ranges during each test run o Emergency shutdown procedures, and
- Detailed description of waste feed.

Finally, the applicant should provide a description of the conditions under which the applicant proposes to operate the incinerator. Since initial permit conditions will be set by this description, the development of a trial burn should be a thoroughly deliberated process.

PERMIT APPLICATION PROCEDURE. RCRA application is generally submitted to the state agency for review. However, if the state does not have Phase II interim or final authorization to permit, the application must be submitted to EPA.

In most cases, it is prudent to submit the application much further in advance than 180 days prior to construction state does not have Phase II interim or final authorization to permit, the application must be submitted to EPA.

In most cases, it is prudent to submit the application much further in advance than 180 days prior to construction. It is a good practice to discuss the project with the regulatory agency as one of the first steps in the incineration permit process. This establishes a working relationship with the agency. This communication should be ongoing throughout the project.

The submitted permit application and all follow-up information are considered public record, and are open to public review. If trade secrets and confidential business information are contained in the application, a specific request must be made to keep this information confidential. Each page containing such information must be stamped, and a justification must be submitted. The reviewing agency will treat confidential information in accordance with procedures in 40 CFR Part 2 (Public Information).

After the initial design phase and development of an application, the application will be submitted to the agency and a permitting fee will be charged. At this point, the application should include Part A, Part B, and the trial burn plan. The agency has 30 days to review the application for completeness. The completeness review determines if the application has addressed all of the

regulatory and procedural requirements. When the agency determines that the application is complete, the next stage is the technical review.

During the technical review, the application will be reviewed by engineers, chemists, and environmental scientists to determine technical merit. After the technical review has been completed, either a draft permit or denial is prepared, and an opportunity for public comment is provided.

If sufficient public interest is expressed, or if the agency determines that additional public input is required, public consultation in the form of a public meeting, public hearing, advisory groups, or other mechanism is provided. The specific mechanism for public input is established by the state if the program has been delegated. Federal public participation requirements are found in 40 CFR Part 25. The agency will determine if the public comments have technical or environmental protection merit.

After the public comment period, the final step is the issuance of a permit with qualifications and requirements necessary to comply with the regulations and performance standards.

A permit will typically be structured to provide for a shakedown, trial burn, and subsequent opportunity for permit modification. After the issuance of a permit and construction, the facility will be allowed a shakedown period on hazardous waste prior to conducting a trial burn. This phase is limited to 720 hours with one allowable extension. The trial burn will follow. It will generally take several months to obtain and evaluate the trial burn data. On submission of the trial burn results to the regulatory agency, the incinerator may continue to operate as specified in the permit. On review of the trial burn data, the agency may require that the application be modified. An additional trial burn could also be required if the data is not acceptable.

WASTE CHARACTERIZATION AND TREATABILITY STUDIES

Of the 265.6 million metric tons of waste generated in the U.S. in 1983, 23.5% of it was incineratable, yet less than 1% was incinerated. The Congressional budget office estimates that today less than 4% of the incineratable hazardous waste is incinerated.

RCRA is a body of regulations developed by the federal government to regulate the handling of hazardous waste. RCRA was intended to fill the gap in environmental regulation left by the Clean Water and Clean Air Act. RCRA does not specifically deal with abandoned sites or closed facilities, nor does it deal with hazardous substances regulated separately (via TSCA or FIFRA). RCRA does address the issue of what can and cannot be landfilled. The so-called "land-ban" portion of RCRA will require, as it expands, that

many wastes previously landfilled will now have to seek other avenues for disposal. Many of these wastes will be incinerated.

Industry-generated incineratable hazardous wastes can be divided into several broad categories that include waste oils, halogenated and non-halogenated solvents, organic liquids, pesticides, herbicides, PCBs, and halogenated and nonhalogenated sludges and solids.

Waste streams can be gas, liquid, solid, or sludge. The first step in waste characterization is to determine the phase of the waste stream. The next step is to determine whether the waste can be handled in bulk or packaged form. Occasionally the mechanical handling problems associated with a particular waste will limit the available treatment options. Waste characterization is a critical step in determining how a waste should be handled. The physical and chemical properties of the waste, together with the regulated and desired treatment standard, are used to determine the best method for waste destruction.

REGULATORY REQUIREMENTS AND DEFINITIONS. A waste stream is considered hazardous when it poses a threat to human health or the environment. This threat posed when a waste stream is improperly treated, stored, disposed, or otherwise mismanaged.

Under RCRA all hazardous waste is solid waste regardless of its actual physical form. Once a hazardous stream has been designated a waste, it is by law a solid waste and RCRA statutes apply unless it has been specifically exempted from regulation. The characterization of the waste for RCRA compliance may or may not be adequate in order for it to be successfully incinerated. Under RCRA a hazardous waste may be a designated or characteristic waste. A designated waste is one that is specifically listed by EPA as hazardous (such as hydrogen cyanide). A characteristic waste is one that exhibits any one of the characteristics of ignitability, corrosiveness, reactivity, or extractive procedure (EP) toxicity.

An ignitable waste is defined as any liquid with a flash point of less than 60°C (140°F), any nonliquid that can cause a fire under certain conditions, or any waste classified by the U.S. Department of Transportation (DOT) as a compressed ignitable gas or oxidizer. An ignitable waste is given the classification number D001. A corrosive waste is defined as any aqueous material that has a pH less than or equal to 2, a pH greater than or equal to 12.5, or any material that corrodes SAE 1020 steel at a rate greater than 6.4 mm/a (0.25 in./yr). A corrosive waste is given the classification number of D002. A reactive waste is defined as one that is unstable, changes form violently, is explosive, reacts violently with water, forms an explosive mixture with water, or generates toxic gases in dangerous concentrations. A reactive waste is given the classification number of D003.

An extractive procedure toxicity (EP Tox) waste is one whose extract contains concentrations of certain constituents in excess of those stipulated by

the Safe Drinking Water Act. A waste that is deemed hazardous due to the results of the EP Tox test is assigned a classification number that reflects the specific reason the waste failed the test. For example, if the extract was found to contain 5 mg/L or more of arsenic, the waste would be classified as D004. If the extract was found to contain 0.02 mg/L or more of endrin, the waste would be classified as D012. If the extract of the waste contained both arsenic and endrin in the aforementioned amounts, it would be given the classification numbers of D004 and D012. If the waste was also ignitable, it would carry the D001 classification along with D004 and D012. A complete list of the maximum concentrations of contaminants for the EP Tox test can be found in 40 CFR Part 261.24.

A waste becomes a designated or listed hazardous waste if it is listed in 40 CFR Parts 261.31, 261.32, or 261.33. The wastes listed in 40 CFR Parts 261.31-33 are subject to certain exclusion limits explained in 40 CFR Part 261.5. Part 261.5 basically provides an exemption from the RCRA statutes for small quantity generators.

Listed hazardous waste can come from specific or nonspecific sources. Wastes such as spent solvents from nonspecific sources are listed in 40 CFR Part 261.31. Sludges and wastes from specific industrial processes are listed in Part 261.32. Commercial chemical products that are "acute wastes" or other commercial products that are being discarded are listed in Part 261.33.

The rationale for listing a particular waste is given in 40 CFR Part 261, Appendix VII. For example, F007, the spent cyanide plating bath solutions from electroplating operations, is a listed hazardous waste. Appendix VII tells why it is listed it contains cyanide. Appendix VIII of 40 CFR Part 261 lists over 400 chemicals that EPA believes to be either carcinogenic or toxic. If a waste contains one or more of the Appendix VIII compounds, it is not necessarily a hazardous waste. To be a hazardous waste, it must be listed or demonstrate one of the four characteristics.

Any mixture of a hazardous waste with a nonhazardous waste is classified as a hazardous waste. Any material derived from the treatment of listed hazardous waste is also a hazardous waste. When a characteristic waste is treated or processed, the product of that treatment is a hazardous waste only if that product displays one of the characteristics.

Subpart C of 40 CFR Part 268, describes the land-ban regulations. The land-ban regulation states that you can no longer bury wastes containing solvents or PCBs, wastes contaminated by the items on the California list, or dioxin containing waste. If a waste fails the toxicity characteristic leachate procedure (TCLP) test, the waste cannot be put in a landfill. Most of the waste that fails the TCLP must be incinerated. The land-ban regulation defines the standard and the methodology that must be used to treat any waste that has failed the TCLP test.

A few examples of waste classification should help illustrate the aforementioned definitions. Suppose we were to come across a container of brown tar-

like sludge. A sample of the sludge is analyzed and found to contain 5 ppm of 1,2-dichlorobenzene. The sludge does not exhibit any of the characteristics and is not a listed waste. It is, therefore, not a hazardous waste.

Now let's take a pint of the commercial product 1,2-dichlorobenzene that we wish to dispose, and add it to the brown sludge. The resultant concentration of 1,2-dichlorobenzene is 5 ppm in the sludge. Is this waste a hazardous waste? The answer is YES! The waste is now a listed waste via the mixture rule. The pint of commercial grade 1,2-dichlorobenzene is a listed waste and carries the classification number U070. As soon as that waste was mixed with the sludge, the sludge becomes a hazardous waste with the classification U070 because of the mixture rule stating that any waste that is the result of mixing a hazardous waste with a nonhazardous waste is now a hazardous waste.

Characterizing and classifying hazardous waste can be difficult. Once the waste has been legally classified, it must be treated designated in 40 CFR Part 268. The analyses that are required to make the hazardous or nonhazardous determination are not always sufficient to determine whether or not the waste can be thermally treated. Sampling and analytical methods are discussed in the next section of this chapter.

It is important to keep in mind that when trying to characterize waste under RCRA, The regulations concerning hazardous waste are still evolving. The land-ban regulations were only recently promulgated and it is expected that the list of land-ban substances will expand. The number of "listed" wastes is also growing. Treatment standards are still evolving. It is conceivable that waste called nonhazardous today may be classified as hazardous in the future.

SAMPLING AND ANALYTICAL METHODS. Part 265.13 of RCRA statute requires that before an owner or an operator treats, stores, or disposes of any hazardous waste he must obtain a detailed chemical and physical analysis of a representative sample of the waste. In addition to those tests required to classify the waste, the heating value, halogen content, sulfur content, and concentrations of lead and mercury must also be determined if the waste is to be thermally treated.

Appendix I of 40 CFR Part 261 describes representative sampling methods. Table 8.4 outlines these methods.

Once the sample has been taken, a number of tests must be performed. Most hazardous waste is characteristic waste. It is ignitable, corrosive, reactive, or EP toxic. Table 8.5 outlines the analytical methods used to determine ignitability, corrosiveness, or reactivity. These methods are also described in 40 CFR Parts 261.21-24. The procedure for the EP Tox test is explained in 40 CFR Part 261, Appendix II. The method used for the TCLP is described in 40 CFR Part 268, Appendix I.

Table 8.4 Representative sampling methods.

Extremely viscous liquid	ASTM standard D140 – 70 crushed or powdered material. ASTM standard D346 – 75 soil or rock-like material. ASTM standard D140 – 69 soil-like material ASTM standard D140 – 65 fly ash-like material. ASTM standard D140 – 76 (ASTM standards are available from ASTM, 1916 Race Street, Philadelphia, PA 19103).
Containerized liquid wastes	“COLIWASW” described in “Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods,” U.S. EPA, Office of Solid Waste, Washington, D.C. 20460. (Copies may be obtained from Solid Waste Information, U.S. EPA, 26 W. St. Clair Street, Cincinnati, OH 45268).
Liquid waste in pits, ponds, lagoons, and similar reservoirs.	“Pond Sampler” described in “Test Methods for the Evaluation of Solid Waste Physical/Chemical Methods.”

Table 8.5 Analytical methods for ignitability, reactivity, or corrosivity.

Ignitability	• D001 • ASTM standard D-93-79 • ASTM standard D-93-80 • ASTM standard D-3278-78, defined in 40 CFR Part 261.21
Corrosivity	• D002 • $\text{pH} \leq 2$ or $\text{pH} \geq 12.5$ • pH method described in 40 CFR Part 260.11 • NACE^a standard TM-01-69, defined in 40 CFR Part 261.22
Reactivity	• D003 • Reacts violently with water • Is unstable and readily undergoes violent changes without detonation • Forms a potentially explosive mixture with water • Generates toxic vapors when mixed with water, cyanide, or sulfur vapors when exposed to low or high pH • Defined in 40 CFR Part 261.23 • Defined in 49 CFR Part 173.51, 49 CFR Part 173.53, or 49 CFR Part 173.88

^a National Association of Corrosion Engineers.

To identify compounds in either Appendix VII or VIII the chemical analysis methods described in “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods” should be used. These methods are found in 40 CFR Part 261.11. Tables 1, 2, and 3 in Appendix III of 40 CFR Part 261

detail the precise method for each component named in Appendix VII and VIII.

Appendix X of 40 CFR Part 261 describes the method for analysis of chlorinated dibenzo-p-dioxins and dibenzofurans.

Figure 8.2 shows one version of a waste data sheet that can be used to collect all the information needed to properly incinerate a liquid waste. Figure 8.3 shows a waste data sheet for a solid. Sludge waste can utilize either the solid or the liquid data sheet depending on the individual sludge.

TREATABILITY STUDIES. What makes a waste amenable to incineration? How should wastes that are not amenable, but designated for incineration, be managed? Wastes that are organic in nature and have high heat contents are ideal for incineration. Inorganic wastes or wastes that contain high levels of volatile metals like mercury and lead are poor candidates for incineration.

Liquids. Liquid wastes with some heating value are perhaps the easiest to incinerate. They can usually be atomized in a burner and combusted with auxiliary fuel if necessary. If the waste is hazardous only because of the characteristic of ignitability, contains low or no ash, is not highly nitrogenated, and does not contain other harmful substances, the waste stream may be suitable for use in a utility boiler. Utility boilers are not usually equipped with particulate or acid gas removal, so the waste must be relatively clean.

Aqueous wastes contaminated with organics can also be incinerated. Since wastes with low or no heating value require substantial amounts of auxiliary fuel be burned with them, it is best to explore the possibility of detoxifying the waste through biodegradation before considering incineration.

If the waste is not biodegradable, and has essentially no fuel value, it can be atomized onto the outer flame envelope of a burner using either auxiliary fuel or a high-BTU waste. A separate source of combustion air must be provided for aqueous wastes that contain more than 2% organics. If not, high levels of carbon monoxide may result.

An aqueous waste may be blended with a high-BTU fuel provided that the two streams are miscible and the resultant mixture is still flammable. The mixture can be atomized and combusted in a standard burner.

In general, it is not necessary to do bench-scale work on liquid wastes. Burners are commercially available for most liquid waste applications. Pilot trials for liquid incineration are advisable whenever there are questions concerning soot formation or destruction removal efficiency (DRE). Unfortunately there are very few test facilities that are permitted to handle RCRA hazardous waste.

Solids. Most of the difficulties encountered in the incineration of solid waste are related to the mechanical handling of the waste and not its thermal proper-

Waste name: _____	Annual production (lb/yr): _____
Process: _____	Frequency of production: _____
Heating value, Btu/lb: _____	Phase at room temperature: _____
Chemical breakdown, percent:	
Carbon: _____	Ionic chlorides: _____
Hydrogen: _____	Total chloride: _____
Oxygen: _____	Fluorine: _____
Nitrogen: _____	H ₂ O: _____
Sulfur: _____	Volatiles: _____
Bromine: _____	Ash: _____
Iodine: _____	Phosphorus: _____
Metal analysis, ppm:	
As: _____	Pb: _____
Ba: _____	Se: _____
Cd: _____	Ag: _____
Cr: _____	Hg: _____
Physical properties:	
Flashpoint, °F: _____	Specific gravity: _____
Total solids, percent: _____	Vapor pressure: _____
pH: _____	Heat of vaporization Btu/lb: _____
Viscosity as F(T) (CPS): _____	Specific heat, Btu/lb/°F: _____
Pumpable: _____	Ash fusion temperature: _____
Boiling point: _____	
Additional information:	
Odor: _____	
Specific chemical compounds: _____	
Toxicity, ingestion, inhalation, dermal, eyes: _____	

Figure 8.2 Liquid waste report.

Waste name: _____	Annual production (lb/yr): _____
Process: _____	Frequency of production: _____
Heating value, Btu/lb: _____	Phase at room temperature: _____
Chemical breakdown percent:	
Carbon: _____	Ionic chlorides: _____
Hydrogen: _____	Volatiles: _____
Oxygen: _____	Fluorine: _____
Nitrogen: _____	H ₂ O: _____
Sulfur: _____	Ash: _____
Total Chlorides: _____	Phosphorus: _____
Bromine: _____	Iodine: _____
Metal analysis, ppm:	
As: _____	Hg: _____
Ba: _____	Pb: _____
Cd: _____	Se: _____
Cr: _____	Ag: _____
Physical properties:	
Melting point, degrees F: _____	Void fraction: _____
Bulk density, lbs/cu ft: _____	Specific heat, Btu/lbs/°F: _____
Pyrophoric: _____	Angle of repose: _____
pH: _____	Ash fusion point: _____
Additional information:	
Shock stability: _____	
Packaging requirements: _____	
Odor: _____	
Toxicity: _____	

Figure 8.3 Solid waste report.

ties. Solid waste is seldom uniform in size or composition, and may have to be "prepared" so that it can be conveyed. If the waste needs to be shredded, pilot-scale work should be done to ensure that the proper shredder has been chosen. If the waste must be conveyed or stored, conveyors and bin activating devices should be pilot tested prior to their selection. Careful attention must also be given to how the solid waste is introduced into the incinerator. Solid waste is generally ram fed into a rotary kiln. A ramming device pushes a batch of solid waste into a chute, from which the waste falls into the kiln by gravity. A slide gate is synchronized with the motion of the ram to provide positive isolation of the feed bin from the kiln. If such positive isolation is not provided, the potential for the preignition of solid waste before it drops into the kiln is very high. The conveying of the solid waste into the incinerator is also complicated by the fact that the solids are often preheated in the feed device due to simple radiation from the incineration chamber. This preheat effect is very hard to simulate in pilot-scale testing, but should not be overlooked.

Solid waste can be incinerated in a wide variety of devices. Solids with heating values in excess of 7000 Btu/lb will usually burn autogenously. Solids with heating values less than 7000 Btu/lb require auxiliary fuel and can present special problems. Usually the solids are spread out on a grate or are lowered onto the floor of a rotary kiln. The auxiliary fuel is fired separately in a burner. It is difficult to distribute combustion air to the solid mass. In the kiln, the solids are tumbled because the kiln rotates. It is still difficult to disperse the solids. As a result it is possible to slag over the outside of a large particle while the inside remains unexposed to either the heat or oxygen. This is why the burn characteristics of the solid is important.

Solids with very high heating values, high ash contents, and high salt contents are especially susceptible to the slag ball phenomena. Their surfaces readily ignite and burn at a very high temperature. The local air distribution at the gas-solid interface and the solid particle size are very important. If the surface is so hot that the ash melts before the solid has completely burned, the ash can encapsulate unburned material.

Pilot trials on solid wastes with high heating values are almost always advisable. Materials handling problems can be worked out in advance and combustion characteristics can be evaluated. The effectiveness of the method of introduction of the solid material can be demonstrated. Rapid consumption of oxygen, resulting in intermittent spikes of carbon monoxide, can occur. The proper charge rate and required solid residence time for total burnout can be established.

Inorganic solids contaminated with organics with little or no heating value are generally not good candidates for incineration. Sometimes, however, these materials must be further treated due to land-ban restrictions. High-temperature incineration will volatilize the metals and is undesirable unless absolutely necessary. Steam stripping or high-temperature air stripping of the

organics from the solids, with subsequent treatment of the contaminated air or steam, should be tried before high-temperature incineration is chosen. The stripping of organics from the inorganics usually depends on the relative volatility of the organics, the ability to expose fresh surface area of the solid to the carrier gas, and the nature of the contamination. Simple bench-scale testing can be used to determine whether or not the solid waste can be treated in this manner.

If the organic portion cannot be stripped from the inorganic portion, then the solid will have to be treated at high temperatures. Solids that have little or no heating value require substantial amounts of auxiliary fuel. The melting point and fluid point of the ash must be determined. If the solid must be melted in order to reach the organic contamination, then the resultant slag must be fluid enough to move out of the incineration device. Bench-scale tests should almost always be conducted to determine whether or not the solid can be thermally treated.

Sludges that can be pumped and are atomizable are best treated as liquids. Sludges that are not atomizable should be treated as solids. Sludges containing high ash contents relative to their combustible portion should be treated as solids regardless of their atomizability. Problems with sludge materials handling usually overshadow any problems encountered with the combustion of the sludges.

Sludges are usually best treated in fluidized beds, unless they have a high salt content. The mixing and grinding action of the bed aids in the dispersion of the sludge, which is usually the factor critical to complete incineration.

Bench-scale tests should be done to determine the treatability of a sludge in a fluid bed. The efficiency of destruction of organics can be measured, and the operability of the unit can be assessed. The test should be of sufficient length to determine whether or not the sludge contains any components that could form low-melting eutectics with the bed material.

The critical question that any bench-scale test should answer is whether or not the waste can be incinerated effectively. Can the desired destruction removal efficiency of the principal organic hazardous constituents be achieved? Is the quality of the residue acceptable? Is the incineration strategy practical? Have the operating conditions been determined? Have the proper emissions data been developed? Once these questions have been answered the treatability of the waste will have been determined.

***T**REATMENT TECHNOLOGIES*

The most important criteria for hazardous waste incinerators is the complete destruction of the major hazardous compounds, although emissions (particulates and chlorides) must also be within acceptable limits. The system must

operate within limits that will not damage the equipment, and the system must be economical.

An adequate degree of destruction (99.99 to 99.9999% for PCBs and dioxin) requires

- Enough residence time,
- A high enough temperature,
- Enough oxygen (or enough hydrogen if burning chlorine or bromine), and
- Sufficient turbulence to mix the waste with the oxygen.

Scrubbers may also be required to remove particulates and other pollutants in the stack gas. Also, the control system must be capable of preventing excessive temperatures that could damage the equipment.

COMBUSTION THEORY. The chemical and thermodynamic properties of the waste that need to be considered in designing an incinerator are elemental composition, net heating value, and moisture content. The percentages of carbon, hydrogen, oxygen, nitrogen, sulfur, halogens, and phosphorus in the waste also need to be known in order to calculate the stoichiometric combustion air requirements and to predict combustion gas flow and composition.

Table 8.6 shows the major reactions that occur in an incinerator. Carbon and hydrogen react with oxygen to form carbon dioxide and water. Water in the feed passes through the system unreacted, except that it can react with halogens (chlorine and fluorine) to form acid gases (HCl and HF). Nitrogen entering with the combustion air passes through the system unreacted. Bromine and iodine tend to pass through the system unreacted. Special control of the compounds may be required, including the introduction of sulfur or sulfur dioxide to the hot zone of the combustion chamber to aid in the conversion to HBr or HI. Sulfur reacts with oxygen to form the acid gas sulfur dioxide. Phosphorus reacts with oxygen to form phosphorus pentoxide.

In addition to the major reactions, carbon, carbon monoxide, free hydrogen, nitrogen oxides, free chlorine, free fluorine, hydrogen bromide, hydrogen iodide, sulfur trioxide, and hydrogen sulfide are also formed in small quantities. These reactions do not need to be considered in calculating combustion gas flows or combustion temperatures, but they can be important in calculating the potential for air pollution and in calculating air pollution control requirements.

Table 8.7 shows the oxygen required and the combustion products formed per pound of the waste components in the feed.

COMBUSTION TEMPERATURE. Combustion must be carried out at a temperature high enough to achieve complete destruction of the waste, but

Table 8.6 Reactions in the incinerator.

$C + O_2$	=	CO_2
$H_2 + 0.5 O_2$	=	H_2O
H_2O	=	H_2O
N_2	=	N_2
$Cl_2 + H_2O$	=	$2HCl + 0.5O_2$
$F_2 + H_2O$	=	$2HF + 0.5O_2$
Br_2	=	Br_2
$Br_2 + H_2 + S$	=	$2 HBr + S$
I_2	=	I_2
$S + O_2$	=	SO_2
$2P + 2.5O_2$	=	P_2O_5

Table 8.7 Reaction stoichiometry.^a

Waste component	Stoichiometric oxygen requirement	Combustion product yield
C	2.67 lb/lb C	3.67 lb CO_2 /lb C
H_2	8.0 lb/lb H_2	9.0 lb H_2O /lb H_2
O_2	- 1.0 lb/lb O_2	—
N_2	—	1.0 lb N_2 /lb N_2
H_2O	—	1.0 lb H_2O /lb H_2O
Cl_2	- 0.23 lb/lb Cl_2	1.02 lb HCl /lb Cl_2 -0.25 lb H_2 /lb Cl_2
F_2	- 0.42 lb/lb F_2	1.05 lb HF /lb F_2 -0.47 lb H_2O /lb F_2
Br_2	—	1.0 lb Br_2 /lb Br_2
I_2	—	1.0 lb I_2 /lb I_2
S	1.0 lb/lb S	2.0 lb SO_2 /lb S
P	1.29 lb/lb P	2.29 lb P_2O_5 /lb P
Air N_2	—	3.31 lb N_2 /lb (O_2) stoichiometric

^a Stoichiometric air requirement = 4.31 x stoichiometric oxygen.

also at a temperature low enough not to damage the refractory in the incinerator.

The heat balance for a thermal destruction system is

- Heat in = Heat out
- Heat in = Fuel value of waste + heat from auxiliary fuel + air preheat, Air preheat = air rate x heat capacity x (T_{air} - T_{ambient})
- Heat out = Heat out stack gas + heat out ash + heat loss, Heat loss is approximately 5% of total heat input, Heat out stack gas = stack gas flow x heat capacity x (T_{gas} - T_{ambient})

RESIDENCE TIME IN THE THERMAL TREATMENT SYSTEM. The average residence time in the incinerator is the incinerator volume divided by the flow rate. The incinerator must be big enough, have enough volume, and have a temperature high enough to allow the waste to complete its combustion before it exits from the stack or flows to a cooler area (scrubber).

A Residence Time. There are a number of features that can affect the gas residence time and subsequently must be controlled

- Incinerator volume in the combustion chamber,
- Feed rate,
- Heating value of the feed,
- Auxiliary fuel firing rate,
- Excess air, and
- Moisture content of the feed (or water injection for cooling).

Solids Residence Time. The above is for a liquid or gas incinerator, an after-burner following a rotary kiln incinerator, or a liquid or gas fired in a kiln. For the rotary kiln itself, you must consider the solids residence time which is a function of the kiln slope and the rate of rotation of the kiln.

For the kiln, the solids residence time for a given feed rate, kiln length, diameter, slope, and rotation rate is given by the following equation:

$$t_K = 0.19 (L/D)/SN$$

Where

L = length, ft;
 D = diameter, ft;
 S = slope, ft/ft; and
 N = rpm.

The L:D ratio is typically 2:10, the slope is 0.03 to 0.09 ft/ft, and the rotation is typically 1 to 5 ft/min; equivalent to an N of 0.03 to 0.3 rpm. The

solids residence time can be hours. It needs to be long enough to completely vaporize any organic wastes in the sludge.

OXYGEN REQUIREMENTS. Items that affect the amount of oxygen required for complete combustion include the reaction stoichiometry, oxygen contained in the compounds in the feed, and excess air.

Of the above, the item most under the control of a thermal treatment system designer or operator is the excess air. The excess air is normally given as a percent. It is the air added in excess of what is required to satisfy the stoichiometry in Table 8.7.

$$\text{Excess air, percent} = (\text{total air stoichiometric air}) / \text{stoichiometric air}$$

The excess air required depends on the amount of turbulence available to mix the oxygen with the waste. The lower the turbulence, the higher the excess air that is required. Thermal destruction systems with poor mixing of the waste and oxygen requiring high excess air are the rotary kiln, fixed hearth, and multiple-hearth incinerators. Units with good mixing that do not require as high an excess air are liquid injection incinerators and fluidized bed incinerators.

TURBULENCE. Turbulence is required to properly contact the waste with oxygen and to make sure that all the waste is exposed to a temperature high enough for destruction. Features that affect turbulence are

- Liquid atomization,
- Agitation of solids,
- Velocity, and
- Design of the reactor internals.

The velocity is a function of the cross-sectional area of the combustion zone and the combustion gas flow rate. If the velocity is not high enough the feed rate can be escalated to increase the combustion gas flow rate. The excess air can be increased (as long as the combustion temperature is high enough), or auxiliary fuel can be fired.

THERMAL TREATMENT TECHNOLOGIES

The following are the most common thermal treatment technologies available:

- Liquid or vapor incinerator (single-chamber unit),

- Catalytic (primarily used for fume and vapor incineration),
- Fluidized bed,
- Rotary kiln,
- Multiple hearth,
- Fixed hearth, and
- Wet air oxidation.

The advantages and disadvantages of the most common types are discussed in Table 8.1.

In general the approach is to try and use the treatment process that is the most economical for the waste. For example, the single-chamber liquid or vapor incinerator is normally the most economical as long as no large solids are present. A solids handling unit such as a fluidized bed or rotary kiln would not be used to treat liquids. Similarly, a fluidized bed unit is normally more economical than a rotary kiln and would be used if all the solids are small enough, or can be shredded small enough for feed to the bed. But rotary kilns are frequently used, even though they are not the lowest cost, if flexibility is required. A rotary kiln unit will burn almost anything.

The possible thermal treatment systems listed in the order of increasing cost are

- Single-chamber incinerators for the destruction of liquid or gaseous wastes. If the waste is a gas or a liquid with a viscosity low enough for atomization in a burner (less than 750 SSU viscosity at the burner), the most economical selection would be a single-chamber incinerator. These units have the lowest investment and tend to have the greatest efficiency because of good mixing in the burners. If the waste has very little ash, dissolved salts, or acid gases this type of unit can be very economical because a scrubbing system may not be required.
- A catalytic incinerator is a modification of a single-chamber unit that can be used to destroy vapors and gases. This type of unit uses a catalyst to allow destruction at a lower temperature than a single-chamber unit and thus can be more efficient in treating dilute vapor streams.
- A fluidized bed incinerator tends to be the most economical unit that can handle solids, sludges, and viscous liquids. A fluidized bed unit tends to have a lower investment than a rotary kiln unit and it tends to have a higher thermal efficiency because of better mixing and better temperature control. A fluidized bed unit would tend to be the first choice in handling wastewater sludges because less fuel would be required to handle the high water content, low-Btu sludge.
- A rotary kiln is the normal choice for commercial units, central treatment units, and any other services where the unit is required to handle

a wide range of wastes, including large solids such as drums or fiber-packs.

- A fixed hearth unit is a competitor to a rotary kiln. This type of unit has been used to handle municipal waste.
- A multiple-hearth unit is a competitor of a fluidized bed unit. A multiple-hearth unit can have a high thermal efficiency handling wet sludges because it utilizes a countercurrent flow.

Two other types of units that are also used are infrared and salt bath units. These are special units that should at least be considered during the screening stage of any project.

BREAKDOWN OF THE TYPES OF THERMAL TREATMENT SYSTEMS IN SERVICE. The results of a 1983 survey⁴ of the hazardous waste incineration industry are given below:

- Single-chamber liquid and vapor incinerators are the most common, accounting for 64% of all the hazardous waste incinerators operating in 1983. This percentage has probably not changed drastically since 1983 since the majority of the new incinerators being installed are of this type.
- In 1983 the second most common hazardous waste incinerators were rotary kilns (17%) and fixed hearth units (12%). Rotary kiln units are under consideration at a number of sites so their percentage has probably increased since 1983.
- Fluidized bed units represented 3% of the units and multiple hearth 2% of the units in 1983. A number of fluidized bed units have been constructed so their percentage is probably on the increase.

LIQUID INJECTION INCINERATORS. A single-chamber incinerator for the destruction of liquid and gaseous wastes is the most economical and most common type of thermal treatment unit. A 1983 survey⁴ found that this type of incinerator accounted for 64% of all the incinerators in service. If suitable for the waste, this type of incinerator should be the first choice for the destruction of hazardous waste.

Design of Liquid Injection Incinerators. A wide variety of units are being marketed. The two major types are horizontally fired and vertically fired units. Tangentially fired units are also available. These incinerators use a refractory-lined chamber where liquid or gaseous wastes are fed through a burner at the inlet end of the chamber. The chamber provides a long enough residence time for the hot combustion gas, with adequate turbulence and adequate excess air, to complete the combustion. Vertical down-fired units may be used to handle salty wastes.

The tangentially fired (vortex) units fire the waste at an angle through the side of the combustion chamber to create a vortex for increased turbulence. These units can handle a higher capacity than the standard horizontal and vertical units because of the greater turbulence, but they also require more maintenance because of increased attack on the refractory. Two of the primary uses for vortex units are the incineration of aqueous waste, which can require greater mixing if the waste is dilute, and to expand units already in service.

BURNERS. To achieve complete destruction, it is critical that the waste be ignited at the inlet end of the combustion chamber. This is achieved by feeding the waste through a burner. The burner mixes the waste with the correct amount of air, atomizes liquids or aqueous waste, and provides a pilot flame to make sure that the waste remains ignited.

High-Btu gases can be handled in a standard burner that mixes the gas with excess air and then lights it. Low-Btu gas may require special burners that mix the waste gas with supplemental fuel to achieve a stable flame temperature.

A liquid will not burn until it vaporizes. To achieve vaporization within an acceptable distance from the end of the burner, liquid burners are designed to atomize the liquid into small drops that vaporize quickly. There are a number of different types of liquid burners that can be used depending on the characteristics (especially the viscosity) of the waste:

- Air atomization is used for small volume, low-viscosity waste.
- High-pressure air or steam atomization is the most common burner.
- Mechanical agitation is used if solids are present in significant quantities.
- Sonic nozzles use high-pressure air or steam to produce sound waves that break the waste into small drops. This type is also used to handle liquids containing solids.

For atomization of liquids, the most important property is viscosity. If the liquid is too viscous, it cannot be pumped to the incinerator. If it is too viscous, it cannot be atomized into small enough drops in the burner. In general, waste can be pumped as long as the viscosity is less than 10 000 SSU, and can be atomized as long as the viscosity is less than 750 SSU. If the waste is between 750 and 10 000 SSU, it may be possible to heat the waste to reduce its viscosity below 750. If the waste cannot be heated or blended with low viscosity wastes to get below 750 SSU, then the waste will need to be handled in one of the other types of incinerators that allow waste to be fed through a lance. Other types of incinerators provide agitation and holdup of the liquids to allow vaporization and destruction. Even with the other types of incinerators, steam atomization can still help to disperse a viscous liquid and improve destruction.

SYSTEM DESIGN. Figure 8.4 shows a typical liquid injection system. The liquid is atomized with air and then fired in a horizontal combustion chamber. In this case, the waste contained significant quantities of inorganic salts (ash) and acid gases so a venturi scrubber is provided to remove particulates and a packed bed scrubber is provided to remove the acid gases from the stack gas. An induced draft fan is used to pull the combustion gases through the system and then discharge them up the stack.

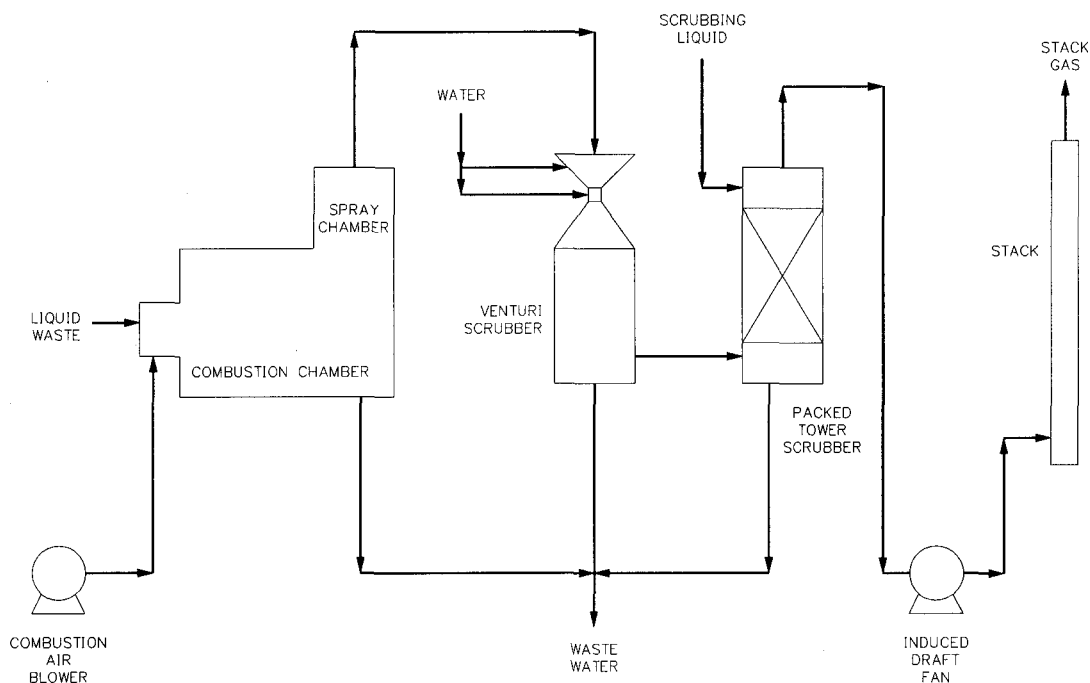


Figure 8.4 Horizontally fired liquid injection incinerator system.

ALTERNATE DESIGN FOR NITROGEN OXIDE CONTROL. Nitrogen oxides (NO_x) formed by the oxidation of atmospheric nitrogen at high temperatures can be controlled by using special, low-temperature burners. However, organically bound nitrogen in the waste cannot be prevented from forming NO_x unless the combustion is carried out in an oxygen deficient (reducing) atmosphere.

The standard approach to handling organically bound nitrogen is to use a two-stage combustion system. Two combustion chambers are used. The first chamber burns the waste in a reducing atmosphere to form nitrogen. The combustion gas is cooled as it leaves the first combustion chamber and then is mixed with excess air to complete the destruction of organics in the gas.

OPERATING CONDITIONS FOR LIQUID INJECTION INCINERATORS.

Liquid injection incinerators operate with residence times in the combustion chamber of between 0.5 and 2.0 seconds,⁵ although a few new units are designed for residence times greater than 2 seconds to provide excess capacity for future expansions or to provide excess residence time in case difficult to destroy wastes are burned in the future.

Operating temperatures range between 800 and 1600°C (1498 to 2938°F). Refractory degradation frequently occurs in the 1400°C (2578°F) range, thus most operation is below that temperature. Special refractories are available with fusion temperatures above 2000°C (3658°F) if required for high-temperature operations.

In theory, liquid and vapor incineration units can operate with only a few percent excess air. Some commercial boilers operate with about 5% excess air. Hazardous waste incinerators normally require a higher percentage excess air because of variations in the heat content and composition of the waste; 20 to 60% is a common excess air for hazardous waste service.⁴

Wastes Applicable for Destruction in Liquid Injection Incinerators. In general, any gas or low-viscosity liquid with little or very small particle solids can be destroyed in a liquid injection incinerator. The limit is that only liquids that can be atomized can be burned.

Gases that can be destroyed are

- Vents from process units or other hazardous waste treatment units that contain organic materials. Continuous vents, vents containing highly toxic compounds, and vents containing acid gases that could not be handled in a flare are all candidates for incineration.
- Vents from other thermal treatment units that do not achieve complete combustion of vapors. Afterburners are really liquid injection incinerators downstream of other combustion units.
- Vents containing burnable particulate matter. This is another afterburner application.

Liquid wastes that can be destroyed are

- Low-viscosity liquids;
- Viscous liquids that can be heated to a viscosity below the 750 SSU maximum possible for atomization in a burner;
- Liquids with solids less than 3.2-mm (0.13-in.) diameter; and
- Aqueous wastes with organic constituents that require destruction.

Wastes that should not be fed to a liquid injection incinerator are liquids too viscous to atomize (greater than 750 SSU), liquids with particles larger than 3.2-mm (0.13-in.) diameter, sludges, and bulk solids.

Liquids containing large quantities of heavy metals may not be good candidates for incineration of any type, because of the potential for excessive concentrations in the stack gas.

Advantages and Disadvantages of Liquid Injection Incinerators. Advantages of liquid injection incinerators include

- Low investment, operating cost, and maintenance;
- High turndown ratio; and
- Fast temperature response to changes in the waste feed rate or changes in the waste characteristics.

Disadvantages include

- Only wastes that can be atomized can be destroyed.
- Particle size must be controlled and burners are susceptible to plugging.
- Burners may not be able to handle wastes that dry and form cakes as they pass through the burner.

CATALYTIC OXIDATION. The design of catalytic oxidation units is very similar to the design of liquid injection incinerators, except that the combustion chamber is filled with catalyst.

Catalytic oxidation units are used primarily to destroy organic materials contained in dilute gas streams. They are frequently economical for dilute streams because the catalyst allows operation at lower temperatures so less fuel is required to heat the inert gas to combustion temperatures.

Design of Catalytic Oxidation Units. Catalytic oxidation units use a refractory-lined chamber where gaseous wastes are fired through a burner at the inlet end of the chamber. The chamber is filled with a catalyst that promotes destruction of the organic content of the waste at lower temperatures than would be possible in liquid injection incinerators.

Historically, most of the catalysts have been noble metals (platinum or palladium) on a porous medium. But newer catalysts have been made of alumina. The catalysts are placed across the flow area in the combustion chamber for good contact with the gas.

The design of a catalytic combustion system is similar to the system for liquid injection incinerators shown in Figure 2. The catalytic oxidation system requires gas cooling and a packed bed scrubber if significant acid gases are present in the waste. However, a venturi scrubber or other particulate

removal device would probably not be required. If enough ash is present to require scrubbing, a catalytic unit probably cannot be used because of potential plugging of the catalyst.

Operating Conditions for Catalytic Oxidation Units. Catalytic oxidation units typically operate at lower temperatures than liquid injection incinerators. Temperatures typically run between 550 and 700°C (1048 and 1318°F). Temperatures above 800°C (1498°F) are not used because of potential degradation of the catalyst.

Wastes Applicable for Destruction in Catalytic Oxidation Units. In general, any gas containing dilute organics is a candidate for destruction in a catalytic unit. Concentrated vents would normally not be a candidate because fuel requirements are low, reducing the economic incentive for a catalytic unit, and combustion temperatures can exceed the design temperature of the catalyst.

Any dilute gas stream leaving a process or hazardous waste treatment step should be a candidate for catalytic oxidation. Catalytic oxidation units can also serve as afterburners for other thermal treatment units.

Gas streams that are not candidates for catalytic oxidation are

- Concentrated gas streams,
- Gas streams containing particulates which can plug the catalyst,
- Gas streams containing vanadium and heavy metals which can foul the catalyst, and
- Gas streams containing large quantities of sulfur or chlorine which can reduce the effectiveness of the catalyst.

Advantages and Disadvantages of Catalytic Oxidation. The advantage of catalytic oxidation is its low fuel requirements for dilute gases.

The disadvantages include

- Units are susceptible to variations in the Btu content of the waste. The catalyst can be destroyed by high-temperature excursions.
- Maintenance can be high because of plugging or poisoning of the catalyst.
- The pressure drop is higher than for liquid injection incinerators, so power costs will be higher.

FLUIDIZED BED INCINERATORS. Design of Fluidized Bed Units. A fluid bed is usually a refractory-lined vessel that is divided into two parts by a distributor plate (Figure 8.5). Air enters the fluid bed through a plenum and is forced through a distributor plate. There are many different distributor plate designs, but one of the more common designs is shown in Figure 8.5.

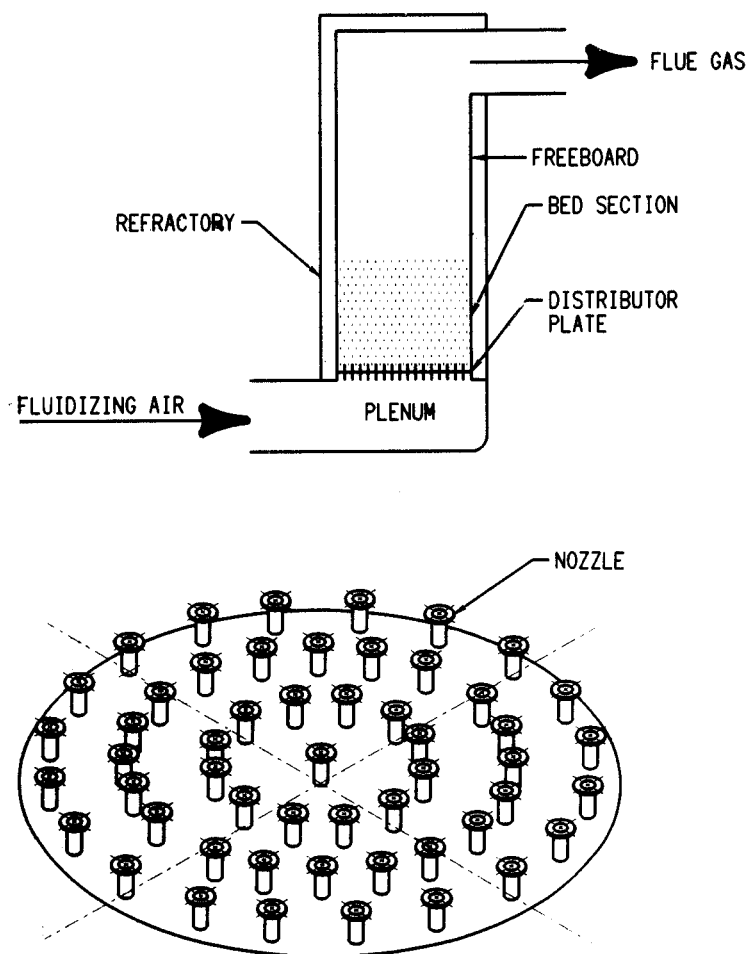


Figure 8.5 Fluid bed incinerator.

Air is forced through the distributor by either a centrifugal or positive displacement blower. The distributor plate is designed such that the ratio of the pressure drop across the distributor to the pressure drop across the bed section is in the range of 0.3 to 0.7.

Above the distributor rests a bed of fine inert material. The objective of the bed material is to provide a medium for rapid heat transfer. Bed depth can vary from 0.6 to 1.8 m (2 to 6 ft), and bed particle sizes can range from 300 μ m to 1.6 mm.

The air, or fluidizing media, that is blown through the distributor plate percolates up through the bed material. When the bed is fluidized it looks as if it is suspended, with gas bubbles rising through it. The pressure drop across the bed increases with increasing air flow rates until it is fluidized.

As the bed fluidizes, it expands. The expanded bed height is generally 1.5 to 2.5 times the static bed height. Once the bed is fluidized an increase in air

flow rate will not appreciably increase the pressure drop across the bed. At the upper limit, if too much air is blown into the bed, the bed material itself will be entrained and transported out of the vessel.

The bed material circulates within the bed and provides excellent dispersion and mixing of the feed materials. Highly viscous liquid wastes can be pumped or conveyed into the top portion of the expanded bed. Solid material can be conveyed into the expanded bed. Above the bed is the section called the freeboard. Particles of bed material are thrown up into the freeboard by bubbles bursting at the top of the bed. The freeboard must contain adequate transport disengaging height so that the bed material can fall back into the bed.

In fluid bed combustion systems, the pressure in the plenum, the pressure above the distributor plate, and the pressure in the lower half of the expanded bed are usually positive. The point of zero pressure usually occurs slightly above the midpoint of the expanded bed. This ensures that the pressure is negative at the point where the feedstock is introduced. The freeboard pressure is usually slightly negative.

The amount of freeboard designed into a fluid bed depends on the operating conditions of the bed. Superficial velocities in the bed section usually average 0.6 to 1.8 m/s (2 to 6 ft/sec). The superficial velocity of the bed section is 1.5 to 2 times the minimum fluidization velocity of the bed material itself. Sometimes the diameter of the vessel is expanded in the freeboard section to slow down the flue gases to prevent the elutriation of bed material.

Operating Conditions for Fluidized Bed Units. Wastes can be destroyed in fluid beds at low temperature because of the high heat and mass transfer rates associated with fluidization. Fluid beds are generally operated between 705 to 982°C (1300 and 1800°F). Temperatures in the bed are fairly uniform, usually within $\pm 2.8^{\circ}\text{C}$ ($\pm 5^{\circ}\text{F}$) of the set point in all parts of the bed. The freeboard temperature in combustion units can run 10 to 93°C (50 to 200°F) higher than the bed temperature. A large difference between the bed and freeboard temperature can be the result of freeboard burning.

The upper limit on bed temperature is set by the fusion temperature of the bed material or the fusion temperature of the ash associated with the feedstock. The lower limit on bed temperature is set by the feedstock itself, but in general is not less than 705°C (1300°F) for combustion processes.

The fluid bed can operate in combustion (oxidizing) or pyrolysis (reducing) mode. Most fluid bed incinerators operate in the combustion mode. Since they operate at inherently low temperature, they normally have low emissions of NO_x emissions.

Wastes Applicable for Destruction in Fluid Bed Units. The fluid bed can be used to destroy a wide variety of wastes, but it is especially useful for processing wet sludges and low-Btu waste. Although the fluid bed can

process solids, the solids must be of fairly small and uniform size and, therefore, often require substantial preparation. Highly viscous liquids can be pumped directly into a fluid bed, but their devolatilization can cause freeboard burning.

Advantages and Disadvantages of Fluid Beds. The main advantage of the fluid bed is that it has a relatively low capital cost. The fluid bed operates at low temperatures and low excess air rates, which translate into reduced operating costs.

The fluid bed has no internal moving parts and, therefore, requires little maintenance. It is ideal for the destruction of wet sludges because the natural bumping and grinding motion of the bed disperses the waste, while the rapid heat and mass transfer characteristics of the bed efficiently dry and combust it. The fluid bed handles low-Btu waste extremely well because it can operate effectively at low excess air rates.

The fluid bed can be operated on a noncontinuous basis (day shift only) because the bed retains heat during a shutdown without the addition of auxiliary fuel.

One of the disadvantages of the fluid bed is that it cannot handle large solid pieces, and fairly extensive preparation of solid waste is required prior to processing. Feeding solid waste to the bed can also be difficult.

Another disadvantage is that it cannot handle wastes with high salt contents. Sodium chloride melts at 800°C (1472°F). If the waste contains sodium sulfate as well as sodium chloride, eutectics that melt at temperatures as low as 538°C (1000°F) can be formed. These low-melting eutectics cause the bed to fuse and defluidize.

Some bed material is lost through attrition due to the natural bumping and grinding motion of the bed.

ROTARY KILN INCINERATORS. Rotary kiln incinerators can handle a wide variety of wastes. The rotating motion of the kiln provides continuous mixing of the charge and promotes thorough destruction of the waste.

Design of Rotary Kilns. A rotary kiln is a refractory-lined cylindrical vessel that lies horizontally on a slight incline. The slope of the kiln can vary from 2 to 5.2%. The slope of the kiln helps to move the solid charge mass along the length of the kiln. Figure 8.6 shows the basic design of a rotary kiln incinerator.

The vessel rotates slowly. Solids, liquids, and sludges can be destroyed in the rotary kiln. Dams are sometimes installed at the discharge end of the kiln to help retain the solid charge. Kilns used for the destruction of hazardous waste have an L:D ratio that varies from 2:1 to 10:1. The length and diameter of the kiln are determined by the residence time requirements of the solid

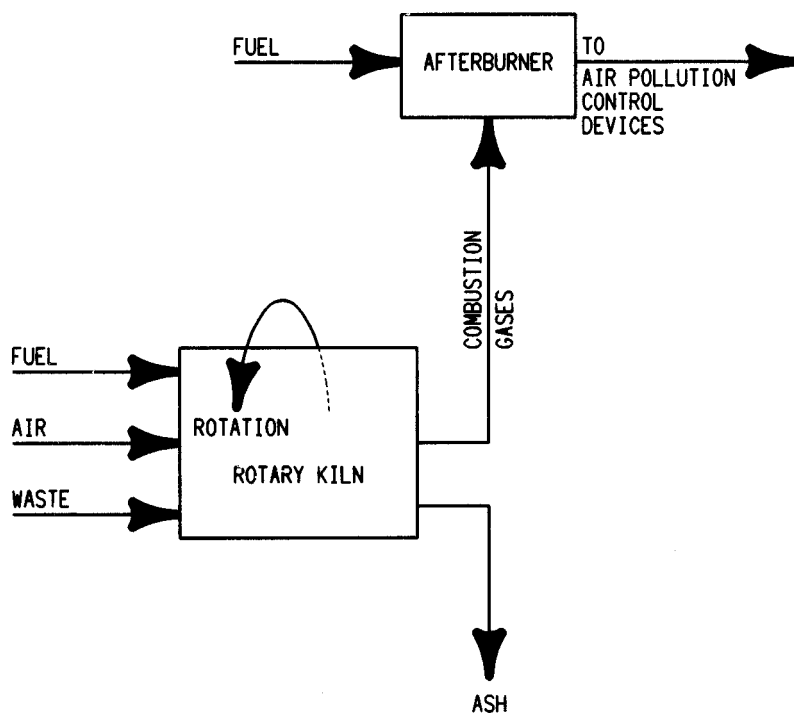


Figure 8.6 Rotary kiln incinerator.

charge and by the charge rate. Residence time can be estimated from the following equation:

$$T = \frac{0.19 \times L}{N \times D \times S}$$

Where

- T = residence time, minutes;
- L = kiln length, ft;
- N = rpm;
- D = diameter, ft;
- S = kiln slope, ft/ft.

The kiln is supported by riders that are like cogged bands around the diameter of the outer shell. The shell is constructed of steel, and surface temperatures on the shell range from 93 to 260°C (200 to 500°F). Temperature profiles in the kiln are a function of the ratio of liquid to solid waste being fired as well as the heating value and moisture content of the waste. High-Btu solids have a tendency to release heat rapidly in the front end of the kiln. Wet solids dry first and have a tendency to release their heat towards the discharge end of the kiln.

The byproduct of rotary kiln incineration is either a solid ash or a liquid slag. The ash or slag drops out of the discharge end of the kiln into a wet trough where the ash is cooled and the slag is solidified and cooled. In slagging kilns, a layer of slag coats the refractory and provides an excellent heat transfer surface as well as a protective coating for the refractory.

Liquid waste or auxiliary fuel is atomized through a primary burner that is mounted on the face of the kiln. The burner can fire either cocurrent or countercurrent to the flow of solid material. Countercurrent firing is used when the solids are very wet so that some fuel economy can be realized. Flame from the primary burner penetrates 20 to 30% of the length of the kiln.

A secondary combustion chamber is usually built after the kiln. The kiln volatilizes and combusts the waste and the secondary combustion chamber completes the oxidation of any gases that escape the kiln unoxidized.

Operating Conditions for Rotary Kilns. Rotary kilns can operate over a wide range of temperatures, but usually fall within the range of 816 to 1649°C (1500 to 3000°F). Kilns can operate in ashing or slagging modes. The characteristics of the ash, together with the operating temperature of the kiln, determine whether the kiln will produce ash or slag as a byproduct.

Kilns usually operate under negative pressure to minimize fugitive emissions and prevent any possibility of leakage of toxic waste into the atmosphere at seal interfaces.

Kilns rotate at speeds in the range of 0.5 to 3 rpm. The rotational speed determines in part the residence time of solid material in the kiln. Solids loading in the kiln vary from 5 to 15% of the internal volume of the kiln.

To reduce operating costs, kilns are operated 24 h/d, 7 d/wk. When the kiln is not being fed waste material, the temperature is maintained by firing auxiliary fuel. Keeping the kiln at operating or near-operating temperature reduces the wear and tear on the refractory which is the single most expensive maintenance item for the kiln.

Wastes Applicable for Destruction in Rotary Kilns. Rotary kilns can handle a wide range of wastes, but are best suited to solid waste. The rotating motion of the kiln serves to constantly expose fresh surfaces of the solid waste to heat and oxygen. Solids that have a tendency to roll out of the kiln can only be incinerated in kilns if dams are installed to prevent the waste from rolling out before it is processed.

Highly aqueous organic sludges are not well suited for destruction in rotary kilns. They tend to form a ring inside the kiln that prevents the discharge of the ash. They also create unprocessed sludge balls.

Advantages and Disadvantages of Rotary Kilns. The main advantages of rotary kiln incineration are that the kiln will accept a wide variety of wastes and provides continuous mixing of the charge materials. The kiln can incin-

erate waste that must be packaged in drums or boxes for any number of reasons. The kiln can incinerate solids, liquids, and sludges. The rotary kiln can operate over a wide range of temperatures to accommodate even the most difficult to destroy wastes. The kiln is a very forgiving piece of equipment.

The main disadvantages of the rotary kiln are that the capital costs involved are very high and they tend to require a lot of maintenance. The refractory inside the kiln is very susceptible to thermal shock and is an expensive maintenance item.

The seals between the stationary walls and rotating cylinder are also high maintenance items. If a container of high-Btu waste is loaded into the kiln and burned rapidly, "puff-out" of the seals could occur because the pressure in the kiln becomes positive. Spikes of carbon monoxide in the exhaust gas can also result from the rapid combustion of containerized waste.

Another disadvantage of the rotary kiln is that it is difficult to control the slagging process in the kiln. If slagging is undesirable, but occurs in the kiln, it is best controlled by limiting the component in the feedstock that is causing the slagging.

MULTIPLE-HEARTH INCINERATORS. Multiple-hearth units have a high thermal efficiency and can be an economical alternative for handling wet sludges. Historically, these units have been used for the incineration of wastewater treatment sludges. A 1983 survey⁴ found that multiple-hearth units represented 2% of all the hazardous waste incinerators in service.

The use of multiple-hearth incinerators in hazardous waste service has been limited by the potential for toxic vapors to evaporate out of the sludge and be discharged up the stack. This can sometimes be corrected by firing gas on the upper hearths, but normally requires a separate afterburner. The conversion of existing units to hazardous waste service has often been limited by a lack of space to install a separate afterburner.

Design of Multiple-Hearth Incinerators. Figure 8.7 shows a typical hearth incinerator. The design includes a refractory-lined shell, central rotating shaft, multiple solid flat hearths, rabble arms to move the waste across each hearth, an air blower, fuel burners (which can be staged up the side of the shell), waste feeding system, and an ash removal system. Lances can be located along the length of the shell to feed viscous liquids. In hazardous waste service, an afterburner would normally be required to complete the destruction of organic materials vaporized in the upper section of the unit.

Sludge or bulk solids can be fed through the furnace using a screw feeder or a flap gate. The rotating air-cooled central shaft, with air-cooled rabble arms, distributes the waste across the hearths and moves it to holes where it can drop to the next lower hearth. The rabble arms also serve to agitate the waste, exposing the entire volume to the hot gases. The waste drops from

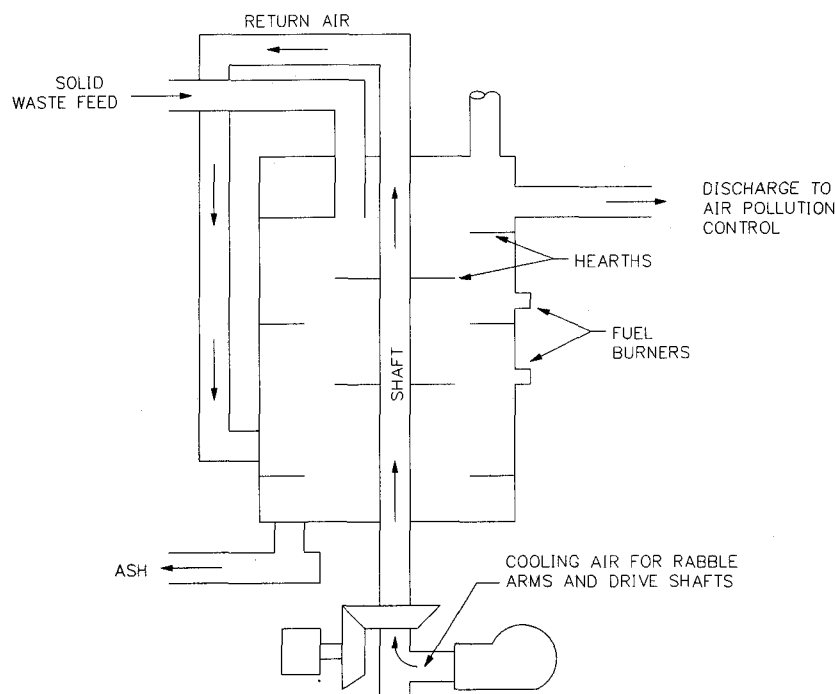


Figure 8.7 Typical multiple-hearth incinerator.

hearth to hearth until it is discharged as ash at the bottom. Liquid or gaseous wastes and auxiliary fuel may be injected into the unit through burners.

A typical system design for hazardous waste service requires a feed preparation and feeding section, separate afterburner (critical), particulate removal system, and packed tower scrubbing system (if acid gases are present in the waste).

Operating Conditions for Multiple-Hearth Incinerators. A multiple-hearth incinerator typically has three operating zones:

- The upper hearths heat up the feed and dry any wet sludges. This zone typically operates between 350 and 550°C (700 to 1050°F).
- The middle zone is where the solids are incinerated. The temperature in this zone typically ranges between 800 and 1000°C (1500 to 1860°F). Waste liquid and gas streams, along with any required supplemental fuel, are fired near the bottom of this zone. Firing can be carried out at individual hearths to control the temperature profile down the zone.

- The bottom zone is where the ash is cooled by transferring heat to the incoming air. This zone typically ranges between 200 and 350°C (420 to 700°F).

If an afterburner is not required, a multiple-hearth unit can be very thermally efficient because of the countercurrent flow. The combustion gas is cooled by exchanging heat with the incoming feed and the ash is cooled by preheating the incoming air. In a properly designed unit both the combustion gas and the ash will exit at below 550°C (1050°F). These low exit temperatures can reduce the fuel firing requirements for wet sludges by 40 to 50% versus the fuel required for a rotary kiln unit.⁶

A multiple-hearth unit can still be thermally competitive with a fluidized bed unit and more efficient than a rotary kiln unit even if an afterburner is required. An afterburner will normally be required in hazardous waste service. The unit still saves energy because of the transfer of heat between the ash and the incoming air. The literature⁶ also indicates that multiple-hearth units do not require such high temperatures in the afterburner because the high residence time within the unit results in more complete destruction of the organic materials in the combustion gas.

The solids residence time is normally very high, resulting in complete destruction of the organic content in the ash.

Wastes Applicable for Destruction in Multiple-Hearth Incinerators.

Most hazardous wastes can be destroyed in a multiple-hearth incinerator (see Table 8.2). The most common application of multiple-hearth units is the destruction of wet sludges where thermal efficiency is important.

Multiple-hearth units cannot handle drums and very large bulky solids. Any drums would need to be emptied and the contents fed to the incinerator. Large bulky solids would best be fed to a rotary kiln or a fixed hearth unit. Multiple-hearth units also are not suited to handle wastes containing fusible ash.

Advantages and Disadvantages of Multiple-Hearth Incinerators. The advantages of multiple-hearth incinerators include

- High thermal efficiency, especially if an afterburner is not required;
- High solids residence time allowing the complete destruction of organic material in the ash;
- Ability to handle a wide variety of waste with a wide variety of chemical and physical properties;
- Maintaining a desired temperature profile by adding fuel burners to any hearth; and
- High turndown ratio (to 35%).

Disadvantages include

- Potential for the discharge of toxic vapors out the stack.
- High investment and high maintenance costs.
- Temperature response is slow because of the long residence time.
- Units are susceptible to thermal shock from feed interruptions or from excess amounts of water in the feed.
- Unsuitable for wastes containing fusible ash, for large bulky solids, or for feeding drums.

FIXED HEARTH INCINERATORS. Historically, fixed hearth units have been used for the incineration of municipal waste. They are ideal for the destruction of large bulky wastes, hazardous waste, and hospital waste. They can handle organically bound nitrogen wastes with minimal NO_x generation. A 1983 survey⁴ found that fixed hearth units were the third most popular hazardous waste units behind liquid injection and rotary kiln units: 12% of the incinerators were fixed hearths.

Other names for fixed hearth units are controlled air, starved air, and pyrolytic units. These names come from the standard practice of operating the solids combustion zone in a reducing (oxygen deficient) atmosphere to minimize NO_x formation.

Design of Fixed Hearth Units. Fixed hearth units employ a two-stage combustion process. Waste is ram fed into the first stage, or primary chamber, where the waste is burned in an atmosphere of less than stoichiometric air. The resultant smoke and pyrolytic vapor products are then passed to the second chamber along with the ash and any unburned solids. In the second chamber (burnout chamber) excess air is added and the remaining organics are destroyed. In hazardous waste service, an afterburner is normally used to guarantee destruction of any organics remaining in the combustion gas.

Figure 8.8 shows a typical fixed hearth incinerator. The unit shown uses a stepped grate system. Rotating grate systems are also available for small units.

GRATE DESIGN. The design of the grate is as critical as the design of the feed system for a fixed hearth incinerator. The grate serves three critical purposes:

- It moves the solids through the incinerator.
- It distributes the solids across the combustion zone.
- It distributes the air in the combustion zone.

Most large fixed hearth systems use stepped reciprocating grate systems.⁷ These systems are constructed from alternating modules of reciprocating and

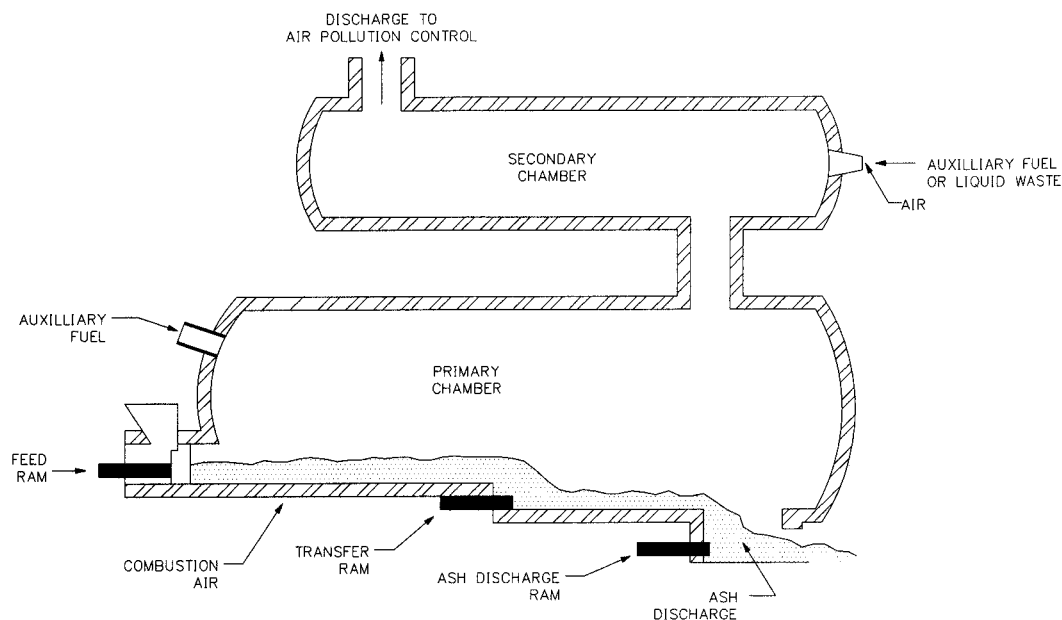


Figure 8.8 Fixed hearth incinerator.

fixed grate bars. The movement of the reciprocating bars rolls and mixes the wastes to allow the hot air to reach all the burning material. The reciprocating bars also serve to move the waste through the unit.

Small modular units are available that can be economical for installation at individual small-quantity generators. These units may use a single reciprocating grate. Rotating grates are also available.

NITROGEN OXIDE CONTROL. Most of the NO_x formation in fixed hearth units comes from organically bound nitrogen in the solid waste. Flame temperatures are normally too low for significant generation of NO_x from the oxidation of atmospheric nitrogen.

Normally NO_x is controlled by the two section design. Since the first stage operates in an oxygen deficient atmosphere, organic nitrogen is reduced to nitrogen. The combustion is then completed in the second stage or afterburner.

SYSTEM DESIGN. In addition to the afterburner, a typical system would also include a quench section, particulate removal, and if significant acid gas is present, a packed bed scrubber.

Operating Conditions for Fixed Hearth Incinerators. Three actions take place inside the units: drying of the solid waste, main combustion, and bur-

nout. Combustion of the solids and the final burnout of all organics in the solids both tend to occur at temperatures of 650 to 1000°C (1230 to 1860°F). Destruction of the organic content of the combustion gases is then carried out in the afterburner at temperatures of 750 to 1100°C (1410 to 2040°F).

Combustion in the first stage, the pyrolytic stage, of the unit is normally carried out at only 50 to 80% of the stoichiometric air. The second stage operates at 50 to 80% excess air, and the afterburner at 100 to 200% excess air.⁷

Wastes Applicable for Destruction in Fixed Hearth Incinerators. As shown in Figure 8.2, a fixed hearth unit can handle almost any type of waste with the possible exception of drums which need to be emptied and the contents fed to the unit. The units also cannot handle wet sludges that will not move well on the grates.

The primary purpose of fixed hearth units is the destruction of wastes containing large bulk solids. This is the reason the units have been so popular for the incineration of municipal waste. The units are also particularly effective in handling solid wastes with large quantities of organically bound nitrogen, since combustion can be staged to minimize NO_x formation.

Advantages and Disadvantages of Fixed Hearth Incinerators. Advantages of fixed hearth incinerators include

- Effective for handling large, bulky solids.
- Can handle solids with high organically bound nitrogen loads with minimal NO_x formation.
- Small modular units can be very economical for the destruction of waste at the site of small quantity generators.

Disadvantages include

- Cannot handle wet sludges that tend to fall through the grate.
- Most of the grates are designed to handle European municipal waste. They can be difficult to operate with hazardous waste or with U.S. municipal waste.
- The grates can be melted if high-Btu waste is suddenly fed into the unit.
- High maintenance costs.

WET OXIDATION. Wet oxidation is a group of processes for oxidizing suspended and dissolved organics in an aqueous waste stream. These processes are used to treat streams that are too dilute to incinerate economically, but are also too toxic to treat biologically.

There are a number of wet oxidation processes available including

- Wet air oxidation,
- Catalyzed wet oxidation,
- Supercritical fluid oxidation, and
- High-temperature wet oxidation.

Of the four types, the wet air oxidation process is commercially available. The other three types may be considered as emerging technologies.

Design of Wet Air Oxidation Systems. Wet air oxidation is the aqueous-phase oxidation of organic substances at elevated temperature and pressure. An oxygen containing gas, usually air, is bubbled through the liquid in a reactor. The temperature is kept high enough for oxidation to occur, and the pressure is kept high enough to prevent evaporation of the water.

Figure 8.9 shows a typical flow scheme for a continuous wet air oxidation unit. The wastewater stream pressure is increased to the system pressure and is fed into the system using a pump. The wastewater passes through a heat exchanger which preheats the waste by exchanging heat with the oxidized effluent. The temperature of the feed is increased to the level required to sustain the oxidation reaction in the reactor. Air is injected into the reactor. As

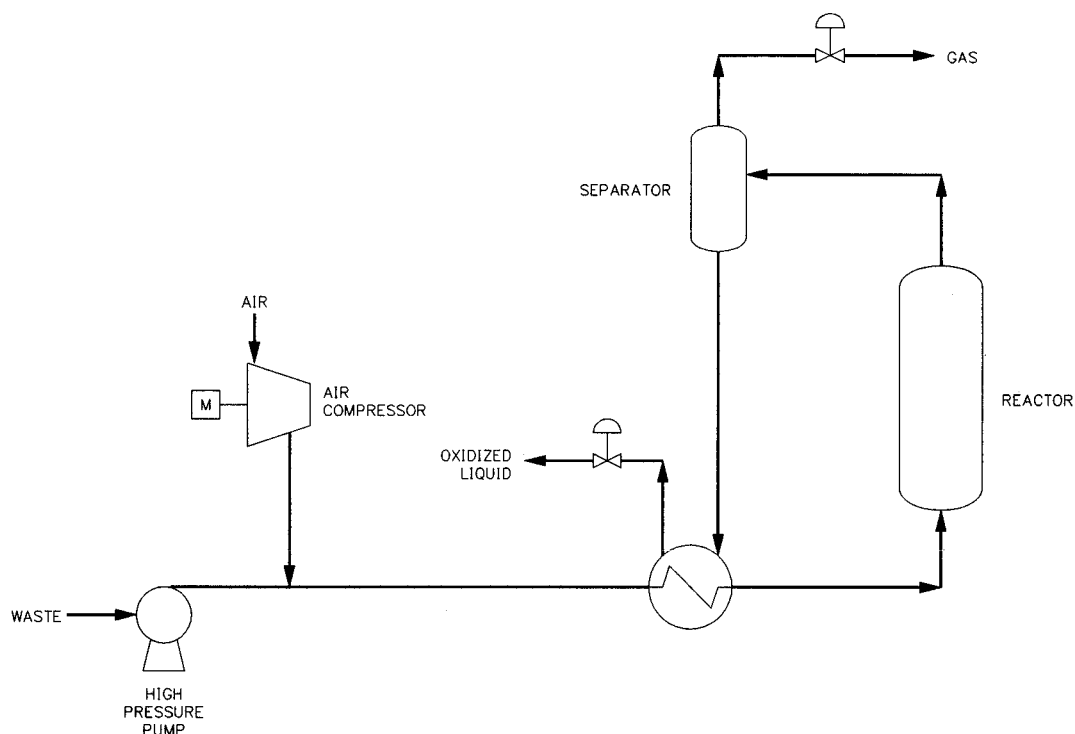


Figure 8.9 Wet air oxidation.

xidation occurs, the heat of combustion is liberated increasing the temperature of the reaction mixture.

Operating Conditions for Wet Air Oxidation. Temperature is the most important variable affecting the oxidation reaction rate. The reaction typically occurs at between 175 and 340°C (370 to 670°F) with about 300°C (600°F) needed to achieve a 95% reduction of COD within a practical reaction time.

The system pressure is maintained high enough to prevent evaporation of the water, typically between 2026 and 30390 kPa (20 and 200 atm).

Wastes Applicable for Destruction Using Wet Air Oxidation. In general, wet air oxidation is most promising for aqueous waste streams that are too dilute for economical incineration or are too toxic for biological treatment. It has potential for any aqueous waste containing nonchlorinated toxic organics. It reportedly does not work well on chlorinated organics.

Specific organic compounds that have reportedly been treated using wet air oxidation are phenols, cyanides, DDT, and nitrosamines.

Advantages and Disadvantages of Wet Air Oxidation. The advantages of wet air oxidation include

- Low energy input. The process can be thermally self-sustaining if the oxygen uptake is above 15 g/L.
- System volumes are small because the liquid phase does not occupy as much space as the gas phase.
- The products of wet air oxidation tend to stay in the liquid phase.

Disadvantages include

- The process reportedly will not handle chlorinated organics.
- The off-gas may require scrubbing, carbon adsorption, or fume incineration to reduce hydrocarbon emissions or odors.

***T*HERMAL TREATMENT SYSTEM AUXILIARIES**

Thermal treatment systems are divided into a number of components, each of which has its own treatment methods. The four major components are

- Feed systems,
- Thermal treatment systems,
- Emission control systems, and

- Ash handling and wastewater treatment.

Each of the above components has a number of possible unit operations or treatment methods that can be used. The approach for selecting a system is to screen the major thermal treatment technologies for applicability to the waste being treated. All the components needed to support the attractive thermal treatment systems are then determined. The system that will treat the desired range of waste streams most economically is then selected.

WASTE RECEIPT, HANDLING, AND STORAGE. Prior to thermal treatment, the handling, storage, and feeding of hazardous waste must be carried out in a manner that is safe, minimizes emissions, and prepares the waste for efficient operation of the thermal treatment system. The physical form of the waste and the type of thermal treatment system determines the required handling, storage, and feed systems.

Gases and Vapors. Gases and vapors are normally received by pipeline from other parts of the plant or treatment system. Storage would normally not be provided. Blowers may be required to move the vapor to the incinerator and some type of flashback protection may be required such as knockout pots, water seal drums, or flame arrestors.

Liquids. Liquids can arrive by pipeline or fiberpack if the liquid is being shipped from within the plant, or by drum or fiberpacks within an “overpack” drum if shipment is coming from outside the facility, by tank truck, or by rail car. Tank cars can hold up to 30 m³ (8000 gal) and rail cars up to 98 m³ (26 000 gal).

Liquids can be burned by feeding fiberpacks or drums directly into a rotary kiln unit, or can be burned by direct injection from a pipeline or from a tank truck or rail car. The normal approach is to transfer the liquid to storage where it can be blended with other compatible liquids that complement the characteristics of the liquid. The liquid would first be sampled and checked for compatibility with other liquids. Compatibility screening is important to prevent unwanted reactions in storage. The liquid can then be blended to produce mixtures that have a low enough viscosity for atomization in a burner. The blending can also be used to smooth out variations in Btu and ash content. The liquids are segregated into the following categories:

- Liquids with a low enough viscosity for feed directly to a burner,
- Liquids that can be fed to a burner if they are heated first,
- Liquids too viscous for feed to a burner so they are placed in storage that will allow feeding directly into a lance, and
- Water solutions that must be atomized into the incinerator.

Sludges. Sludges can be received, sampled, and blended in much the same manner as liquids. The main difference is that sludges will normally be fed through a lance into the incinerator instead of being atomized in a burner. The sludges will frequently require agitation in storage and will require circulation loops in any piping to keep the solids from settling out and plugging the system.

Solids. Solids can arrive in fiberpacks from within the plant, in drums or in fiberpacks inside overpack drums if shipment is from outside the plant, or in dump trucks.

The feeding of solids is one of the most critical variables in the design of a thermal treatment system. The feeding of solids that have been segregated to smooth out variations can have a major impact on the capacity of the system.

Drums or fiberpacks are normally sampled before being fed to the incinerator. Any liquids would be decanted to minimize the potential for sudden heat releases when the drum is fed into the incinerator. The drums can also be segregated to smooth out waste feed. For example, a group of drums containing halides can be segregated and fed over a period of time to smooth out the generation of acid gases and thus stay within emission limits. If drums cannot be fed directly into the system, it may be necessary to transfer material from the drum into fiberpacks, shred the drum or fiberpack, or dump the material out of the drum or fiberpack.

Bulk solids need to be stored and then fed into the system. The solids can be pushed into the incinerator with a ram feeder or can be elevated with cranes or conveyors and then dumped into the incinerator.

Any type of solid feed system requires the use of an air lock to prevent sucking air into the incinerator during feeding.

AIR POLLUTION CONTROL DEVICES. The primary products of combustion in a thermal treatment process are carbon dioxide and water. However, there frequently are small amounts of pollutants in the stack gas leaving the combustion chamber that must be removed using air pollution control devices.

The selection of the proper air pollution control device is dependent on a number of factors including

- Federal regulations, which are the most important factor in the selection of a control device,
- Type of waste being burned,
- Type of incinerator,
- Public opposition to installation of the treatment system, and
- Capital cost and operating cost (economics).

The federal,⁸ state, and local regulations define the maximum emission rate (lb/hr or concentration) that is allowed, although public opposition may require the use of lower emission rates. The permit for the treatment system will document the emission rates that must be achieved.

Air pollution control is divided into five main areas:

- Final destruction of organics,
- Combustion gas conditioning,
- Particulate removal,
- Acid gas removal, and
- NO_x control.

FINAL DESTRUCTION OF ORGANICS. A number of the thermal devices (fluidized bed, single-chamber liquid and vapor, and catalytic incinerators) achieve essentially complete combustion of the organics present in the waste. Complete destruction is defined as 99.99% to 99.9999% destruction depending on the application. However, a number of treatment devices do not achieve complete combustion of vapors within the primary combustion chamber (rotary kiln, fixed hearth, and multiple-hearth incinerators) and require additional equipment to achieve emission requirements.

Where required, the control of organic pollutants is normally achieved by final combustion in an afterburner. An afterburner is a simple combustion chamber that provides for the destruction of the combustion gas.

Combustion Gas Conditioning. Venturi scrubbers are capable of handling the hot gases that come from combustion devices. Most of the particulate and acid gas removal devices require that the gas be cooled before it reaches the emission control devices.

There are five primary ways to cool the combustion gas:

- A quench,
- Heat recovery boiler,
- Combustion air preheat,
- Recycle of stack gas, and
- Dilution with ambient air.

Historically, a quench has been used because it is a simple device. Heat recovery is economical, but was not common because the primary goal of the thermal treatment system was to destroy waste. Operators have resisted placing an additional piece of equipment in the process that could reduce the service factor of the process. However, more than 50% of the new systems contain some type of heat recovery.

A quench is a device where water is sprayed into the gas stream. The water evaporates to cool the gas. Some type of contact is required, which can

be as simple as spraying water into the duct leaving the combustion chamber. For more critical applications, a tower can be used with water sprayed into the top of the tower.

If the thermal treatment system is located in a plant where there is a demand for steam, a waste heat boiler may be an economical option. The presence of alkaline salts or other slagging compounds may require special designs, such as water-wall boilers, firetube boilers, or boilers with finless tubes.

If there is no demand for steam, the thermal efficiency of the system can still be improved by installing combustion air preheaters. This type of device is common on fired heaters and has also been used successfully with municipal wastewater sludge incinerators. Again, the presence of alkaline salts may effect the design and applicability of this type of heat recovery.

Particulate Removal. This can be one of the more critical areas in the design of a thermal treatment system. Research by EPA indicates that thermal treatment systems almost always achieve their design destruction of organic material, but do not always achieve their design removal of particulates. There are a number of reasons why systems do not achieve the desired particulate removal efficiencies including

- The particulates may be too small for the particulate removal equipment selected.
- Compounds may be present that vaporize in the combustion chamber and then recondense in the emission control equipment under conditions where the condensation forms very fine particles.

Examples of compounds that may vaporize in the combustion chamber are lead, organic phosphates, and low boiling alkaline salts (if combustion is carried out above the boiling point of the salt). It is critical that analysis for these compounds be carried out during the waste characterization phase of the project.

Table 8.3 lists the most common particulate control devices in thermal treatment systems. If very fine particle removal is required, electrostatic precipitators or bag houses may be required. These devices can remove particles down to 0.1 μm . A number of commercial units and systems that remove very fine (down to 0.1 μm) particulates are now using venturi scrubbers for the primary removal device followed by an electrostatic precipitator. A possible alternative to this is the use of a bag filter.

VENTURI SCRUBBERS. A venturi scrubber is a constricted area (throat) in the duct where scrubbing liquid is introduced. Exhaust gas from the combustion chamber enters the venturi where it is accelerated in the throat to a velocity of approximately 30 to 120 m/sec. The high velocity gas atomizes

the liquid into fine drops that have a high surface area for contact with the particles. One variation of a venturi is a patented model that uses mixing nozzles to shatter the liquid into even finer drops for higher particulate removal efficiency.

Venturi scrubbers are not good for acid gas removal because they only provide one theoretical stage of scrubbing; versus 10 stages possible with packed towers. But venturies do provide some removal and may be adequate if acid gas concentrations are not much higher than the levels allowed in the permit.

Venturi scrubbers can be very efficient for the removal of particles down to 1 μ m in size with a pressure drop of 7.5 to 12.4 kPa (30 to 50 in. H₂O). Particles down to 0.2 μ m can be removed but with a pressure drop of over 24.9 kPa (100 in. H₂O). At pressure drops this high it tends to be more economical to use bag houses or electrostatic precipitators.^{9,10}

BAG HOUSES. Bag houses, or fabric filters, utilize cloth bags to filter the particulates from the combustion gas stream. The bag house contains a number of bags manifolded so that while part of the bags are filtering, other bags can be discharging solids.

The cloths used for the bags are temperature sensitive, so it is critical that the gas be cooled upstream of the bag house. Bag houses do not remove any acid gases. If acid gases are present, an additional air pollution control device, such as a packed scrubber, is needed.

Bag houses are very efficient at removing fine particles with a low pressure drop: down to 0.1- μ m particles at a pressure drop of only 0.5 to 1.5 kPa (2 to 6 in. H₂O).⁹ Their initial investment cost is higher than for a venturi, but the operating cost and energy cost is lower. The larger the combustion gas flow, the more likely that a bag house will be economical.

ELECTROSTATIC PRECIPITATORS. Electrostatic precipitators use electricity to charge particles and separate them from the gas stream. Negatively charged gas ions are formed between emitting and collecting electrodes by applying a sufficiently high voltage to the electrodes to produce a corona discharge. Suspended particulates are charged by bombardment and migrate toward the collection plates.

Electrostatic precipitators can be dry or wet. The wet units use a water spray to help collect the particles and wash them off the collecting plate. The dry units have the advantage of collecting the particulates in a dry form. The wet units are able to achieve some acid gas removal, although high gas concentrations require upstream removal using equipment such as a packed bed.

Both types of electrostatic precipitators are capable of removing fine particles with low pressure drops: down to 0.1- μ m particles at pressure drops as low as 0.25 kPa (1 in. H₂O).⁹

Acid Gas Removal. Acid gases that frequently need to be removed are SO_x , HX , and X_2 with X being chlorine, bromine, iodine, or fluorine. The most common scrubbing medium is caustic although lime can be substituted for caustic, and water can be used for the more soluble compounds, such as hydrochloric acid.

Packed beds are the most common device for acid gas removal, although spray towers, venturi scrubbers, and wet electrostatic precipitators can be used if acid gas concentrations are low. Dry scrubbing systems that use lime, sodium carbonate, or proprietary reagents in a dry form are also available.

Fluidized bed incinerators frequently do not require the use of separate acid gas scrubbing systems. Lime can be added directly to the bed in the incinerator to react with the gases before they leave the system.

PACKED BED SCRUBBER. A packed bed scrubber is a vessel filled with packing. The scrubbing liquid enters at the top of the vessel. The combustion gas normally enters at the bottom for countercurrent upward flow, but can enter at the side in a cross-flow mode. A plate scrubber is a modified version of a packed tower. The plate scrubber uses plates to promote contact between the liquid and vapor, instead of packing. The plate towers are less efficient than packed towers but can be used with higher particulate loadings because they are less susceptible to plugging.

Packed beds can remove particulates but do not have a high efficiency if the particles are less than $10\text{ }\mu\text{m}$. The normal particle size leaving solid waste incinerator ranges from 5 to $10\text{ }\mu\text{m}$.⁵

Packed beds can achieve better than a 99% removal of acid gases. The height of the bed and the pressure drop depends on the percent removal required. In general, the pressure drop is less than 7.5 kPa ($30\text{ in. H}_2\text{O}$).

SPRAY TOWERS. Spray towers are vessels in which a liquid is atomized, at the top, using high pressure nozzles. The atomized liquid forms fine droplets that scrub out particulates and provide a high surface area for acid gas removal.

Spray towers are the simplest and least expensive gas scrubbing device. They are low efficiency, however, and can be used for only the simplest particulate and acid gas scrubbing requirements. Their most common use is as a quench upstream of other air pollution control devices.

Nitrogen Oxide (NO_x) Control. Nitrogen oxides can come from two sources in thermal treatment systems: from the high temperature oxidation of nitrogen in burners, or from the oxidation of organic nitrogen in the waste.

Nitrogen oxide formed in the burners is controlled by using low temperature burners, a type of burner commonly used in plant fired heaters to control NO_x .

Scrubbing systems are available for removing nitrogen oxides from combustion gases, but these systems are not in widespread use.

The most common method of controlling NO_x from the burning of organic nitrogen compounds is to use a two-stage combustion system. The initial combustion is carried out in an oxygen deficient (reducing) atmosphere that tends to reduce the organic nitrogen to nitrogen. The second stage of combustion is then carried out with excess air to complete the destruction of any organic compounds.

Fluidized bed incinerators can provide both stages within a single chamber; a reducing atmosphere is used in the bed with excess air added above the bed. However, most thermal treatment units require two combustion chambers with cooling between the chambers.

ASH HANDLING AND WASTEWATER TREATMENT. **Ash Handling.** In a properly designed thermal treatment system, the ash leaving the combustion system should not contain organic material. Inorganic components in the waste are not destroyed, although they may be oxidized into other compounds.

The inorganic materials exit the thermal treatment system either as bottom ash from the combustion chamber, in scrubber water, or as fly ash from the air pollution equipment. Unless demonstrated otherwise, these ashes should be considered as hazardous waste and handled as such.

The ash from the combustion chamber and the fly ash must both be discharged without letting significant quantities of air into the treatment system. For fly ash and treatment systems where all the ash particles are small, removal can be accomplished using rotary air locks. When large solids are present, such as drums or the rings from fiberpacks, large discharge systems such as airlocks or water seals are required (the ash can drop directly into a vat of water).

Ash is normally either air cooled or quenched with water as it leaves the system. Air-cooled ash is then conveyed to drums or dumpsters for transfer to a landfill for disposal. Any ash that still contains organic material can be recycled back to the thermal treatment system. Some systems routinely recycle ash to make sure combustion is complete. If necessary, the ash can be chemically treated or stabilized before it goes to the landfill.

Ash that is quenched in water can be handled as part of the wastewater treatment system.

Wastewater Treatment. Quench water and scrubber effluents are normally combined for treatment. Depending on the waste and the scrubbing system used, the wastewater can contain particulates, acidic or alkaline wastewater, and dissolved salts.

Neutralization of acidic or alkaline wastewater is common along with clarification to remove suspended solids. The solids may require thickening

or filtration to produce a dry cake for landfill with the ash. Chemical treatment may be required to precipitate heavy metals at their lowest solubility levels.

After treatment the wastewater usually contains high concentrations of dissolved salts and may need dilution with other wastewaters before discharge. In some facilities, the water is disposed of by incineration (recycled to the thermal treatment system), especially in cases where water must be injected to cool the products of combustion.

***E*MERGING TECHNOLOGIES**

Emerging technologies are new processes which have not been used extensively on a commercial scale. These are processes "which were found to offer innovative approaches to waste treatment."¹¹

The emerging technologies discussed in this section are

- Infrared thermal destruction,
- Wet oxidation,
- Molten glass,
- Molten salt,
- Electric reactors, and
- Plasma systems.

INFRARED THERMAL DESTRUCTION. Infrared thermal destruction is a proprietary process that has been used to regenerate activated carbon. It currently is undergoing testing as an emerging technology for the thermal destruction of hazardous waste.

Process Description. An infrared thermal destruction system uses the same processing steps as most of the other treatment technologies: a feed system, a combustion chamber, an afterburner to complete the destruction of organics in the combustion gas, an air pollution control system, ash handling, and wastewater treatment.

The combustion chamber utilizes a belt to move the solid waste through the chamber where it is heated by infrared heating elements. Rotary rakes or cake breakers stir the material to ensure adequate mixing.

Air is supplied to the combustion chamber through burners spaced along the length of the chamber. Additional air and supplemental fuel is added through burners in the afterburner.

Operating Conditions. Temperatures and residence times for infrared units are similar to those for the other thermal treatment units. Temperatures in both the combustion chamber and the afterburner run about 1000°C (1858°F).

The combustion gas flow can be lower for the infrared unit than for the other thermal treatment units if supplemental fuel is required. Since the solids are heated with infrared units, the combustion gas does not include the products from combustion of the supplemental fuel. This can be a significant percentage of the total stack gas when solids low in organic content, such as contaminated soil, are being treated.

Wastes Applicable for Treatment by Infrared Destruction. The primary application for infrared units is the treatment of solids with a low organic content. However, any solids that can be processed to a state where they can be spread out on the belt are candidates for infrared destruction.

Wastes that are not applicable to infrared destruction are drums, bulk solids, and sludges (which tend to run or cake on the belt).

Advantages and Disadvantages of Infrared Thermal Destruction Units.

Advantages of infrared thermal units include

- Lower fuel requirements for treating solids with low organic content,
- Smaller afterburner and air pollution control facilities because of the lower stack gas flow, and
- Low velocity, which results in less solids entrainment.

Disadvantages include

- Drums or bulky solids cannot be handled without pretreatment.
- Maximum temperatures are limited by the design temperature for the belt.
- Belt maintenance requirements.

WET OXIDATION. Wet oxidation is a group of processes for oxidizing suspended and dissolved organics in aqueous streams. One of the processes in this group, wet air oxidation, is already in commercial use and was described in Chapter 5. Emerging wet oxidation processes include

- Catalyzed wet oxidation,
- Supercritical fluid oxidation, and
- High-temperature wet oxidation.

Catalyzed Oxidation. Catalyzed wet oxidation uses ions, nitrate, bromide, and sometimes copper to catalyze the reaction of organics with oxygen. A continuous stirred tank reactor contains the catalyst solution. Air and waste are continuously pumped into the reactor where the oxidation takes place. The heat of oxidation is removed by boiling off water, which can be condensed and returned to the reactor.

A catalyzed system operates at a lower temperature and pressure than the wet air oxidation system discussed in Chapter 5 and thus can economically treat very dilute solutions. Typical operation parameters are a temperature of 200 to 300°C (420 to 600°F) and pressures of 7091 to 14 182 kPa (70 to 140 atm).

Advantages of these systems include

- Low energy input.
- Nonvolatile organics remain in the reactor until they are destroyed.
- Vent gases are low in volume.

A disadvantage is that the vent gases may require further treatment to reduce volatile organics or odor.

Supercritical Fluid Oxidation. Supercritical fluid oxidation is a high-temperature, high-pressure wet oxidation. Above the critical temperature (374°C (730°F)) and critical pressure (22 083 kPa (218 atmospheres)) of water, organic materials and gases are completely miscible with water. Under these conditions, reaction occurs very rapidly.

High-pressure pumps are used to feed the aqueous solution of slurry to the reactor. Oxygen is supplied in the form of compressed air, which can be fed through an eductor where it serves as the motive force to recycle reactor effluent. The recycled effluent preheats the feed to start the reaction.

The system typically operates in the range of 600 to 650°C (1140 to 1230°F) and 25 325 kPa (250 atm).

Advantages of supercritical fluid oxidation include

- Low energy consumption.
- Rapid reaction allows short residence times and thus smaller equipment.
- Enhanced solubility of air and oxygen eliminates the need for two-phase flow.
- The complete oxidation of organics can eliminate the need for off-gas processing.
- Many inorganic constituents precipitate out under supercritical conditions.
- The hot, supercritical water formed by the heat of combustion can serve as a high-temperature heat source.

High-Temperature Wet Oxidation. This is another form of supercritical wet oxidation. The process uses a vertical, underground tubular reactor. Two concentric tubes are used. The waste is pumped down the inner tube where it is heated by the treated waste flowing up through the annulus. An electrode

at the bottom of the tube provides additional electric heating plus cathodic protection.

Advantages of these systems include low energy consumption and the fact that the pressure is contained in standard tubing.

MOLTEN GLASS. Molten glass processes use a pool of molten glass as the transfer medium to thermally destroy organics. The main advantage of this technology is that the residue from the process is nonleachable (glass). The combustion conditions for organics appear to be at least as good as those in hazardous waste incinerators, plus the inorganic residue and ash is incorporated into the glass. This technology could possibly be an attractive way to handle wastes containing toxic metals, if the metals can be contained in glass.

There are two different methods for supplying heat to the molten glass. The first is using a Joule heated glass melter. This technology sets up an electric current with the molten glass as the resistance element. This avoids the need to transfer heat from a heating element, or from hot gas, to the glass.

This process is most attractive for the destruction of contaminated soils containing toxic metals. The soils can be fed directly into the process, avoiding the need for a pretreatment step.

The second method is an electromelt pyro-convertor. This process uses the heat of combustion of the waste combined with the heat from submerged electrodes to heat the glass. Wastes, including bulk solid wastes, can be rammed into the unit where they burn on the surface of the glass. The units are designed to provide residence times long enough for complete combustion before the combustion gases leave the system. Filters are used to remove particulates from the flue gas. The particulates are periodically returned to the unit for incorporation in the molten glass.

Molten glass units operate in the range of 1200 to 1260°C (2220 to 2330°F). Advantages of molten glass units include

- Toxic metal residues are contained in a potentially nonleachable block of molten glass.
- Combustion gas volumes are low because supplemental heat is added using electricity (there is no stack gas flow from the combustion of supplemental fuel).

MOLTEN SALT. Molten salt is a process where waste material is injected beneath a bed of molten sodium carbonate for incineration. The molten bed reportedly allows combustion at lower temperatures. Also, the salt serves as a scrubbing medium for acid gases.

The process consists of injecting the material to be burned along with air under the surface of a pool of molten salt. Halogens, phosphorus, sulfur, and arsenic react with the sodium carbonate and remain in the melt.

The process operates at about 900°C (1680°F) and either at atmospheric or elevated pressure. The advantages of this process include

- Low-temperature operation reduces fuel consumption.
- Low-temperature operation reduces NO_x formation.
- Acid gases are retained in the salt bed.

ELECTRIC REACTORS. Electric reactor processes pyrolyze waste contaminants off of particles such as soil through the use of an electrically heated fluid wall reactor. Heat transfer in these units is dominated by radiation rather than by conduction or convection, therefore, oxidation is quite rapid.

Feed is dropped into the top of the reactor. As it flows downward, it is heated by electrodes. Inert purge gas enters through porous walls in the reactor to prevent molten waste from fouling the sides of the reactor.

The reaction normally occurs with less than stoichiometric oxygen (pyrolytic conditions) to minimize the formation of nitrogen oxides. The reaction occurs at about 2200°C (4020°F).

The advantages of electric reactors include

- Reduced residence times and thus smaller system volumes.
- Residue formation tends to be nonleaching.
- Low NO_x formation.
- Low stack gas flow rates since supplemental heat is from electricity, not supplemental fuel firing.
- High percent destruction of waste because of the high operating temperatures.

PLASMA SYSTEMS. Plasma systems use the extremely high temperatures of plasma (a hot, ionized gas) to destroy waste materials.

One process utilizes an electric arc to ionize air and heat it to 28 000°C (50 458°F). As the activated components of the plasma decay, they transfer their energy to waste materials that are heated and destroyed.

A second process preheats oxygen before it mixes with the waste. The heat of combustion of the waste then raises the temperature of the waste to about 2760°C (5030°F).

An advantage of this system is that reaction rates are very fast, allowing the use of small equipment.

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Chapter 9

Process Integration

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***I**NTRODUCTION*

Selection of treatment options depends on the nature of the hazardous material, the required effluent concentration levels, and economic considerations. Hazardous materials can exist as a solid, liquid, or vapor. The available treatment alternatives for hazardous materials include biological, physical, chemical, and thermal treatment. Each of these has been discussed previously in this manual. The integration of this information into treatment train options is the objective of this chapter.

Hazardous materials can be found in natural or man-made environments. Typical examples include groundwaters, surface waters, soils, construction materials, new and waste materials storage, wastewater streams, and the work place and ambient air. Stringent environmental laws passed in recent years for the protection of human health and the environment have brought many formerly "safe" materials into the hazardous materials classification.

Traditional industrial wastewater treatment addresses the disposal of hazardous materials in liquid form from the relatively simplistic viewpoint of gross contaminant reduction. Many of the same treatment methods can be

used but greater personal protection and lower effluent concentrations are required.

Traditional solid wastes collection, processing, and disposal have not been totally applicable to hazardous materials. The requirements for solidification before disposal, manifesting, disposal, and cataloging at Class I dump sites have been a far more complex process than picking up solid wastes and transporting them to a sanitary landfill. Part of the reason for the stricter laws has been the environmental problems currently associated with former landfill sites.

Air pollution control technology has also been affected by the requirements of hazardous materials control. Detection levels have been lowered, the types of materials monitored has increased, and a general awareness of the dangers of air pollution in the workplace and community has resulted in improvements in control and monitoring technologies.

Economic considerations governing hazardous waste treatment must be applied on a total accounting basis so that all relevant capital, operating, and maintenance cost factors are considered. In addition to concern for product, process, and facility life, there may also be uncertainties as to treatment level and liabilities associated with permit violations. Designing for zero discharge of pollutants, if chosen by management, avoids the issues of future imposition of higher stringencies, the costs associated with permitting and monitoring, and other factors influencing costs. Thus, all treatment options should be considered when evaluating costs.

Hazardous waste processing frequently involves retrofitting into an existing plant structure and is highly site specific. Costs may exhibit bias based on layout because of long piping runs for utilities. Usually, a lack of accurate "as-built" drawings adds to cost because of unknown interferences.

Industries have given a great deal of attention to avoiding the hazardous waste problem in a number of ways. These include product substitution of a nonhazardous manufactured product, process modification, or reagent change resulting in the generation of lesser quantities or less toxic byproducts. Another is "bottling up" which results in zero discharge and includes attention to fugitive emissions, leakage and reuse of recycle, or recycle of materials elsewhere in the plant. It is a continuing process and one requiring sensitivity when dealing with the problem of managing the wastes that must be generated. The subject of waste reduction is discussed in Chapter 3.

An examination of economics is usually worthwhile when considering the question of waste minimization. Also, issues of expansion in an existing treatment facilities can be addressed, as can the issue of pretreatment in a plant generating a unique waste load that could impact the larger system.

Consideration of any particular process on paper alone is particularly difficult because of the low concentrations of hazardous materials that must typically be managed. General references are available to suggest possible processes. These include the "Standard Handbook of Hazardous Waste Treat-

ment and Disposal, and compendia from U.S. Environmental Protection Agency (EPA) and WPCF. More detailed consideration of alternatives may be possible using the latest published data in WPCF's Literature Review.⁵ There is, however, no substitute for bench- or pilot-scale testing using actual waste streams, slip streams, or composite samples of the wastes to be managed. These data may be used to design a full-scale treatment process with the aid of process simulation software. These cover such topics as solids handling, reactors, physical properties, sizing, costing, and general unit operations. Treatability testing is necessary to demonstrate the feasibility, the control parameters, and the treatment costs for any potentially applicable treatment train. Site-specific costs for construction and operation of the treatment train are also important when selecting the combination of treatment technologies that achieves the desired results for the least cost.

WASTE CHARACTERIZATION

Characterizing a waste to determine the appropriate cost-effective treatment requires both a description of the waste's composition in terms of its chemical nature, its liquid and solid matrix, and a definition of hazardous versus nonhazardous streams and the possible segregation or combining of waste streams.

The selection of possible processes is largely determined by the chemical nature of the waste and the matrix within which it occurs. Regardless of the matrix, a mass balance is required to initiate development of an adequate process train to handle a waste stream.

Depending on the hazardous material of concern, the mass balance outlets may vary greatly. For example, the mass balance for copper from an electroplating operation focuses on wastewater, sludge, scrubbers, etch wastes, and product incorporation. A mass balance for Freon 113 focuses on fugitive emissions and still bottoms quantities.

A well-constructed material balance requires attention to flow and chemical variability and allows assessment of amenability of the streams to be segregated or combined for treatment. Variability is an important factor in the design of a process unit. Segregation has a less obvious economic impact. The concept is to treat substreams before combining them to affect processing on a smaller volume of waste and to facilitate or avoid interfering with downstream processing. A convenient example is plating waste treatment where hexavalent chrome is reduced to trivalent, and cyanide-bearing streams are oxidized upstream of the point at which these streams are combined with other metal-bearing streams which then flow into a precipitation process.

There may be questions about the toxicity of a particular waste stream if constituents are not listed wastes or incorporate more than one waste listed as

hazardous. Opportunities for delisting under appropriate, detailed EPA procedures should not be ignored particularly at the discharge end of the waste treatment process.

TREATMENT PROCESS SELECTION

The standards to which wastes must be treated for release are closely related to considerations for ultimate disposal or reuse of material. If recovery, reuse, or delisting options are to be considered, they should be carefully evaluated. Options for zero discharge or nonhazardous wastewater discharge to a POTW or a receiving body (NPDES) should likewise be thoroughly understood. Disposal options for solids and sludges provide similar alternatives, such as composting, landfill cover and hazardous versus nonhazardous landfills, and options for on-site, permitted disposal via a properly licensed facility and contractor.

RCRA applies to all considerations that have cradle-to-grave management of hazardous waste from generator to disposal. Use of environmental counsel is suggested in developing an overall plan. Most states are now authorized to administer RCRA. Standards higher than the federal regulations can now be required by the states.

Processes for treating hazardous materials must be evaluated in light of multimedia interactions so that the hazardous components of the wastes are concentrated and isolated for treatment and transferred from one matrix to another. Items to consider during unit process selection are

- How to manage mixed waste streams with the potential of conflicting treatment goals,
- Equipment fouling,
- Generation of a toxic byproduct or intermediate, and
- Low residual concentration requirements.

An example considers volatile organic compounds (VOCs) and metals in a dilute waste stream. To remove volatiles with a stripping process, metals may have to be removed first to avoid fouling the stripping operation. Precipitation of the metals, however, would coprecipitate or sorb some of the organics in the flow of the metal precipitates. In this example, metals are concentrated by precipitation but the presence of organics may affect the way in which the solids are subsequently treated. VOCs are stripped and transferred into a different media, an air stream or water vapor stream, and then concentrated by reabsorption onto carbon or by cooling into a condensate. The condensate or the carbon, now organic rich, require further treatment. If the VOCs were accompanied by semivolatiles or nonstrippables requiring further treatment that treatment could also produce other waste streams, perhaps a solid phase,

that could be combined with the metal precipitates of the earlier treatment step.

The challenge of simultaneously considering multimedia interactions, plus trying to avoid unnecessary generation of recycle or waste byproduct streams, is complicated by the very low concentrations of toxic compounds in waste streams. Frequently, concentrations in the part per billion (g/L) range are intolerable for compounds of concern; parts per trillion (ng/L) is not uncommon as a target treatment level. As analytical techniques are improved, detection levels lowered, and health effects experience is gained, one can only expect greater concern for very low allowable limits of hazardous materials.

In selecting processes to remove contaminants of concern, one must look at process performance for a majority of a class or family of compounds that are present or specific removal for particular compounds of concern. The complexity and reliability of the treatment step must next be considered. The ability of the process to accept a wide range of stream variability and other off-design operating expectations need to be addressed. Ease of testing and demonstration are part of the selection process. Ease of integration with existing or planned facilities is important so that space requirements, piping runs, utilities, and waste stream utilization are all optimized. All of these aspects can be related to economics.

Where there is a regulatory interface, documentation, planning detail, and compatibility with existing permits must also be taken into account. If one is able to demonstrate a proven technology application in a situation, it will be easier to develop the desired working relationship with regulatory authorities.

LIQUIDS TREATMENT PROCESS. In considering a general scheme of treatment train selection, it is perhaps helpful to consider an overall processing strategy that can be summarized as follows:

The first step is to phase-separate, and generate oil-free aqueous and water-free oil streams. Solids may settle out in the process and so may gaseous streams be generated. All will be relatively free of the other phases or matrices; the aqueous stream will be diluted, and the organic will be concentrated and may consist of sinkers and floaters with respect to the aqueous phase. All will be relatively homogeneous permitting ease of further treatment.

The next step is to remove metals. Metals lead to poisoned biological treatment and interfere with physical treatment due to scaling. Removal of volatile metals will remove constraints on possible thermal processes later in the sequence. Removal of organic-complexed metals from the oil stream will likewise not inhibit use of thermal processes.

Then the various treatment combinations with organics that may be present must be considered. Segregation into categories such as the following may be helpful:

- Volatile and semivolatile,
- Biorefraction PNAs, dioxins, and pesticides, and
- Chlorine-containing compounds.

Finally, polishing treatment may be required to attain the requisite levels of dissolved anions and cations. Proven technology exists in membrane, thermal, and ion exchange processing.

DILUTE ORGANICS. The organics portion of a waste stream can be treated by a number of oxidation processes including biological, wet air oxidation, chemical and advanced, UV and ozone, or peroxide. They can also be concentrated by stripping into overheads and by absorption onto carbon, resin, or zeolite, and subsequently treated as part of the matrix to which they are removed. Contaminant-specific processes have been developed for problems such as PCBs. Where PCBs are present, the major process will be PCB-specific and the others will provide pretreatment to enable that process to work.

Activated carbon has been used extensively for removing dilute organics. It can be applied with relatively little engineering because it can be “changed out” and replenished easily with fresh material on initial breakthrough. If carbon is the selected major process step, then pretreatment becomes focused on extending the life of the carbon between change outs. For example, one might air strip VOCs to avoid loading the absorption sites with those organics.

Table 9.1 shows some of Calgon’s operating experience with carbon. In this table, benzene is readily removable by carbon; benzene is also readily removable by air or steam stripping. Phenol is shown as readily sorbed; it is also easily biologically oxidized. One has to choose judiciously among competing processes so that all the compounds of concern are removed most economically.

CONCENTRATED ORGANICS. The fate of toxic organics is logically thermal destruction. As with conventional combustion processes, atomization parameters, heating value, and flame temperature are important parameters in hazardous liquid incineration. With hazardous wastes, elevated flame temperatures and long residence times are the rule; pyrolytic or two-stage combustion is common. Where chlorine-containing organic waste is present, elaborate gas cleaning systems are used. The presence of volatile metals in the organic can further complicate combustion to the point where potential incineration contractors cannot accept anything but low levels of contained metals according to their air permits. When considering a multiplicity of organic wastes, one must look at the miscibility or homogeneity of the mixture. Also, the flash points must be considered because the inherent safety is dependent on the most volatile component in the mixture.

Table 9.1 Carbon influent and effluent.

	Occurrences	Influent concentration range	Carbon effluent concentration achieved
Carbon tetrachloride	4	130 µg/L – 10 mg/L	< 1 µg/L
Chloroform	5	20 µg/L – 3.4 mg/L	< 1 µg/L
DDD	1	1 µg/L	< 0.05 µg/L
DDE	1	1 µg/L	< 0.05 µg/L
DDT	1	6 µg/L	< 0.05 µg/L
Cis-1,2-dichloroethylene	8	5 µg/L – 4 mg/L	< 1 µg/L
Dichloropentadiene	1	450 µg/L	< 10 µg/L
Disopropyl ether	2	20 – 30 µg/L	< 1 µg/L
Tertiary methyl-butylether	1	33 µg/L	< 5.0 µg/L
Diisopropyl methyl phosphonate	1	1250 µg/L	< 50 µg/L
1,3-dichloropropene	1	10 µg/L	< 1 µg/L
Dichlorethyl ether	1	1.1 µg/L	< 1 µg/L
Dichloroisopropylether	1	0.8 µg/L	< 1 µg/L
Benzene	2	0.4 – 11 mg/L	< 1 µg/L
Acetone	1	10 – 100 µg/L	< 1 µg/L
Ethyl acrylate	1	200 µg/L	< 10 µg/L
Trichlorotrifluoroethane	1	6 mg/L	< 1 µg/L
Methylene chloride	2	1 – 21 mg/L	< 100 µg/L
Phenol	2	63 mg/L	< 1 µg/L
Orthochlorophanel	1	100 mg/L	< 1 µg/L
Tetrachlorethylene	10	3 µg/L – 70 mg/L	< 1 µg/L
Trichlorethylene	15	5 µg/L – 16 mg/L	< 1 µg/L
1,1,1-trichloroethane	6	60 µg/L – 25 mg/L	< 1 µg/L
Vinylidene chloride	2	3 µg/L – 4 mg/L	< 1 µg/L
Toluene	1	3 – 7 mg/L	< 10 µg/L
Xylene	1	0.2 – 10 mg/L	< 101 µg/L

SOLIDS. Industrial solid waste streams that contain hazardous wastes cover such a wide range that generalization is difficult. Examples include electric air furnace (EAF) dust, machine shop floor sweepings, and refinery oil and water separator sludges. The ultimate fate of these materials is unclear because of EPA's land ban. Two things are clear, however. Maximum attention will be given to resource recovery. The EAF dust might be resmelted to remove zinc, lead, and cadmium so that the residual nonhazardous focus will be on volume and toxicity reduction. The ultimate fate of these wastes will be dependent on economic factors. Processing by incineration in combination with ash fixation will become more widely available as the land ban is implemented.

A ***N INTEGRATED TREATMENT PROCESS***

An integrated hazardous waste treatment process flow diagram is presented in Figure 9.1. The influent is assumed to consist of an oil and water mixture with settleable solids. Heavy metals are present in low concentrations. Dilute VOCs are dissolved in the aqueous phase. Step 1 is to separate the phases for treatment. In this example, the solids are separable without special processing and the liquid phases are immiscible and not emulsified. Use of an API separator is therefore suggested to produce three matrices for further processing. Alternative processes might include dissolved air flotation (DAF) to hasten separation in a stilling basin. Floating oils would be recovered. These could be recycled by a used oil processor or used as fuel in the plant, assuming the metals content is low enough. Note that zero halide content promotes favorable consideration of burning.

The aqueous phase in this example contains low concentrations of organics and heavy metals. Options for treating this stream include biological oxidation if there is capacity in an existing wastewater treatment plant, chemical oxidation with UV and ozone if a small remote processing unit might be appropriate, air stripping of volatiles to a carbon absorption unit, or if waste steam is conveniently available stripping to a concentrated liquid phase in a condenser. It should be noted that high heavy metal concentrations could obviate biological oxidation without pretreatment because of concern for poisoning the microorganisms and also air stripping because of likely scaling of treatment equipment. Absence of halides favors the use of ozone; if present, objectionable chloro-organics could be formed.

In this example, air stripping would be a relatively inexpensive process but one coupled with the need to dispose of or regenerate the carbon. One option would be to thermally desorb the organic off the carbon and then feed the concentrated vapors to a thermal destruction unit. Finally, the aqueous phase could be treated in an ion exchanger to remove the low concentrations of metals. In this example it is worth noting how heavy metals, if present in high concentrations, would completely change the process sequence or alter unit process selection. Settleable solids from the initial treatment unit would contain sorbed organic that would be to some extent coprecipitated. The solid is "unknown" in this example. Incineration could be a candidate process, but inadequate characterizing will not suffice. In this case more data would be a necessary next step.

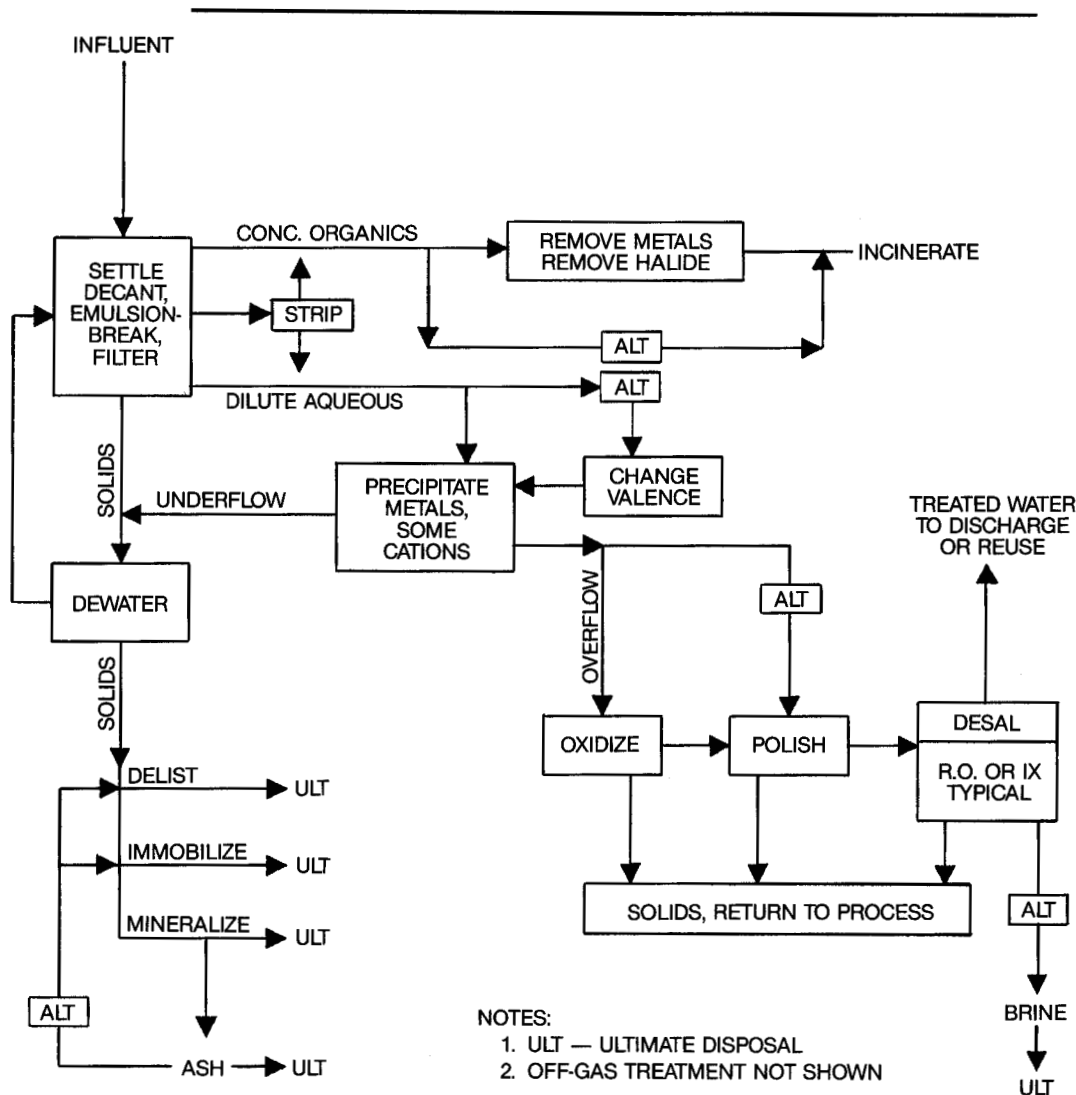


Figure 9.1 Hazardous waste treatment process flow diagram.

CASE STUDY

There is not one standard solution to the characterization and treatment of a hazardous waste stream. Selection of treatment options is dependent on the nature of the hazardous material and its treatability, the required effluent concentration levels, and economic considerations.

The following case study is for an industrial plant that stores its operating chemicals, consisting of solvents and other hydrocarbons, in above-ground and below-grade process vats and tanks. The fugitive waste streams (spills and leaks) are often the most difficult to identify and to handle. The follow-

ing are several approaches that can be used to collect the necessary information and several treatment options that have been used to handle the problem.

DATA COLLECTION. The design of a treatment system requires the collection of data about the material to be treated. A treatment problem usually has a beginning that may not appear to be a major problem. The following is a summary of the steps that are often followed when a fugitive waste stream is noticed. It is presented in a chronological framework.

TANK OR SUMP REMOVALS. The manager of the industrial facility has noticed that an underground tank or sump is losing product, or a process change requires that the underground tank or sump be removed or replaced. The plant manager may call either a consultant or contractor.

When the underground tank or sump is removed it is found that contamination exists in the area. The work area may be either fenced or lined with plastic and filled with clean materials while the samples are being analyzed by the laboratory. The decision to fence or backfill is often one of safety, and the expected time before the remediation work, if any, will be undertaken.

When the soil and water sample results come from the laboratory with concentrations in excess of the allowable limits it is necessary to complete a site investigation to determine the lateral and vertical extent of the contamination so that remediation options can be developed.

SITE INVESTIGATIONS. The investigation and remediation of contaminated soil and water may be handled by different methods. Since the soil is often the source of the on-going release of contaminants into the groundwater, the characterization and remediation of the soil contamination should be handled first.

Two basic approaches are available for the site investigation. When possible a vapor probe study or soil gas survey is used to determine the lateral extent of the soil contamination. Using the vapor probe data, the quantity of soil to be treated or removed can be determined. If the contamination is deep or cannot be detected with the vapor probe equipment, soil and water samples can be collected by drilling and the samples analyzed in the laboratory.

The vapor probe method is inexpensive, very flexible for pursuing contamination paths, provides immediate results, and does minimum damage to the site. The typical cost for a study is \$3000 to \$6000/day. The method does have depth limitations and does not provide laboratory analysis. It is a good method to use to define the limits of the soil contamination since laboratory samples will be taken during the site excavation and monitoring well installations. The lateral extent of groundwater contamination is not detected using

this method, but the quality of the water will be determined by the required monitoring wells around the excavation site.

The use of drilling equipment and laboratory analysis of the samples can greatly increase the cost and accuracy of the site investigation. Drilling also allows for better definition of the vertical extent of the contamination. Since a limited number of borings can be completed in a given day, the equipment is not as flexible as tracking near-surface contamination plumes. Both soil and water contamination can be tracked with this method.

SOIL REMEDIATION. Soil contamination can be handled by several methods. Specific site conditions, including soil type, rainfall, and groundwater depth, will affect the selection of a treatment option. Typical options include

- *In situ* aeration, chemical treatment, or biological treatment,
- Excavation and transportation to a Class I or Class II disposal site, depending on the concentrations in the soil, or
- Excavation, on-site treatment by aeration, chemical, or biological processes, and disposal as clean soil.

UNDERGROUND TANK PROJECT. A typical work site for an underground fuel tank is shown in Figure 9.2. An estimate was prepared for the quantity of construction work to be completed, and the costs for soil removal, treatment, and disposal were determined. These data are given in Table 9.2. The costs of consultant supervision and report writing were not included.

Once the soil contamination problem is solved, several monitoring wells must be installed around the excavation site. Generally these are 2 to 4 in. (5 to 10 cm) in diameter. Generally three wells are required to ensure that one well is installed down-gradient from the excavation site. The costs for well installations and quarterly monitoring for 1 year are given in Table 9.3.

GROUNDWATER CONTAMINATION. If the monitoring well samples are clean the project is complete. If hydrocarbon contamination is found in the water samples, additional site investigation and groundwater remediation is required. The number of additional borings and monitoring wells required to determine the extent of the contamination cannot be determined in general terms. However, the basic approach is to drill additional monitoring wells in the down-gradient direction until the extent of the contamination plume is determined.

Once the extent of groundwater contamination has been determined, and the degree of contamination has been assessed, the treatment system is designed. Additional information is needed about the site to determine the water quality, flow rate, and disposal path.

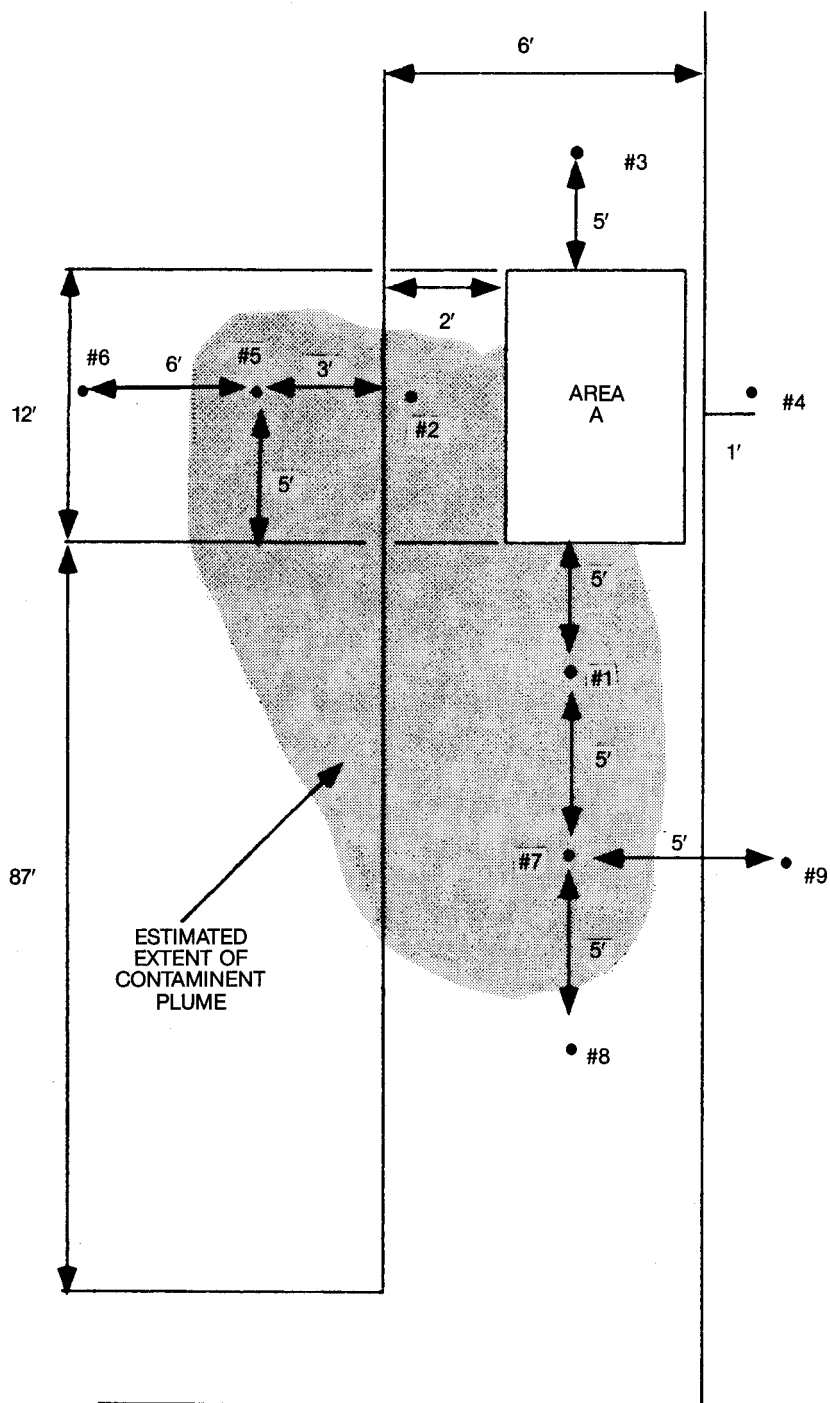


Figure 9.2 Underground storage tank site investigation.

Table 9.2 Contractor costs for soil remediation and site work.

Description	Quantity	Units	Unit price	Total
Concrete removal	232	sq ft	2.00	464.00
Rock backfill removal	27	cu yd	30.00	810.00
Excavation soil removal	81	cu yd	30.00	2 430.00
Surface soil removal	13	cu yd	30.00	390.00
Gravel backfill placement	121	cu yd	20.00	2 420.00
Conc. sidewalk placement	174	sq ft	5.00	870.00
Conc. curb and gutter	32	ln ft	15.00	480.00
Total site work				\$7 860.00
Soil remediation—bioremediation				
Soil treatment	94	cu yd	60.00	5 640.00
Soil disposal	94	cu yd	30.00	2 820.00
Freight	94	cu yd	20.00	1 880.00
Total				\$10 340.00
Hazardous waste disposal alternatives				
Class I landfill	141	tons	185.00	\$26 085.00
Class II landfill	141	tons	115.00	\$16 215.00
(includes freight charges)				

Table 9.3 Monitoring well installation.

Install one 2-in. (5-cm.) monitoring well to 30 ft, collect soil and water samples.

Monitoring well

Professional labor	1 500.00
Lab analysis, three soil and one water sample.	
Analyze for TPH, BTEX	864.00
Drilling contractor	1 450.00
Other direct costs	125.00
Total	\$3 939.00

Quarterly monitoring

Collect quarterly water samples for 1 year from one well and analyze for TPH and BTEX. Annual cost.

Professional labor	800.00
Lab analysis, four water samples. Analyze for TPH and BTEX.	864.00
Other direct costs	100.00
Total	\$1 764.00

The geologic data collected during the installation of the soil borings and monitoring wells yields information necessary for the design of the groundwater pumping system. Specific pumping capacity and the radius of influence are commonly determined by the use of a pumping test. An existing monitoring well can be used for the pump test, but generally a larger and deeper well is required to provide sufficient drawdown to create an adequate

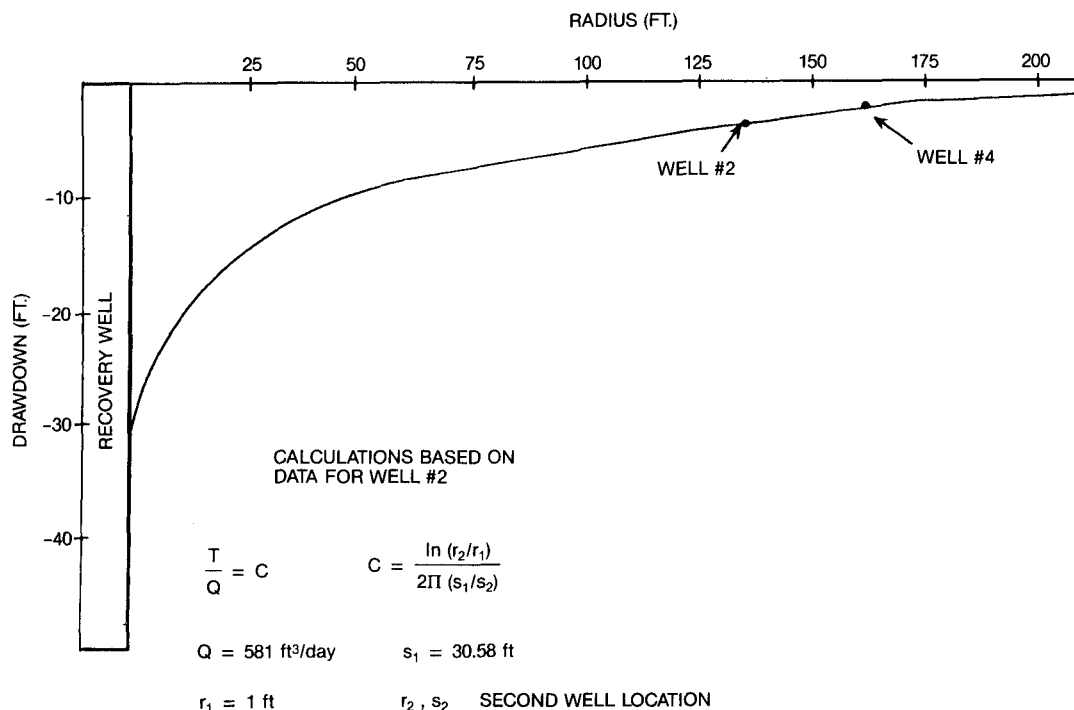


Figure 9.3 Drawdown curve.

radius of influence for the collection of the contaminated water. A typical drawdown curve is shown in Figure 9.3.

Once the pumping rate has been determined, the groundwater treatment system can be designed. Figure 9.4 shows a system designed to extract floating product, treat the groundwater, and reinject the treated water into an infiltration gallery up gradient from the recovery wells. The cost of the treatment system is given in Table 9.4.

The treatment of the groundwater will be continued until the necessary level of cleanup is achieved. Often the groundwater can be cleaned to an acceptable level and the equipment shut off. The monitoring wells will still be evaluated for at least 1 year and the equipment may need to be turned on again if contamination levels start to increase.

CHLORINATED ORGANICS. Solvent contamination in groundwater can require a major cleanup effort even when the concentrations are very low. Typical treatment systems often involve air stripping and carbon adsorption. The treatment costs associated with this type of cleanup are given in Table 9.5.

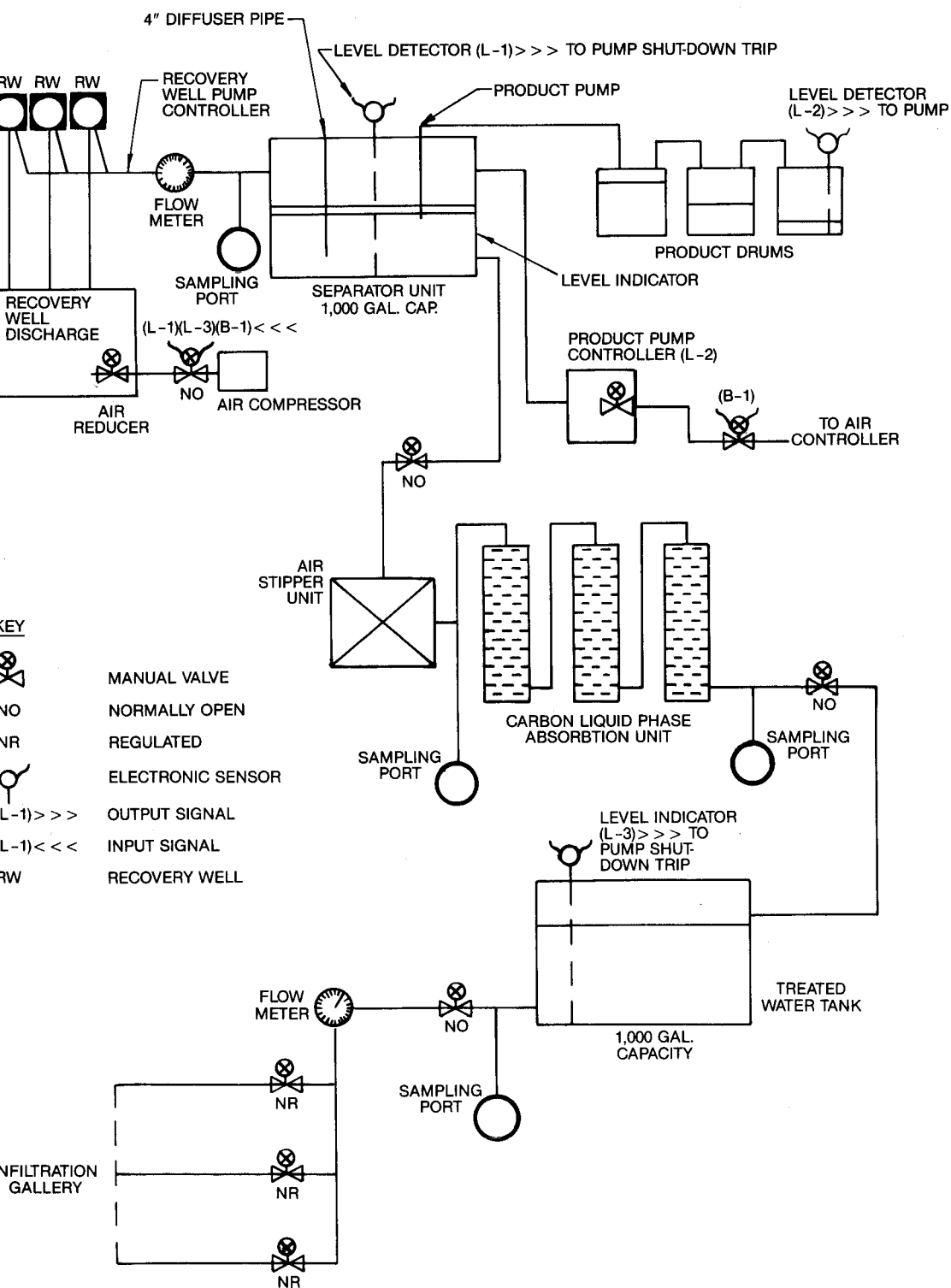


Figure 9.4 Groundwater treatment system.

Table 9.4 Cost of groundwater treatment system for fuel contamination.

Phase I Groundwater recovery wells and remediation plan

Labor		
Professional staff		\$25 800
Clerical		\$1 000
Cartographer		\$600
	Subtotal	\$27 400
Other direct costs		
Driller—Labor and well materials		\$12 250
Laboratory analysis—eight water, two soil samples. Analyze for BTEX and TPH.		\$2 160
Equipment rental		\$700
Travel and per diem		\$1 600
Shipping		\$100
Miscellaneous materials		\$100
Permit application fees		\$600
Printing and computer		\$300
	Subtotal	\$17 810
	Total Phase 1	\$45 210

Phase II Installation, operation, and maintenance

	Total 24 months	3 year additional	Total 36 months
Labor			
Professional staff	\$33 840	\$20 000	\$53 840
Clerical	1 800	1 000	2 800
Cartographer	900	500	1 400
Subtotal	\$36 540	\$21 500	\$58 040
Other direct costs			
Remedial systems components	\$43 000	\$4 300	\$47 300
Remedial area construction	4 000	400	4 400
Regulatory charges	500	500	1 000
Travel and per diem	3 500	2 000	5 500
Subcontractor labor	1 000	1 000	2 000
Carbon drum disposal	4 000	2 500	6 500
Laboratory analysis	16 000	4 000	20 000
Subtotal	\$72 000	\$14 700	\$86 700
Subtotal Phase II	\$108 540		\$144 740
Total Phase I + II	\$153 750		\$189 950

Table 9.5 Cost of groundwater treatment system for chlorinated organics.

• Install large diameter recovery well, develop, sample, and install well head.	\$10 000.00
• Install all underground piping and electrical and connect to services.	16 000.00
• Install pumping and treatment system.	50 000.00
• System startup and compliance sampling.	7 500.00
• System operation and monitoring for 3 years.	130 000.00
• Total	<u>\$213 500.00</u>

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Appendix A

Acronyms and Abbreviations

The hazardous waste treatment field uses many acronyms and abbreviations, as do many technical fields. This list contains the most frequently used acronyms and abbreviations.

Acronym	Definition
AA	Atomic Absorption
AA	Assistant Administrator (ARCS)
ABN	Acid/base neutral semivolatile compound
ACGIH	American Conference of Governmental Industrial Hygienists
ACM	Asbestos Containing Material
ACS	American Chemical Society
AEA	Atomic Energy Act
AG	Attorney General
AGI	American Geological Institute
AGT	Above-Ground Tank
AHERA	Asbestos Hazard Emergency Response Act
AIC	Acceptable Intake for Chronic Exposure
AIChE	American Institute of Chemical Engineers
AISE	Acceptable Intake for Subchronic Exposure
AISI	American Iron and Steel Institute
ALR	Action Leakage Rate
ANOVA	Analysis of Variance
ANSI	American National Standards Institute
AOC	Area of Contamination

Acronym	Definition
APCD	Air Pollution Control Device
API	American Petroleum Institute
APR	Air-Purifying Respirator
AQCR	Air Quality Control Region
AQMA	Air Quality Maintenance Area
ARAR	Applicable or Relevant and Appropriate Regulations
ARCS	Alternative Remedial Contracting Strategy
ASTM	American Society for Testing and Materials
ASTSWMO	Association of State and Territorial Solid Waste Management Official
ATSDR	Agency for Toxic Substances and Disease Registry
AWMD	Air and Waste Management Division
AWQC	Ambient Water Quality Criteria
BAP	Benzo (a) pyrene
BART	Best Available Retrofit Technology
BAT	Best Available Technology
BDAT	Best Demonstrated Available Technology
BDL	Below Detectable Limits
BEIs	Biological Exposure Indices
BEJ	Best Engineering Judgement
BHP	Biodegradation, Hydrolysis, and Photolysis
BMP	Best Management Practice
BNA	Bureau of National Affairs
BNA	Base Neutral/Acid Semivolatile Compound
BOD	Biochemical Oxygen Demand
BRB	Bromofluorobenzene
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
BTGA	Best Technology Generally Available
BTU	British Thermal Unit
CA	Cooperative Agreement (ARCS)
CA	Corrective Action
CAA	Clean Air Act
CAER	Community Awareness and Emergency Response
CAM	Contract Administration Manager (ARCS)
CAMU	Corrective Action Management Unit
CAP	Capacity Assurance Plan
CAPA	Critical Aquifer Protection Area
CASAC	Clean Air Scientific Advisory Committee
CBO	Congressional Budget Office
CBOD	Carbonaceous Biochemical Oxygen Demand
CDC	Centers for Disease Control
CEL	Continuous Exposure Limit

Acronym	Definition
CEM	Continuous Emission Monitor
CEMS	Continuous Emission Monitoring System
CEPP	Chemical Emergency Preparedness Program
CEQ	Council on Environmental Quality
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CERCLIS	Comprehensive Environmental Response Compensation and Liability Information System
CFR	Code of Federal Regulations
CGI	Combustible Gas Indicator
CGL	Comprehensive General Liability
CHEMNET	Mutual aid network of chemical shippers and contractors
CHEMTREC	Chemical Transportation Emergency Center
CHLOREP	Mutual aid group of chlorine shippers and carriers
CHRIS	Chemical Hazardous Response Information System
CIS	Contract Information System
CI	Chlorine
CLP	Contract Laboratory Program
CMA	Chemical Manufacturers Association
CMI	Corrective Measures Implementation
CMS	Corrective Measures Study
CN	Cyanide
CO	Consent Order
COC	Chain of Custody
COD	Chemical Oxygen Demand
COE	Army Corps of Engineers
CPE	Chlorinated Polyethylene Polymer
CPE-A	Chlorinated Polyethylene Alloy
CPF	Carcinogenic Potency Factor
CPS	Centipoise
CPSR	Contractor Purchasing System Review
CQA	Construction Quality Assurance
CR	Polychloroprene (Neoprene)
CRC	Contamination Reduction Corridor
CRC (2nd)	Community Relations Coordinator
CRDL	Contract Required Detection Limit
CRL	Central Regional Laboratory (Region 5)
CRP	Community Relations Plan
CRZ	Contamination Reduction Zone
CSPE	Chlorosulfonated Polyethylene Polymer (Hypalon)
CWA	Clean Water Act

Acronym	Definition
CZMA	Coastal Zone Management Act
DAF	Dilution/Attenuation Factor
DBCP	1,2-dibromo-3-chloropropane
DC	Direct Current
DCA	Deoxycorticosterone acetate or Dichloroethylene
DCE	Dichloroethylene
DCM	Dichloromethane
DDT	Dichlorodiphenyltrichloroethane
DEC	Department of Environmental Conservation
DERA	Defense Environmental Repair Act
DERP	Defense Environmental Restoration Program
DFTPP	Decafluorotriphenyl Phosphine
DI	Distilled or Deionized
DL	Detection Limit
DMP	Data Management Plan
DMR	Discharge Monitoring Report
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOD	Department of Defense
DOE	Department of Energy
DOT	Department of Transportation
DQO	Data Quality Objective
DRE	Destruction and Removal Efficiency
DWPL	Drinking Water Priority List
DWRD	Drinking Water Research Division
EA	Environmental or Endangerment Assessment
EAF	Electric Arc (or Air) Furnace
EC	Emergency Coordinator
ECAO	Environmental Criteria and Assessment Office
ED	Electrodialysis
ED10	10% Effective Dose
EDB	Ethylenedibromide
EDD	Enforcement Decision Document
EDF	Environmental Defense Fund
EDR	Electrodialysis Reversal
EECA	Engineering Evaluation and Cost Analysis
EHS	Extremely Hazardous Substance
EIL	Environmental Impairment Liability (Insurance)
EIS	Environmental Impact Statement
EM	Electromagnetic
EMA	Emergency Management Agency
EMI	Emergency Management Institute

Acronym	Definition
EMSL	Environmental Monitoring and Support Laboratory
ENR	Engineering News Record
EOC	Emergency Operating Center
EOD	Explosive Ordnance Disposal
EOP	Emergency Operations Plan
EP	Extraction Procedure toxicity
EPA	Environmental Protection Agency
EPAAR	Environmental Protection Agency Acquisition Regulation
EPCRA	Emergency Planning and Community Right-to-Know Act
EPDM	Ethylene Propylene Diene Monomer
EPIC	Environmental Photographic Interpretation Center
EQA	Environmental Quality Act
ERA	Expedited Response Action
ERB	Environmental Response Branch
ERC	Emergency Response Coordinator
ERCS	Emergency Response Cleanup Service
ERD	Environmental Response Division
ERP	Emergency Response Plan
ERRB	Emergency and Remedial Response Branch
ERRIS	Emergency and Remedial Response Inventory System
ERT	Emergency Response Team
ESATs	Environmental Service Assistance Teams
ESBEP	Environmental Services Branch (EPA)
ESD	Environmental Services Division
ESP	Electrostatic Precipitator
EXOH	Ethanol
EZ	Exclusion Zone
FAAS	Flame Atomic Absorption Spectroscopy
FEMA	Federal Emergency Management Agency
FFDCA	Federal Food, Drug, and Cosmetic Act
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FIT	Field Investigation Team
FML	Flexible Membrane Liner
FOIA	Freedom of Information Act
FP	Facilities Plan
FPR	Federally Permitted Release
FR	Federal Register
FRC	Functional Residual Capacity
FRP	Fiberglass Reinforced Plastic

Acronym	Definition
FS	Feasibility Study
FSP	Field Sampling Plan
FTGs	Field Technical Guidelines
FWPCA	Federal Water Pollution Control Act
FWQC	Federal Water Quality Criteria
FWS	Fish and Wildlife Service
GAC	Granular Activated Carbon
GACC	Granular Activated Carbon Column
GAO	Government Accounting Office
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GEMS	Graphical Exposure Modeling System
GIS	Geographic Information System
gpm	Gallons per Minute
GWSS	Groundwater Supply Survey
HAZMAT	Hazardous Material
HCB	Hexachlorobenzene
HCL	Hydrochloric Acid
HCS	Hazard Communication Standard
HDPE	High-Density Polyethylene
HEA	Health Effect Assessment
HEP	Habitat Evaluation Procedure
HEPA	High-Efficiency Particulate Air (filter)
HH	High Hazard
HHE	Health Hazard Evaluation
HM/HW	Hazardous Material/Hazardous Waste
HMCRI	Hazardous Materials Control Research Institute
HMIR	Hazardous Material Intelligence Report
HMIS	Hazardous Materials Information System
HMR	Hazardous Material Regulations
HMTA	Hazardous Materials Transportation Act
HOCs	Halogenated Organic Compounds
HQ	Headquarters
HRS	Hazard Ranking System
HRSD	Hazardous Response Support Division
HSCD	Hazardous Site Control Division (EPA Headquarters)
HSI	Habitat Suitability Index
HSL	Hazardous Substances List
HSP	Health and Safety Plan
HSWA	Hazardous and Solid Waste Amendments (to RCRA)
HU	Habitat Unit
HWAC	Hazardous Waste Action Coalition

Acronym	Definition
HWDF	Hazardous Waste Derived Fuel
HWEB	Hazardous Waste Enforcement Branch
HWSF	Hazardous Waste Storage Facility
IAG	Interagency Agreement
ICARs	International Civil Aviation Regulations
IDD	Internal Due Diligence (Audit)
IDLH	Immediately Dangerous to Life and Health
IEM	Inhalation Exposure Methodology
IEMS	Integrated Emergency Management System
IFR	Interim Final Rule
IM	Inquiry Memorandum (ARCS)
IPL	Interim Priorities List (now NPL)
IPM	Integrated Pesticide Management
IQRPE	Independent, Qualified, Registered, Professional Engineer
IR	Installation Restoration (USATHAMA's RI/FS)
IRMS	Installation Restoration Management System
IRP	Installation Restoration Program
ISSA	Intra- or Interservice Support Agreement
IWS	Ionizing Wet Scrubber
JIT	Just In Time
JOSH	Job Occupational Safety and Health
LA	Load Allocation
LAER	Lowest Achievable Emission Rate
LCP	Laboratory Certification Program
LCRS	Leachate Collection and Removal System
LCS	Low-Cost Solution
LD50	Quantity of a substance administered either orally or by skin contact necessary to kill 50% of exposed animals in laboratory tests within a specified time
LDPE	Low-Density Polyethylene
LDR	Land Disposal Restriction
LEL	Lower Explosive Limit
LEPC	Local Emergency Planning Committee
LFL	Lower Flammable Limit
LL	Liquid Limit
LLDPE	Linear Low-Density Polyethylene
LOD	Limit of Detection
LOQ	Limit of Quantitation
LQMP	Laboratory Quality Management Plan
LRT	Liquid Release Test
LSC	Liquid Sample Concentration

Acronym	Definition
LUST	Leaking Underground Storage Tank
LVZ	Low-Velocity Zone
MAD	Maximum Applicable Dose
MAL	Maximum Allowable Level
MBAS	Methylene Blue Active Substance
MBE	Minority Business Enterprise
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MCP	Municipal Compliance Plan
MCRT	Mean Cell Residence Time
MDL	Minimum Detection Limit
MDL	Method Detection Limit
MDWL	Maximum Drinking Water Level
MED	Minimum Effective Dose
MEFR	Maximum Expiratory Flow Rate
MF	Membrane Filter
MF	Microfiltration
mg	Milligram
mgd	Million Gallons per Day
mg/L	Parts per Million
MIT	Mechanical Integrity Test
mL	Milliliter
MMS	Minerals Management Service
MMT	Million Metric Tons
MPN	Most Probable Number
MPRSA	Marine Protection Resource and Sanctuaries Act
MS	Mass Spectrometer
MSDS	Material Safety Data Sheet
MSHA	Mining Safety and Health Administration
MSW	Municipal Solid Waste
MSWLF	Municipal Solid Waste Landfill
MVV	Maximum Voluntary Ventilation
MWTA	Medical Waste Trading Act of 1988
NAAQS	National Ambient Air Quality Standards
NACE	National Association of Corrosion Engineers
NAMS	National Air Monitoring Station
NAS	National Academy of Sciences
NCATH	National Campaign Against Toxic Hazards
NCDC	National Climatic Data Center
NCIC	National Cartographic Information Center
NCP	National Contingency Plan
NCRIC	National Chemical Response and Information Center

Acronym	Definition
NCSL	National Council of State Legislatures
ND	Not Detected
NDD	National Decision Document
NEIC	National Enforcement Investigations Center
NEPA	National Environmental Policy Act
NESHAPs	National Emission Standards for Hazardous Air Pollutants
NETC	National Emergency Training Center
NFPA	National Fire Protection Association
NFRAP	No Further Remedial Action Planned
NGA	National Governor's Association
NGVD	National Geodetic Vertical Datum
NHMP	National Human Monitoring Program
NIAID	National Institute of Allergy and Infectious Diseases
NIH	National Institutes of Health
NIOSH	National Institute for Occupational Safety and Health
NIPDWR	National Interim Primary Drinking Water Requirements
NIPDWS	National Interim Primary Drinking Water Standards
NIRS	National Inorganics and Radionuclides Survey
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NOAEL	No Observed Adverse Effect Level
NOD	Notice of Deficiency
NOEL	No Observed Effect Level
NOMS	National Organics Monitoring Survey
NORS	National Organics Reconnaissance Survey
NOV	Notice of Violation
NPDES	National Pollutant Discharge Elimination System
NPDWR	National Primary Drinking Water Regulations
NPDWS	National Primary Drinking Water Standards
NPL	National Priorities List
NPO	National Program Office
NPS	National Pesticide Survey
NRC	National Response Center
NRC	Nuclear Regulatory Commission
NRDAM/CME	Natural Resource Damage Assessment for Coastal and Marine Environments
NRDC	National Resource Defense Council
NRT	National Response Team
NSF	National Sanitation Foundation
NSF	National Strike Force

Acronym	Definition
NNS	National Stock Number
NSP	National Screening Program
NSPS	New Source Performance Standards
NSWMA	National Solid Waste Management Association
NTIS	National Technical Information Service
NTNCWS	Nontransient Noncommunity Water System
NTP	National Toxicology Program
NTU	Nephebretric Turbidity
NWF	National Wildlife Federation
NWS	National Weather Service
NWWA	National Water Well Association
O&M	Operation and Maintenance
OAR	Office of Air and Radiation
OBA	Oxygen Breathing Apparatus
ODA	Ocean Dumping Act
ODW	Office of Drinking Water
OECD	Office of Enforcement and Compliance Monitoring
OERR	Office of Emergency and Remedial Response
OEW	Ordnance and Explosive Waste
OGWP	Office of Groundwater Protection
OHMTADS	Oil/Hazardous Materials Technical Assistance Data System
OLM	Organic Leachate Model
OMEP	Office of Marine and Estuarine Protection
OMPC	Office of Municipal Pollution Control
OPA	Office of Policy Analysis
OPMO	Office of Program Management and Operations
OPP	Office of Pesticide Programs
OPTS	Office of Pesticides and Toxic Substances
ORD	Office of Research and Development
ORM	Otherwise Regulated Material
ORP	Office of Radiation Programs
ORS	Ordnance Ranking System
OSC	On-Scene Coordinator
OSD	Office of the Secretary of Defense
OSHA	Occupational Safety and Health Act
OSOT	Oil Spill Operations Team
OSR	Office of Standards and Regulations
OSW	Office of Solid Waste
OSWER	Office of Solid Waste and Emergency Response
OTA	Office of Technology Assessment
OTS	Office of Toxic Substances

Acronym	Definition
OURM	Operable Unit Remedial Measures
OUST	Office of Underground Storage Tanks
OVA	Organic Vapor Analyzer
OW	Office of Water
OWPE	Office of Waste Programs Enforcement
OWRS	Office of Water Regulation and Standards
PA	Preliminary Assessment
PA/SI	Preliminary Assessment/Site Inspection
PAC	Powdered Activated Carbon
PAH	Polycyclic Aromatic Hydrocarbons
PAIR	Preliminary Assessment Information Rule
PAL	Preventive Action Limit
PAPR	Powered Air-Purifying Respirator
PCA	Tetrachloroethane
PCBs	Polychlorinated Biphenyls
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzo furans
PCE	Tetrachloroethylene
PCP	Pentachlorophenol
PDP	Preliminary Determination Phase
PDS	Personnel Decontamination Station
PE	Performance Evaluation
PE	Polyethylene
PEIS	Programmatic Environmental Impact Statement
PEL	Permissible Exposure Level
PFE	Potency Factor Estimate
PFLT	Paint Filter Liquids Test
PFS	Phased Feasibility Study
PHC	Principal Hazardous Constituents
PHRED	Public Health Risk Evaluation Database
PIAT	Public Information Assist Team
PIRP	Public Information Response Program (or Plan)
PN	Public Notification
PNA	Polynuclear Aromatics
POHCs	Principal Organic Hazardous Constituents
POLs	Petroleum, Oil, and Lubricants
POTWs	Publically Owned Treatment Works
POU	Point-of-Use Technologies
ppb	Parts per Billion
PPE	Personal Protective (Clothing and) Equipment
ppm	Parts per Million
ppt	Parts per Trillion

Acronym	Definition
PQL	Practical Quantitation Level
PRP	Potentially Responsible Party
PSD	Prevention of Significant Deterioration (Air)
PSTN	Pesticide Safety Team Network
PTA	Packed Tower Aeration
PVC	Polyvinyl Chloride
PWS	Public Water System
PWSS	Public Water System Supervision
QA	Quality Assurance
QA/QC	Quality Assurance/Quality Control
QAMS	Quality Assurance Management Staff
QAPP	Quality Assurance Project Plan
QARMP	Quality Assurance Reference Materials Project
QC	Quality Control
QCP	Quality Control Plan
QCSR	Quality Control Summary Report
RA	Remedial Action
RACT	Reasonably Available Control Technology
RAP	Remedial Action Plan
RAP	Response Action Program
RAS	Routine Analytical Service
RBC	Rotating Biological Contactor
RCP	Regional Contingency Plan
RCRA	Resource Conservation and Recovery Act of 1978
RCS	Regulated Chemical Substance
RD	Remedial Design
RD/RA	Remedial Design/Remedial Action
RDCO	Regional Document Control Officer
RDF	Refuse Derived Fuel
REEP	Reasonable Extra Efforts Program (Air)
REL	Recommended Exposure Limit
REM	Remedial Planning
REM/FIT	Remedial Planning/Field Investigation Team
RFA	Request for Application
RFD	Reference Dose
RFI	RCRA Facility Investigation
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
RIA	Regulatory Impact Analysis
RITTA	RCRA Integrated Training and Technical Assistance
RLL	Rapid Extremely Large Leakage
RLSC	Regional Laboratory Services Coordinator

Acronym	Definition
RM	Regional Manager (ARCS)
RMCL	Recommended Maximum Concentration Limit (Water)
RMICs	Recommended Maximum Impurity Concentrations
RO	Reverse Osmosis
ROD	Record of Decision
RQ	Reportable Quantity
RRT	Regional Response Team
RSPA	Research and Special Programs Administration
RSPO	Remedial Site Project Officer
RTP	Reinforced Thermosetting Plastic
RTR	Reinforced Thermosetting Resin
RV	Residual Volume
RWS	Rural Water Survey
SAB	Science Advisory Board (of EPA)
SAP	Sampling and Analysis Plan
SAR	Supplied-Air Respirator
SARA	Superfund Amendments and Reauthorization Act of 1986
SARMs	Standard Analytical Reference Materials
SAS	Special Analytical Services
SBIR	Small Business Innovative Research
SCAP	Superfund Comprehensive Accomplishments Plan
SCBA	Self-Contained Breathing Apparatus
SCS	Soil Conservation Service
SDI	Silt Density Index
SDI	Subchronic Daily Intake
SDL	Sample Detection Limit
SDWA	Safe Drinking Water Act
SDWAA	Safe Drinking Water Act Amendments
SERC	State Emergency Response Commission
SHERP	Safety, Health, and Emergency Response Plan
SI	Site Inspection
SI units	International System of Units
SIC	Standard Industrial Category
SIM	Selected Ion Monitoring
SIP	State Implementation Plan (Air)
SITE	Superfund Innovative Technology Evaluation
SLAMs	State and Local Air Monitoring Stations
SLN	Special Local Needs
SM	Site Manager (ARCS)
SMCL	Secondary Maximum Containment Level

Acronym	Definition
SMCRA	Surface Mining Control and Reclamation Act
SMO	Sample Management Office
SMOA	Superfund Memorandum of Agreement
SMWP	Sampling and Monitoring Work Plan
SNARL	Suggested No Adverse Response Level
SNUN	Significant New Use Notice
SNUR	Significant New Use Rule
SOC	Synthetic Organic Chemical
SOP	Standard Operating Procedure
SOQ	Statement of Qualifications
SOW	Statement of Work
SP	Sampling Plan
SPCC	Spill Prevention Control and Countermeasures
SPE	Solid Phase Extraction
SPHEM	Superfund Public Health Evaluation Manual
SQGs	Small Quantity Generators
SS	Suspended Solids
SSA	Sole Source Aquifer
SSB	Support Services Branch
SSC	Site Safety Coordinator (SSHO, SSO, and HSO)
SSC	Scientific Support Coordinator
SSHO	Site Safety and Health Office (SSC, SSO, and HSO)
SSO	Site Safety Officer (SSC, SSHO, and HSO)
SSSP	Site-Specific Safety Plan
SSU	Saybolt Seconds Universal (viscosity measurement)
STAPPA	State and Territorial Air Pollution Program Administration
STAR	Stability Array
STEL	Short-term Exposure Limit
STORET	Storage and Retrieval for Water Quality Data
SW	Solid Waste
SWDA	Solid Waste Disposal Act
SWMUs	Solid Waste Management Units
T-EPDM	Thermoplastic EPDM
TAG	Technical Assistance Grant
TAL	Target Analyte List
TAT	Technical Assistance Team
TBC	(Advisories) To Be Considered
TCA	Trichloromethane
TCDD	Tetrachlorodibenzo (p) dioxin, 2,3,7,8- (Dioxin)
TCE	Trichloroethylene
TCL	Target Compound List

Acronym	Definition
TCLP	Toxicity Characteristic Leaching Procedure
TDD	Technical Directive Document
TDS	Total Dissolved Solids
TECP	Totally-Encapsulated Chemical Protection
TEGD	Technical Enforcement Guidance Document
TEP	Typical End-Use Product
TGD	Technical Guidance Document
THM	Trihalomethane
TIC	Tentatively Identified Compound
TKN	Total Kjeldahl Nitrogen
TLD	Thermoluminescence Detector
TLV	Threshold Limit Value
TLV-C	Threshold Limit Value-Ceiling
TLV-STEL	Threshold Limit Value-Short-Term Exposure Limit
TLV-TWA	Threshold Limit Value-Time Weighted Average
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
TOH	Total Organic Halogen
TOX	Total Organic Halide
TPH	Total Petroleum Hydrocarbon
TPQ	Threshold Planning Quantity
TRDs	Technical Resource Documents
TRI	Toxic Release Inventory
TSCA	Toxic Substances Control Act
TSD	Toxic Substance Disposal
TSD	Treatment, Storage, and Disposal
TSDFs	Treatment, Storage, and Disposal Facilities
TSP	Total Suspended Particulate
TSS	Total Suspended Solids
TTO	Total Toxic Organics
TTUs	Transportable Treatment Units (hazardous waste)
TUAC	Total Unburned Hydrocarbons
TWA	Time Weighted Average
UCR	Unit Carcinogenic Risk
UEL	Upper Explosive Limit
UF	Ultrafiltration
UFL	Upper Flammable Limit
UHWM	Uniform Hazardous Waste Management
UIC	Underground Injection Control
UNAMAP	User's Network for Applied Modeling of Air Pollution

Acronym	Definition
USA-CERL	U.S. Army Construction Engineering Research Laboratory
USALMC	U.S. Army Logistics Management Center
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency
USC	U.S. Code
USCG	U.S. Coast Guard
USCS	Unified Soil Classification System
USDA	U.S. Department of Agriculture
USDI	U.S. Department of Interior
USDW	Underground Source of Drinking Water
USGS	U.S. Geological Survey
USNRC	U.S. Nuclear Regulatory Commission
USPIRG	U.S. Public Interest Research Group
UST	Underground Storage Tank
UV	Ultraviolet
VOA	Volatile Organic Acid
VOC	Volatile Organic Compound
VOST	Volatile Organic Sampling Train
VTSR	Verified Time of Sample Receipt
WAO	Wet Air Oxidation
WAP	Waste Analysis Plan
WLA	Wasteload Allocation
WMDDRD	Waste Minimization Destruction/Disposal Research Division
WMP	Waste Minimization Program
WP	Work Plan
WPCF	Water Pollution Control Federation
WQA	Water Quality Act of 1987
WQC	Water Quality Criteria
WRAP	Waste Reduction Assessment Program
WREAFS	Waste Reduction at Federal Sites
WRITE	Waste Reduction Innovative Technology Evaluation

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