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TECHNOLOGICAL OPTIONS FOR MANAGEMENT OF HAZARDOUS
WASTES FROM U.S. DEPARTMENT OF ENERGY FACILITIES

by

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ABSTRACT

This report provides comprehensive information on the technological options for management of hazardous wastes generated at facilities owned or operated by the U.S. Department of Energy (DOE). These facilities annually generate a large quantity of wastes that could be deemed hazardous under the Resource Conservation and Recovery Act (RCRA). Included in these wastes are liquids or solids containing polychlorinated biphenyls, pesticides, heavy metals, waste oils, spent solvents, acids, bases, carcinogens, and numerous other pollutants. Some of these wastes consist of nonnuclear hazardous chemicals; others are mixed wastes containing radioactive materials and hazardous chemicals.

Nearly 20 unit processes and disposal methods are presented in this report. They were selected on the basis of their proven utility in waste management and potential applicability at DOE sites. These technological options fall into five categories: physical processes, chemical processes, waste exchange, fixation, and ultimate disposal. The options can be employed for either resource recovery, waste detoxification, volume reduction, or perpetual storage. Detailed descriptions of each technological option are presented, including information on process performance, cost, energy and environmental considerations, waste management of applications, and potential applications at DOE sites.

1 INTRODUCTION

Hazardous Waste Generation in the United States

Over 6×10^9 tons of solid waste are produced annually in the United States. At least 40×10^6 tons of these wastes contain toxic chemicals, many of which are man-made chemical compounds that may possess mutagenic, carcinogenic, teratogenic, or acutely toxic properties. Unfortunately, certain technological and scientific breakthroughs have had the adverse impact of

increasing the presence of these toxic chemicals in our environment by many orders of magnitude. Prior practices for disposing of wastes containing these chemicals demonstrated that little consideration had been given to the possibility of future generations coming into contact with these toxic species.

Hazardous Waste Generation from Energy Industry

The most frequently cited examples of inadequate waste management are those of chemical industries; however, the energy development sector may also have problems with toxic waste disposal if precautions are not taken. Efforts are under way to develop and improve technologies that produce liquid and gaseous products from coal and liquids from oil shale. These coal-use initiatives run counter to many environmental initiatives and, except for their possible impact on air quality, these energy developments will most affect environmental initiatives on solid waste generation. Present federal initiatives call for approximately 2×10^9 tons of coal to be mined by 2000.

The amount of coal cleaning wastes, fly ash, and scrubber sludge to be disposed of from conventional combustion, already estimated at 66×10^6 tons per year, will escalate dramatically to more than 200×10^6 tons per year. Of perhaps greater importance, however, is that 600×10^6 tons of coal per year will be converted to synfuels by 2000. It is estimated that up to 50×10^6 tons of solid waste will be generated from these conversion processes. Although much of the waste from these processes will contain ash and scrubber sludge, new types of wastes will also be produced. In particular, the reducing nature of the conversion processes will produce appreciable amounts of coal char, tars, and oils. These wastes could contain considerable amounts of organic chemicals that are toxic or carcinogenic. In addition to coal, oil shale development will produce 180×10^6 tons per year of solid wastes by 1995. Continuing problems will also exist in disposing of nuclear fuel-cycle wastes and drilling brines and muds from domestic oil and gas production.

In addition to these fuel wastes, many transformers and capacitors contain polychlorinated biphenyls (PCBs) either as concentrated liquids or as oils contaminated with PCBs. The wastes arising from these are presently controlled under the Toxic Substances Control Act (TSCA), although the authority for disposal of these wastes may be transferred to Resource Conservation and Recovery Act (RCRA) regulations. Regulations promulgated under RCRA will control disposal of all the wastes mentioned above. RCRA provides for criteria that designate certain solid wastes as hazardous. Wastes with this designation require special handling and disposal. It is believed that waste streams from many energy-producing processes will be deemed hazardous under RCRA criteria. It should be noted that the Solid Waste Act of 1980 will allow for a three-year moratorium on designation of conventional coal combustion wastes under RCRA.

In addition to solid fossil-fuel wastes, there are a variety of solid wastes from the nuclear fuel cycle. High-level wastes (HLW) can be either (1)

intact spent fuel assemblies removed from a reactor or (2) the wastes generated as a result of spent-fuel reprocessing. A 1000-MW light-water reactor annually discharges about 30 metric tons of spent fuel from the present once-through fuel cycle. Currently, commercial spent-fuel assemblies are stored at the reactor site until a decision on the question of spent-fuel reprocessing is made. If the nuclear fuel cycle is closed and spent reactor fuel is reprocessed to recover uranium and/or plutonium, a different type of HLW will become the bulk of the wastes generated. Reprocessing wastes contain 84% by weight of fission products and 16% by weight actinide wastes. In addition to decreasing the volume of wastes that must be disposed of, spent-fuel reprocessing reduces the amounts of transuranic elements in the waste. However, the consequent reduction in waste-disposal risk achieved by reprocessing and recycling must be balanced against the new risks entailed in using plutonium in the active fuel cycle and in processing large quantities of radioactive materials.

Transuranic (TRU) wastes result primarily from spent-fuel reprocessing and fuel assembly refabrication; very little is generated by the once-through fuel cycle. Transuranic wastes are currently defined as material containing more than 10 nanocuries of TRU activity per gram of material. Because of their long half-lives, TRU wastes must be isolated from the biosphere for time periods similar to those for HLWs, i.e., 10^3 to 10^6 years. However, problems associated with heat generation and temperature increases are absent, and since TRU wastes are easier to handle than HLWs, the operational demands on disposal systems designed for TRU waste alone would be more modest than those associated with an HLW repository.

In contrast to TRU wastes, low-level wastes (LLWs) are defined as those containing less than 10 nanocuries of TRU activity per gram of material. (In fact LLWs may be entirely free of TRU activity.) LLWs, however, might have potentially hazardous amounts of fission products. LLWs are generated in all phases of the nuclear fuel cycle and in other operations that utilize radioisotopes. Disposal of LLWs consists of burial in shallow pits; 14×10^6 metric tons of commercial and 46×10^6 metric tons of defense-related LLWs have already been buried. It is anticipated that the annual production of LLW wastes will triple to 321,000 m^3 by 1990. Many of these wastes will be mixed wastes, i.e., LLW mixed with toxic or potentially toxic chemical wastes.

The final category of nuclear wastes involves those generated upon the retirement of a nuclear facility. The process of decommissioning/decontamination is a potential source of large quantities of radioactive wastes. The volume of LLW (no TRU) that might result after the shutdown of an 1160-MW reactor could vary from 60 m^3 under a mothballing procedure, to 23,000 m^3 for complete removal and dismantling.

Hazardous Waste Generation at DOE Facilities

The Department of Energy's (DOE's) facilities, like many large manufacturing industries, generate a large quantity of hazardous wastes. Approximately 150 sites operated or owned by DOE are presently believed to have waste streams that could be deemed hazardous under RCRA (Resource Conservation and Recovery Act). According to a recent survey, these sites annually produce some 400×10^6 pounds of nonnuclear hazardous waste and 770×10^6 pounds of mixed hazardous waste containing radioactive materials. These waste streams include some 30×10^6 pounds of wastes containing PCBs, and disposal of these wastes will continue to be a significant portion of waste disposal effort at several facilities. In addition to PCB wastes, a large variety of other hazardous wastes require treatment and disposal: waste oils, spent solvents, acids, bases, asbestos, coal tars, coal liquids, heavy-metal-containing liquids, and many others. The hazardous waste generation data compiled based on the recent DOE survey of 45 sites are presented in Table 1.1.

The regulations promulgated under RCRA require that hazardous waste be managed in an environmentally accepted manner. Currently DOE has taken the position that the RCRA does not apply to those DOE facilities regulated under the Atomic Energy Act (AEA). This position applies to nonradioactive waste streams as well as mixed waste streams. Regardless of RCRA applicability, DOE must subscribe to waste management practices that are comparable to those required under RCRA and consistent with other state and federal laws. In meeting the proper disposal guidelines, DOE facilities will need to examine disposal options and state-of-the-art practices.

The Office of Operational Safety (OOS) of the U.S. Department of Energy is charged with providing support and assistance to DOE organizations in conforming with environmental regulations. In meeting the criteria under these regulations, OOS staff develops policy and provides DOE facility staff with advice, information, and technical support in order to enable proper conformance with environmental regulations. The current and future RCRA regulations for management of hazardous waste streams from DOE facilities are (or are expected to be) some of the most stringent environmental regulations to be developed.

Purpose and Organization of This Report

This report, prepared under a program sponsored by DOE/OOS, identifies and evaluates various options for management of hazardous wastes at DOE

Table 1.1 Hazardous Waste from DOE Facilities^a

Major Category	Type	Annual Generation (tons)	Contents/Wastes
Organic	Waste oils	480	
	PCBs	2000	
	Halogenated spent solvents	840	Tetrachloroethane, tetrachloroethene, trichloroethylene, trichloroethene, trichloromethanethiol, chloroform, etc.
	Nonhalogenated spent solvents	500	Methanol, ethanol, toluene, xylene, kerosene, acetone, methylethyl ketone, metnylisobutyl ketone, etc.
	Unspecified solvents	140	
	Others	310	Acetonitrile, cyanides, benzo(a) pyrene, creosote, coal tars, coal liquids, gasifier wastewater, etc.
Inorganic	Asbestos	60	
	Metal-containing	10,220	Mercury, chromium, cadmium, sodium, arsenic, lead, barium, silver, etc.
	Acids	86,300	HCl, H ₂ SO ₄ , HNO ₃ , HI, HF, HBI ₄ , etc.
	Bases	250	KOH, NaOH, NH ₄ OH, etc.
	Others	1,127,700	Spent pickle solution, wastewater treatment sludge, cooling water blow-down, etc.
Unspecified		67,000	

^aCompiled by ANL based on the DOE preliminary survey of 45 sites.

facilities.* These options include resource recovery, detoxification, volume reduction, fixation, and land disposal. The resource recovery alternative pertains to the treatment of wastes for recovery of material or energy. It is obviously attractive not only from the standpoint of conserving material and energy resources now beginning to be recognized as finite, but also as a potential means of reducing the quality of hazardous wastes requiring disposal. The detoxification alternative interposes a step prior to disposal that makes the waste stream innocuous, so that low-cost disposal methods become applicable. The volume reduction alternative simply reduces the magnitude of the waste disposal problem, permitting efficient utilization of available land burial sites. Fixation is applicable to liquid or semiliquid wastes to produce solid material prior to disposal, aiming to improve the handling and physical characteristics of the wastes, and to limit the solubility of pollutants contained in the waste. Landfill disposal is thus far the most commonly used means for management of solid/hazardous wastes. The primary purpose here is to provide information that facilitates development of acceptable landfill disposal practices as a measure to contain hazardous wastes.

Nearly 20 unit processes/management methods are evaluated in this report. These options were selected due to their potential or proved applicability to the specific hazardous wastes being generated at DOE sites. They are categorized into five categories and presented in the following sections.

*Currently available technologies for management of PCB-containing wastes are assessed in a separate ANL report - Fradkin, L., and S. Barisas, *Technologies for Treatment, Reuse, and Disposal of Polychlorinated Biphenyl Wastes*, Argonne National Laboratory Report (ANL/EES-TM-168), January 1982. Another Argonne report - Tanzman, E., B. LaBrie, and K. Lerner, *Overview of Hazardous Waste Regulations at Federal Facilities*, for the U.S. Department of Energy (ANL/EES-TM-182), May 1982, provides an overview and current development of federal laws and regulations concerning hazardous waste management and an assessment of current status of state hazardous waste management programs.

2 PHYSICAL TREATMENT PROCESSES FOR RECYCLING OR VOLUME REDUCTION

The physical treatment processes described in this section are resin adsorption, dissolution (leaching), liquid-liquid extraction, membrane processes (ultrafiltration and reverse osmosis), distillation, steam distillation, steam stripping, and evaporation. These physical technologies are either phase separation processes or component separation processes, and are potentially useful in volume reduction or resource recovery. They were chosen due to their potential or proved applicability to the specific hazardous wastes being generated at several DOE sites.

2.1 RESIN ADSORPTION

2.1.1 Description of Technology

2.1.1.1 Basic Concepts

Adsorption on synthetic resins is considered here primarily as a process for the removal of organic chemicals from liquid waste streams; a separate section on ion-exchange resins, which are used for removal or recovery of inorganic ions, appears elsewhere in this report.

Waste treatment by resin adsorption involves two basic steps: contacting the liquid waste stream with the resins and allowing the resins to adsorb the solutes from the solution; and regenerating the resins by removing the adsorbed chemicals, a process that is often effected by simply washing the resin with the proper solvent.

The chemical natures of the various commercially available resins are quite different; perhaps the most important variable in this respect is the degree of their hydrophilicity. The adsorption of a nonpolar molecule onto a hydrophobic resin (e.g., a styrene divinylbenzene-based resin) results primarily from the effect of Van der Waals forces. With less-hydrophobic resins, other types of interactions such as dipole-dipole interaction and hydrogen bonding are also important.¹

Although it is not possible to predict accurately the degree of adsorption that will take place in any specific case, it is useful to generalize that hydrophobic or nonpolar molecules (or portions of molecules) are attracted to hydrophobic surfaces, and that hydrophilic or polar molecules are attracted to hydrophilic surfaces.

In resin adsorption, the strength of the attractive forces between the solute molecules and the resin is usually weaker than that associated with solute adsorption on carbon. Consequently, the resin can be more easily

regenerated and the adsorbed substances can be more easily recovered than in carbon adsorption. With carbon, thermal regeneration is usually required, which generally means that solutes cannot be recovered.

2.1.1.2 Process Description

Resin adsorbents are used in much the same way as granular carbon adsorbents. A typical system for treating low-volume waste streams consists of two fixed beds of resin. One bed will be on stream for adsorption while the second is being regenerated (see Fig. 2.1). In cases where the adsorption time is much longer than regeneration time, one resin bed plus a hold-up storage tank is generally used.

Fig. 2.1 Resin Adsorption Process for the Removal and Recovery of Phenol from Water

The adsorption bed is usually fed by downflow at flow rates in the range of 0.25 to 2 gal/min/ft³ of resin; this is equivalent to 2-16 bed volumes per hour, and thus contact times are in the range of 3-30 min. Linear flow rates are in the range of 1-10 gal/min/ft². Adsorption is stopped when the bed is fully loaded and/or the concentration in the effluent rises above a certain level.

Regeneration of the resin bed is performed in situ with basic, acidic, or salt solutions or nonaqueous solvent. Basic solutions may be used for the removal of weakly acidic solutes and acidic solutions for the removal of weakly basic solutes; hot water or steam may be used for volatile solutes; methanol and acetone are often used for the removal of nonionic organic solutes. A prerinse and/or a postrinse with water are required in some cases. As a rule, about 3 bed volumes of regenerant will be required for resin regeneration, although as little as 1.5 bed volumes may suffice in certain applications.

The regenerating solvent is usually recovered unless (1) the solute-laden solvent can be used as a feed stream in some industrial process at the plant or (2) the cost of the solvent is low enough so that it may be disposed of after a single use. Organic solvents are usually recovered by distillation, which of course allows recovery of the solute too, if that is desired.

Resin lifetimes may vary considerably, depending on the nature of the feed and regenerant streams. Regeneration with caustic is estimated to cause a loss of 0.1 to 1% of the resin per cycle;² replacement of resins at such installations may be necessary every 2-5 y, and in this case lifetimes will be limited by slow fouling or oxidation resulting in a loss of capacity; actual experience indicates that lifetimes of more than five years are obtainable.

2.1.1.3 Special Characteristics

Environmental Impacts. Disposal of the used regenerant solution or the extracted solutes when they are not recycled must be addressed. For example, when highly colored wastewaters are treated, the used regenerant solution (containing 2-4% caustic plus the eluted wastes) is not recycled and must be disposed of, usually by evaporation and incineration. In another case, when pesticides are removed from water, regeneration is effected by an organic solvent. In this case, the solvent would be recovered (probably by distillation) resulting in a concentrated waste (still bottoms) to be disposed of (probably by incineration). Where incineration is used for the eventual destruction of the wastes, the environmental impacts would be on air quality (from incinerator emissions), energy use (for the incinerator fuel), and land use (for the disposal of unburned residues).

Energy Requirements. Energy requirements are most significant when both solvent and solute are recovered by distillation. Up to three distillation columns may be needed (see, for example, the system shown in Fig. 2.1). If, additionally, the influent solute concentration is high, frequent bed regeneration may be required and large quantities of steam will be used for the distillation columns. Electricity requirements will also increase. In such a case, energy requirements may account for over half of the direct operating costs. In systems where distillation is not required, the energy requirements consist only of electricity for pumps, stirrers, and controls and may only account for about 5% of the direct operating costs.

Barriers to Implementation. The following are expected to be barriers to implementation of resin adsorption:

- Generally lower adsorption capacity than activated carbon (surface areas are smaller);
- Susceptibility to certain poisons such as oxidants or organic foulants that are not efficiently removed by the regenerant;
- The necessity of keeping suspended solids in the influent low enough to prevent clogging in the bed; and,
- The relatively high cost of the resins vs. the cost of activated carbon.

Cost. The costs of wastewater treatment by resin adsorption can vary widely depending on the nature of waste being treated and the system design. As with carbon adsorption systems, two primary variables in the process economics are the resin exhaustion rate (i.e., the amount of resin required to treat a given volume of liquid) and the superficial liquid retention time (i.e., the time that the liquid takes to fill the volume of the resin bed.) For a given flow, influent concentration, and resin, the capital and operating costs will depend almost entirely on these two variables. The operating costs are determined primarily by the resin exhaustion rate because this rate will set the frequency of regeneration required. The total capital costs will be determined primarily by the superficial liquid retention time because this time will set the size (or number) of the resin beds required.

2.1.2 Applications

2.1.2.1 General Discussion of Applications

Resin adsorption (excluding ion exchange with inorganic species) is expected to be applicable to the removal of organic solutes from aqueous wastewater and of organic or inorganic solutes from nonaqueous liquid wastes. Table 2.1 summarizes actual and potential waste treatment applications.

Resins have proved to be very efficient for color removal (primarily color associated with organic molecules) and to be capable of decreasing chemical or biological oxygen demand (COD or BOD) by a significant fraction at the same time. When one or more solutes of commercial value are present in high enough concentrations to merit consideration of recovery, resins should be considered because it is relatively easy to recover certain solutes following resin adsorption.

Resins may be designed to be selective. For example, special resins may be made that will (1) selectively remove aromatics from linear hydrocarbons (especially hydrophilic ones), (2) selectively remove amines from other hydrocarbons, (3) selectively remove weak organic acids from other

Table 2.1 Waste Treatment Applications of Resin Adsorption

Physical Form of Waste	Hazardous Components	Component Concentration
<u>Actual Applications</u>		
Aqueous Solution	Phenols	High
	Color (plus some COD & BOD)	High
	Explosives (TNT, DNT, HMS, RDX)	Low
	Pesticides (e.g., endrin)	Low
	Chemical carcinogens	Very Low
	Chlorinated hydrocarbons (e.g., ethylene dichloride)	Low
<u>Potential Applications</u>		
Aqueous Solution	Almost any organic chemical	Low-High
Aqueous Solution	Some inorganic chemicals (?)	Unknown
Nonaqueous Solution	Some inorganic or organic chemicals (?)	Unknown

hydrocarbons, and (4) selectively remove macromolecules (e.g., dye bodies) from wastewaters containing other material.

If an adsorption process is desirable for a moderate-to-high-volume waste stream, and carbon cannot be regenerated in such an application, then resin adsorption may be more economical: e.g., with munition plant wastewaters that contain explosives, thermal regeneration of carbon is not safe and chemical regeneration of carbon is not practical; thus carbon adsorbent would have to be thrown away.

High levels of inorganic dissolved solids can pose problems for carbon adsorption systems. These inorganic solids may deposit on the carbon during thermal regeneration and cause severe scaling, resulting in appreciable loss of activity. This deposition is not a problem with resins, since they are not thermally regenerated, although they may require a prerinse with water before regeneration with solvents.

2.1.2.2 Potential Applications to DOE Waste Streams

Removal of Pesticides from Wastewaters. Resin adsorption can be used to reduce pesticide concentration from 1 part per million (ppm) to less than 1 part per billion (ppb). Isopropanol can be used for resin regeneration, and can be distilled for solvent recovery.

Removal of Carcinogens from Wastewater. Trace levels of chemical carcinogens may be removed from wastewaters by resin adsorption. In this case, resin adsorption is more desirable than carbon adsorption because the leakage rate is lower. Methanol may be used to regenerate the resin bed.

Removal of Chlorinated Hydrocarbons from Wastewaters. Resin beds have been found to be effective at removing ethylene dichloride from wastewaters. Tetraethylene dichloride is removed from the resin with a steam regeneration procedure.

2.2 DISSOLUTION (LEACHING)

2.2.1 Description of Technology

2.2.1.1 Basic Concept

Dissolution is the complete or partial transfer of one or more components from a solid phase into a liquid phase in contact with the solid. The

liquid phase may consist of a consumable active reagent in a carrier solvent or a simple solvent alone. The most frequently used carrier solvent for dissolution of inorganic species is water, because it aids in holding the dissolved species in solution and is by far the least expensive solvent.

In dissolution, the major intended product is an aqueous stream that requires further treatment for separation, recovery, stabilization, or destruction of the species leached from the solids. Hence, dissolution is only a first step in recovering resources from waste.

The dissolution reaction involves some degree of chemical transformation of the species being dissolved. The driving force for the reaction is the formation of a more stable solvated species or the transformation of one of the species by a reagent. An example of the former is the selective dissolution of water-soluble salts from an otherwise water-insoluble solid, whereas an example of the latter is the dissolution of a water-insoluble metal carbonate salt in an acid, accompanied by the formation and evolution of carbon dioxide from the solution.

2.2.1.2 Process Operation

In the dissolution process, the solids are placed in contact with the reagent in a mixer for a length of time that is determined by the kinetics of the particular reaction taking place, following which the slurry is separated. Heat may be applied to speed up the process and to provide increased solubility.

There are various methods of bringing the liquid and solids into contact. The mode most used in waste processing is batch leaching. This process involves loading a mixer with appropriate amounts of solids and solvent, mixing until leaching is complete, and then separating the phases.

Dissolution operations make use of common mixing and separating equipment. Mixers include both impeller-driven and air-lift types; separating equipment includes thickeners and various filters. Materials of construction must be appropriate for the solvent being used. Extremely corrosion-resistant materials may be required for processes designed to recover corrosion-resistant alloys from machining wastes.

A wide variety of reagents can be used. However, economic considerations dictate that only a very few are widely used in waste processing. The major categories of reagents are as follows:

- Acids - Sulfuric, hydrochloric, nitric, and phosphoric are all useful to one degree or another in the dissolution of basic salts (hydroxides, oxides, carbonates) of metals. Sulfuric acid is by far the most widely used; hydrochloric acid is used where complexing is needed.

- Bases - Sodium hydroxide is the principal base; however, lime and sodium sulfate can also be used to yield dilute solutions. Sodium hydroxide is used to dissolve metallic aluminum.
- Complexants - Ammonia, ammonium salts, and sodium cyanide are used commercially as leaching agents for copper and nickel from ores. Carbon dioxide is also used with ammonia in leaching copper and nickel.
- Oxidants - Air (O_2) and chlorine are most widely used; air has been used frequently as an oxidant in leaching copper ores. Chlorine finds use with hydrochloric acid in dissolving corrosion-resistant metals such as cobalt/nickel alloys.

The solids can be treated with two or more solvents sequentially for selective removal of different species. This process can be particularly useful where removal of a valuable component will result in simultaneous leaching of undesirable materials. For example, a solid composed of the mixed hydroxides of nickel, copper, and chromium (III) can be leached initially with ammonium carbonate to remove nickel and copper, and then the chromium can be removed with a sulfuric acid leach.³

Another type of dissolution process involves the use of fused salts as solvents. Such materials have been used as chemical reaction media and have some useful solvent and electrochemical properties. However, the energy cost and the large amounts of salts required make their use in waste processing highly unlikely at this point.

2.2.1.3 Economic and Environmental Characteristics

The cost of dissolution can vary greatly, depending on the material being dissolved and the reagents and operating conditions required to handle it. To illustrate the costs, a sample economic analysis was done by Arthur D. Little, Inc. in 1976.⁴ The sample application consisted of dissolution of a 10,000-lb/day feed stream of dry, mixed metal-liming sludge solids from metal finishing, containing 3.2% copper, 3.6% nickel, 7.3% chromium, 5.6% zinc, and 0.4% cadmium. The chemical form of the metals and the remainder of the solids were unspecified. The listed metals were dissolved in aqueous sulfuric acid in a batch mode operating 24 h/day, 350 days/y. The operation required two stainless steel reactors, each of 1100 gal capacity. The required resources included energy, water, and labor, as well as sulfuric acid. Quantities of resources and the associated costs are shown in Table 2.2.

The actual costs for this application at the present time would be higher than the 1976 costs shown in Table 2.2. However, the illustration

Table 2.2 1976 Cost Estimates for Dissolution Treatment System^a

Cost Category	Annual Quantity	Unit Cost, \$	Annual Cost (1976)
<u>Variable Costs</u>			
Operating Labor	2,200 man-hours	12.00/h	\$ 26,400
Electricity	300,000 kWh	0.02/kWh	6,000
Heat	7×10^9 Btu	$2/10^6$ Btu	14,300
Chemicals			
H ₂ SO ₄	750 tons	53.25/ton	42,750
H ₂ O	3.5×10^6 gal	0.20/100 gal	700
Maintenance (3%)			2,400
Total Variable Costs			\$ 92,550
<u>Fixed Costs</u>			
Taxes and Insurance (2%)			1,600
Capital Recovery			13,200
Total Fixed Costs			\$ 14,800
Total Operating Costs			\$107,000

^aSource: Ref. 4.

serves to point out a conclusion that is generally well established in hydro-metallurgy practice, namely that such processes are extremely chemical-intensive. The cost for clean sulfuric acid is approximately 40% of the processing costs. If there are any extraneous acid-consuming substances present such as excess lime or sodium carbonate, then the acid consumption will be increased in proportion to the content of those substances.

Use of clean acid reagents other than sulfuric acid will result in even higher reagent costs, and may also require special corrosion-resistant equipment.

Waste processing offers ample opportunity to utilize waste reagents that frequently are available at substantially lower cost. In general, the cost of such reagents is related to the nature and amount of impurities present, including water and other solvents. In some cases, the producers of such wastes will pay to have them removed. Examples of waste reagents are waste acids (sulfuric and hydrofluoric) from petrochemical alkylation processes and waste hydrochloric acid from chlorination processes.

Such waste reagents can be utilized in many treatment processes where the impurities contained in the reagents will not interfere with subsequent processing steps or result in the necessity for additional processing steps. For example, dilute sulfuric acid contaminated with heavy metals probably could be used for leaching of metal-containing sludges without problems. However, sulfuric acid containing much organic matter, as is often found in spent alkylation acid, might well introduce sufficient organics into the process stream to upset subsequent separation steps such as precipitation or ion exchange. In addition, the organics thus added might necessitate an additional treatment step in order to render the aqueous stream suitable for discharge or reuse.

The energy requirements for dissolution are relatively minor: principally electricity for mixing and pumping, and possibly steam or another source of heat to aid the dissolution process.

There are few environmental problems associated with dissolution. Emissions to water are not significant, provided that the liquors used and produced are properly conveyed to the next processing step with no inadvertent losses. No land disposal problems are anticipated, provided that any leached solids that have been made suitable for landfill disposal are adequately washed to remove leach liquor prior to such disposal. Emissions to air would be significant only when gas is evolved during dissolution. Such gas evolution may be the result of the intended dissolution reaction, as in release of carbon dioxide during dissolution of carbonates in acid, or of an unintended reaction, as in reaction of traces of sulfides in the waste to give hydrogen sulfide. There are no special land use factors associated with the usual modes of dissolution. The only safety problems that might arise involve handling the loaded leach liquor and reagents.

2.2.2 Applications

2.2.2.1 Current Commercial Applications to Waste Treatment

There appear to be relatively few commercial applications of dissolution to waste treatment; it is mostly used, in commercial operations, for recovery of bulk materials rather than for selective stripping of minor constituents.

One application involves the production of various zinc and iron chemicals for agricultural and other uses, by using waste acids to dissolve skimmings from galvanizing operations and flue dusts containing zinc and iron.⁵ Commercially valuable products realized from such processes include zinc sulfate, zinc ammonium sulfate, ferrous ammonium sulfate, and ferric sulfate. The reactions are carried out in batch operations.

A commercial operation for the recovery of metallic copper scrap involves dissolution of the material in ammonia/ammonium carbonate solution with air oxidation.⁶

Commercial applications of leaching have generally been predicted upon a fairly constant composition of the feed solids, and upon large-volume operations. In contrast, in waste processing, very little may be known about the composition and contents of the waste. This problem is illustrated by work at Battelle on leaching of metal sludge.³ Sludges that were somewhat similar in composition behaved rather differently during leaching, and even sludges from the same source varied markedly in metal content and in leaching properties. Techniques used successfully for ores of supposedly similar composition did not work as well as expected with sludges.

In order to cope with these problems, it may be necessary to employ stronger acids and oxidants than desirable. Even so, having more information on the solids composition would permit a more knowledgeable selection of possible reagents and conditions before starting tests. These composition data must include all major substances, as well as the components to be dissolved, and should include the chemical identity of the latter where possible.

Some thought must also be given to treatment prior to dissolution. Although grinding and milling may be too expensive for waste treatment, simple mixing may improve the homogeneity of the material, thereby ensuring that leaching conditions established on one portion will be applicable to all others.

2.2.2.2 Potential Applications to DOE Wastes

Dissolution is applicable to a wide variety of waste forms and qualities. Present commercial and laboratory applications have centered on those wastes that have sufficient metal value for economic recovery. Dissolution may be applicable to

- Dry solids, such as metallic wastes (metal machining waste), dry powders (flue dust, flyash), and ashes (incineration, coal combustion);
- Slurries, such as scrubber slurries, metal machining slurries (electrochemical machining, for example), and sludges (hydroxide and liming sludges from metal finishing processes, frequently having solids contents in the 1 to 10% range); and
- Organics, such as metallized and metal-containing polymer wastes.

The technique may be applied over a range of situations, from the removal of a major component of a solid waste to removal of minor or trace components.

2.3 LIQUID-LIQUID EXTRACTION

2.3.1 Description of Technology

2.3.1.1 Basic Concepts

Liquid-liquid extraction is the separation of one or more components of a liquid solution by contact with a second immiscible liquid called the solvent. If the component(s) in the original liquid solution distribute themselves differently between the two liquid phases, separation will result, and it is this principle upon which separation by liquid-liquid extraction is based.

Solvent extraction can theoretically be used for any solute concentration, though there may be restrictions at times, depending on the specific solute and solvent involved. For example, when the solute and solvent are miscible with each other in all proportions, there exists an upper limit of solute concentration (in the feed solution) above which it is not possible to extract any solute with that solvent. Extraction may be easier, in a practical sense, at low solute concentrations, because lower solvent-to-feed ratios could probably be used, and a solvent with very low solubility in the raffinate (i.e., the feed solution after it is extracted) could be used, thus eliminating the need for recovery of solvent from the raffinate. On the other hand, low-concentration aqueous solutions are likely to be more economically treated either by adsorption (e.g., with carbon or resins) or by stripping.

2.3.1.2 Process Description

The liquid-liquid extraction process is shown schematically in Fig. 2.2. As Fig. 2.2 indicates, reuse of the extracting solvent (after solute removal) and recovery of that portion of the extracting solvent that dissolves in the extracted phase are usually necessary aspects of the process. Solvent reuse is necessary for economic reasons; the cost of the solvent is generally too high to permit one-time use. Recovery of solvent from the extracted water, or raffinate, may be omitted if the concentration in the water to be discharged is not harmful, or if the solvent lost does not represent a high cost. The end result of solvent extraction is to separate the original solution into a treated stream (the raffinate) and a recovered solute stream (which may contain small amounts of water and solvent). Solvent extraction may thus be considered a recovery process, because the solute chemicals are generally recovered for reuse, resale, or further treatment and disposal.

Fig. 2.2 Schematic Diagram of Solvent Extraction of Wastewater

The first step, extraction, brings the two liquid phases (feed and solvent) into intimate contact to allow solute transfer either by forced mixing or by countercurrent flow resulting from density differences. The extractor will also have provisions to allow separation of the two phases after mixing.

One output stream from the extractor is the solute-laden solvent; some water may also be present. Solute removal may be via a second solvent extraction step, distillation, or some other process. For example, a second extraction, with caustic, is sometimes used to extract phenol from light oil, which is used as the primary solvent in dephenolizing coke plant wastewaters. Distillation is more common, except where problems with azeotropes are present. In certain cases, it may be possible to use the solute-laden solvent as a feed stream in some industrial processes, thus eliminating solute recovery. This is apparently the case at some refineries, where crude or light oil can be used as a solvent (for phenol removal from water) and later processed with the solute in it. Other similar applications probably exist and are particularly attractive since they eliminate one costly step.

There are two major categories of equipment for liquid extraction.

- (a) Single-stage equipment where the fluids are mixed, extraction occurs, and the insoluble liquids are settled and separated. A cascade of such stages may then be arranged. A single stage must provide facilities for mixing the insoluble liquids and for settling and decanting the emulsion or dispersion that results. In batch operation, mixing, settling, and decanting may take place in the same or in separate vessels. In continuous operation, different vessels are required.

- (b) Multistage equipment, where the equivalent of many stages may be incorporated into a single device or apparatus. Countercurrent flow is produced by virtue of the difference in densities of the liquids. With few exceptions, the equipment takes the form of a vertical tower, which may or may not contain internal devices to influence the flow pattern. Other forms of equipment include centrifuges, rotating discs, and rotating buckets. Depending upon the nature of the internal structure, the equipment may be of the stagewise or continuous-contact type.

2.3.1.3 Special Characteristics

Environmental Impacts. There are no major environmental impacts associated with the proper use of solvent extraction. Solvent extraction is almost always used for material recovery (for resale or reuse), and thus may be of some environmental benefit.

When one or more solutes are recovered from aqueous wastes, minor impacts can result from small losses of the solvent (to the air and/or water) and of heat (e.g., from stripping or distillation). In addition, solvent extraction systems seldom produce a raffinate that is suitable for direct discharge to surface waters, and thus a polishing treatment is generally required; biological treatment suffices in many cases.

When mixed organic liquids are treated principally for the recovery of one component (e.g., the more valuable halogenated hydrocarbons), current economic forces may make the purification of other components (as required for resale or reuse) impractical, and a waste for disposal will result.

Energy Requirements. Energy consumption for a solvent extraction process will be minimal if solvent extraction is the only process required; electric power is needed for feed and solvent pumps and possibly a stirrer or column agitator. When the overall process also includes recovery of solvent and solute by stripping, distillation, or adsorption, then significant amounts of additional energy, both steam and electricity, will be required for such units. It is estimated that solvent extraction may be less energy-intensive than steam stripping (a competing process), especially when the material to be removed by stripping makes up a major fraction of the feed solution.

Barriers to Implementation. For aqueous solutions, if a solute is present in concentrations higher than about 10%, it is likely that solvent extraction, although still possible, may become impractical. This could be true, for example, if the solute has a strong hydrophilic nature and thus

requires the use of a solvent that is also somewhat hydrophilic, to obtain a respectable extraction efficiency. The use of such a solvent would probably lead to problems with recovery of solvent from the raffinate.

Cost. Costs of extraction processes vary widely and are in general least when a system can be designed so that one, or just a few, extraction stages are required.

2.3.2 Applications

2.3.2.1 General Discussion

Present applications are concentrated in two areas: the recovery of phenol from aqueous wastes, and the recovery of halogenated hydrocarbons from organic solutions containing other water-soluble components. Extraction in the former case is with an organic solvent and in the latter case with water.

Valuable organic solutes in concentrations ranging from a few hundred ppm to a few percent may be economically treated. Competing processes include adsorption and stripping. Organic solutions containing a mixture of water-soluble and nonwater-soluble components may be economically treated by extraction with water. Here stripping or distillation are competitors when the vapor pressures of the two components are far enough apart.

Solvent extraction should be regarded primarily as a process for treating concentrated, selected, and segregated waste streams where material recovery is possible to offset process costs. Solvent extraction, when carried out on the more concentrated waste streams, seldom produces a treated effluent (the raffinate) that can be directly discharged to surface waters; some form of final polishing is usually needed. Solvent extraction cannot compete economically with biological oxidation or adsorption in the treatment of large quantities of very dilute wastes, and it will have trouble competing with steam stripping or the recovery of volatile solutes present in moderate to low concentrations.

Nevertheless, solvent extraction is a proven method for the recovery of organics from liquid solutions, and is the process of choice in some cases. Table 2.3 summarizes the areas of actual and potential applicability.

There are relatively few insurmountable technical problems with solvent extraction. The most difficult problem is usually finding a solvent that best meets a long list of desired qualities, including low cost, high extraction efficiency, low solubility in the raffinate, easy separation from the solute, adequate density difference with the raffinate, no tendency for emulsion formation, nonreactivity, and nonhazardousness. No one solvent will meet all the desired criteria, and therefore compromise is necessary. A wide range of extraction equipment is available today, and space requirements are not large.

Table 2.3 Areas of Actual and Potential Applicability of
Solvent Extraction Removal and Recovery of Organics

Physical Form of Waste	Solute Recovered
<u>Wastes that have been treated</u>	
Aqueous Solution	Phenol, acetic acid, salicylic and other hydroxyaromatic acids, petroleum oils
Organic Solution	Methylene chloride from isopropyl alcohol, Freon™ from oil and alcohol or acetone, mixed chlorinated hydrocarbons from alcohol or acetone
<u>Wastes that may be treated</u>	
Aqueous Solutions (containing one or a few solutes)	Any valuable organic solute present in moderate to high concentration. Candidates include phenols, acids, alcohols, amines, glycols, tetrahydrofuran, and dimethylformamide.
Organic Solutions (containing a mixture of water-soluble and non-water-soluble components)	Water-soluble components including low-molecular-weight alcohols, ketones, amines, ethers, phenols, etc. Nonwater-soluble components including simple hydrocarbons, halogenated hydrocarbons, oils, and other high-molecular-weight organics, which may contain a hydrophilic functional group.

2.3.2.2 Potential Applications to DOE Waste Streams

Recovery of Phenol. Removal of phenol and related compounds from wastewaters is the principal application;⁷⁻¹⁶ proved applications are to petroleum refinery wastes, coke-oven liquors, and phenol resin plant effluents. Extraction reduces phenol concentrations from levels of several percent down to levels of a few parts per million. Removal efficiencies of 90 to 98% are possible in most applications, and with special equipment (e.g., centrifugal and rotating-disc contactors) removal efficiencies around 99% have been achieved. Commonly used solvents are crude oil, light oil, benzene, toluene, and "benzol"; less common but more selective solvents are isopropyl ether, tricresyl phosphate, methyl isobutyl ketone, methylene chloride, and butyl acetate. When crude or light oil is used, the phenol is not always recovered (i.e., the solvent is not recycled); the phenol is destroyed in downstream

operations. Alternatively, extraction with light oil may be followed by recovery of phenol via extraction of the oil with caustic; in this case, the phenol is recovered as sodium phenolate.

Recovery of Alcohols. A proven application involves the reclamation of Freon™ solvents. The waste material arrives as a mixture of oil, Freon,™ and other solvents (e.g., acetone or alcohol), which is then extracted with water to recover Freon.™ The material is sold for about half the price of new Freon.™

A second example involves the removal of water-soluble alcohols from a waste of mixed chlorinated hydrocarbons via extraction with water. Simple mixer-settlers are commonly used, and the process yields a salable-quality chlorinated hydrocarbon.

Recovery of Oil from Quench Water. De-oiling of quench waters from petroleum operations via solvent extraction has been developed by Gulf Oil Corporation.⁷ The quench water, containing about 6000 ppm of dissolved and emulsified oil, is extracted with a light aromatic oil, and the extract is recycled for refinery processing. Additional treatment of the water is necessary before it is reused.

Concentration of Sludges with the Recovery and Recycling of Oil. A novel process employing solvent extraction is currently being developed to remove essentially all of the water and oils from inorganic and organic sludges.^{17,18} The process, called Basic Extractive Sludge Treatment (B.E.S.T.), converts sludges with 0.05% to 60% solids to three output streams consisting of very dry solids (4-5% moisture), a clear water effluent, and recovered oils, if present in the original sludge. The process train includes (1) extraction of water (and oils) from the sludge with an aliphatic amine at low temperatures (50°F), (2) removal of solids with a centrifuge followed by drying of solids (and solvent recovery), (3) heating the solvent/water/oil mixture to 120° to force phase separation, (4) steam stripping of the water phase for solvent recovery, and (5) distillation of the solvent phase for oil recovery. A mobile test-and-demonstration facility has been constructed, which can treat 1500 gal/day. Several different types of sludges have been successfully processed.

2.4 MEMBRANE PROCESSES

2.4.1 Description of Technology

2.4.1.1 Basic Concepts

A membrane is defined as a phase that acts as a barrier between other phases. It can be a solid, a solvent-swollen gel, or even a liquid. The applicability of a membrane for separation depends on differences in its permeability to different compounds. In Table 2.4, a survey is given of membrane separation processes and their principal driving forces and applications.

Ultrafiltration and reverse osmosis are the processes that find the most application in recovery and recycling of wastes, and therefore this section will address these two processes. The basic principle of separation by ultrafiltration and reverse osmosis is illustrated in Fig. 2.3. Flowing past a porous membrane is a solution containing two solutes; one consists of molecules small enough to pass through the membrane, and the other of larger molecules that cannot pass through. Pressure is applied to the upstream side of the membrane (which has a mechanical support), and the larger molecules are restrained by the membrane. A solution concentrated in the retained solute is collected from the upstream side, and a solution of the small-molecule solute and solvent is collected from the downstream side of the membrane. Where only a single solute is present and cannot pass through the membrane, the liquid collected downstream is (ideally) pure solvent.

Ultrafiltration employs porous membranes in which the pore sizes have been adjusted to exclude passage of material commonly of the size range 1-10 nm while permitting passage of solvent and smaller particles. Expressed another way, ultrafiltration is applicable to separations where the particles being separated are about one to two orders of magnitude larger than the solvent molecules. Thus, ultrafiltration techniques are suitable for separation of large soluble molecules (e.g., proteins, macromolecules), dispersion,

Table 2.4 Membrane Separation Processes

Process	Driving Force	Function of Membrane
Ultrafiltration	Pressure	Selective to molecular size and shape
Reverse Osmosis	Pressure	Selective transport of water
Electrodialysis	Electric Potential	Selective to certain ions
	Gradient	
Dialysis	Concentration	Selective to solute

Fig. 2.3 Schematic Diagram of Membrane Separation Process

colloids, and suspensions from solvent and small dissolved molecules such as inorganic salts. Operating pressures for ultrafiltration commonly range from 10 to 100 psi.¹⁹

Reverse osmosis involves the separation of solute molecules of the same order of magnitude as the solvent molecules (less than 1 nm). Reverse osmosis employs so-called semipermeable membranes, which are permeable to water but not permeable (or only slightly so) to dissolved substances. The "pores" of the reverse osmosis membrane are very small -- of the dimensions of the water molecule. Separations by reverse osmosis commonly require pressures substantially in excess of the osmotic pressure of the solutions being separated, and therefore usually much higher than the pressure required for ultrafiltration. For example, an operating pressure of 800 psig is specified for DuPont's Permasep® B-10 Permeator, with a feed of 30,000 mg/L NaCl.²⁰

The two techniques can complement each other and may even be used in tandem in the same installation. For example, ultrafiltration could be used for the first step in purification of an aqueous waste, to remove suspended particles, colloids, emulsified oils, protein molecules and the like. In the second step, reverse osmosis would be used to remove dissolved salts and other

small molecules from the aqueous permeate. Both techniques are receiving increasing attention in many fields because of their ability to effect concentration and separation of aqueous systems with relatively low expenditure of energy -- less than required for distillation or evaporation. Reverse osmosis finds extensive use as a low-energy alternative to distillation in the preparation of potable water from brackish water and seawater. Attention is focused here on ultrafiltration, because of its applicability to recovery and recycling of waste streams, although the basic concepts of reverse osmosis will also be discussed.

2.4.1.2 Process Description

Reverse Osmosis. The heart of a reverse osmosis plant for industrial waste is the reverse osmosis modules (Fig. 2.4). These devices are assembled into racks to accommodate the desired flow rate. Reverse osmosis is induced

Fig. 2.4 Reverse Osmosis Plant Flowsheet

by applying a high pressure to a suitable thin membrane, which rejects the salt molecules and passes a relatively salt-free water stream. The remaining salt solution is concentrated and flows out of the system.

Rinse water from specific processes can be treated using reverse osmosis, and the purified water returned for more rinsing; the concentrates, possibly after further concentration by evaporation, are extracted for disposal. For cyanide- or chromium-containing rinse water, however, suitable membrane materials are not yet commercially available.

Care must be exercised with reverse osmosis systems so that the waste does not contain certain colloidal substances or heterogeneous matter; otherwise, these may in time reduce the permeability of the membrane.

Ultrafiltration. Ultrafiltration installations closely resemble those described for reverse osmosis. The range of pore sizes in the ultrafiltration module, however, limits its use to removal of finely emulsified oils or suspended solids from the feed stream, in contrast to reverse osmosis, which can also concentrate dissolved salts through use of extremely fine membrane elements (hyper-filtration).

Streams in the flux range of 5 to 50 gal/day/ft² of membrane enter the module. Fouling by microorganisms or organic deposits is minimized by the scouring action of the feed stream. Operating pressure is in the range of 10 to 100 psig, compared with the 50 to 1,500 psig necessary for reverse osmosis. Back-flushing is conducted regularly to maintain adequate flow rate.

2.4.1.3 Special Characteristics

Membrane processes are energy-efficient alternatives to evaporation and distillation, and they can produce high-purity streams. There is no gaseous or solid waste from a reverse osmosis plant, and the only liquid waste is the concentrated brine or solute solution, which may be recycled or disposed of in an acceptable manner. However, the throughput of a membrane process is small, and the capital cost can be high. For example, the total installed cost of a reverse osmosis unit to treat 30 gal/min of wastewater can be in the range of $\$1 \times 10^6$ (1981 basis).

Reverse Osmosis. Cellulose acetate membranes have been the most frequently used in the past, but polysulfones and polyamides (e.g., nylon) are increasingly popular for use at high pH values. Because of the susceptibility of the flow system to plugging and erosion, it is common to preprocess feed water, if necessary, to remove oxidizing materials (e.g., iron and manganese salts), to filter out particulates, and to remove oils, greases, and other film formers. If there is likelihood of fouling by microorganisms,

chlorination or ultraviolet treatment may be employed as well to insure that maximum flux rates are obtained.

Table 2.5 indicates typical salt rejection rates for a cellulose acetate membrane. Flux rates (at 400-600 psi) range from about 5 to 20 gal/day/ft². Care must be taken that precipitation, and especially scale formation, does not take place on the membrane surface. Water treatment, including chlorination, pH control, and filtering (of particles about 1-25 μ m, depending on system) may be required, as discussed earlier.

Most important of all, virtually any potential application must be piloted in order to ensure that its chemistries are well understood and that no unknown factors will arise later.

Ultrafiltration. Ultrafiltration membranes are asymmetric structures, possessing an extremely thin selective layer (0.1-1.0 μ m thick) supported on a thicker spongy substructure. Controlled variation of fabrication methods can produce membranes with desirable retention characteristics for different separation applications. Indeed, it has become possible to tailor membranes with a wide range of selective properties. For example, tight membranes can retain organic solutes of 500-1000 molecular weight while allowing passage of most inorganic salts. Conversely, loose membranes can discriminate between solutes of 1,000,000 and 250,000 molecular weight.

Membranes can be made from various synthetic or natural polymeric materials. These range from hydrophilic polymers such as cellulose to very hydrophobic materials such as fluorinated polymers. Polyarylsulfones and inorganic materials have been introduced to deal with high temperatures and pH values. Membranes of this type are in many respects similar to reverse osmosis membranes except for the openness of their pores. Other forms and materials are available as well, including porous zirconia deposited on a porous carbon substrate or porous ceramic tubes. The latter two systems, while more expensive than the former, can be used at very high pH values and high temperatures.

2.4.2 Applications

2.4.2.1 General Discussion of the Application of Membrane Processes to Waste Streams

Reverse Osmosis. Reverse osmosis may be used to concentrate dilute solutions of many inorganic and some organic solutes. Preprocessing may be necessary to optimize pH, remove strong oxidants, and filter out suspended solids and film formers. The processing equipment is commercially available, with a large number of competitive suppliers. In general, reverse osmosis

Table 2.5 Reverse Osmosis Rejection Parameters:
Cellulose Acetate Membrane

Solute	Symbol	Percent Rejection	Maximum Concentration, Percent
CATIONS			
Sodium	Na^+	94-96	3-4
Calcium	Ca^{+2}	96-98	a
Magnesium	Mg^{+2}	96-98	a
Potassium	K^{+1}	94-96	3-4
Iron	Fe^{+2}	98-99	a
Manganese	Mn^{+2}	98-99	a
Aluminum	Al^{+3}	99+	5-10
Ammonium	NH_4^{+1}	88-95	3-4
Copper	Cu^{+2}	96-99	8-10
Nickel	Ni^{+2}	97-99	10-12
Strontium	Sr^{+2}	96-99	---
Hardness	Ca and Mg	96-98	a
Cadmium	Cd^{+2}	95-98	8-10
Silver	Ag^{+1}	94-96	a
ANIONS			
Chloride	Cl^{-1}	94-95	3-4
Bicarbonate	HCO_3^{-1}	95-96	5-8
Sulfate	SO_4^{-2}	99+	8-12
Nitrate	NO_3^{-1}	93-96	3-4
Fluoride	F^{-1}	94-96	3-4
Silicate	SiO_2^{-2}	95-97	---
Phosphate	PO_4^{-3}	99+	10-14
Bromide	Br^{-1}	94-96	3-4
Borate	$\text{B}_4\text{O}_7^{-2}$	35-70 ^b	---
Chromate	CrO_4^{-2}	90-98	8-12
Cyanide	CN^{-1}	90-95 ^b	4-12
Sulfite	SO_3^{-2}	98-99	8-12
Thiosulfate	$\text{S}_2\text{O}_3^{-2}$	99+	10-14
Ferrocyanide	$\text{Fe}(\text{CN})_6^{-3}$	99+	8-14

Table 2.5 (Cont'd)

Solute	Molecular Weight	Percent Rejection	Maximum Concentration, Percent
ORGANICS			
Sucrose	342	100	25
Lactose	360	100	25
Protein	$\geq 10,000$	100	10-20
Glucose	198	99.9	25
Phenol	94	c	--
Acetic Acid	60	c	--
Lactic Acid	90	c	--
Dyes	400 to 900	100	--
Biochemical oxygen demand	(BOD)	90-99	--
Chemical oxygen demand	(COD)	80-95	--
Urea	60	40-60	Reacts similar to a salt
Bacteria & virus	5,000-100,000	100	
Pyrogen	1000-5000	100	
GASES			
Carbon Dioxide	CO ₂	---	30-50
Oxygen	O ₂	---	c
Chlorine	Cl ₂	---	30-70

^aMust watch for precipitation, other ion controls maximum concentration.

^bExtremely dependent on pH; tends to be an exception to the rule.

^cPermeate is enriched in the material due to preferential passage through the membrane.

should be considered whenever one must concentrate a waste stream that contains dissolved salts or organic materials to permit their reuse or to reduce the volume of the waste stream prior to evaporation or other disposal.

Ultrafiltration. Ultrafiltration is a membrane separation system capable of segregating dissolved or suspended material from a liquid stream on the basis of the size. These species may range from large organic molecules (molecular weight about 1000) to larger agglomerations.

Ultrafiltration presently has commercial applicability in several industrial situations and is increasing its markets. There are several suppliers of equipment offering a wide range of designs and membrane materials.

Ultrafiltration has genuine utility in certain waste treatment applications, generally those involving the separation of high-molecular-weight solutes or suspended materials from an aqueous stream. Under optimum conditions it can produce a recyclable concentrate and "innocuous" permeate. However, costs may be high (both operating and capital) and operating conditions and plant design must be carefully tailored to the application. Careful piloting is a prerequisite. Nonetheless, ultrafiltration has demonstrated unique capabilities in oil/water separation, electropaint recovery, and the dairy processing industry, and it is certain that new applications will continue to be developed.

2.4.2.2 Potential Applications of Membrane Processes to DOE Waste Streams

The applicability of a membrane process to a DOE waste stream depends on the size of the stream, concentration, location, and a number of other factors. Each application will be site-specific and must be evaluated on its own merits. The following are potential applications of membrane processes to DOE waste streams.

Recovery of Waste Oils. It is believed that increased use of ultrafiltration could make a substantial contribution to the recovery of waste industrial oils. Annual sales of industrial oils in the United States amount to 2.5×10^9 gallons per year. Of this total, only 50×10^6 gallons are recovered, with 1.2×10^9 gallons being burned or dumped. Much of the oil is used in the form of oil/water emulsions. Ultrafiltration affords a means for recovery and concentration of oil and water from these emulsions.¹⁹ Concentrations of recovered oil can range from 30 to 60%, with only 10 ppm of oil in the water permeate.¹⁹ The remaining oil in the permeate could be cleared up by biological treatment.²¹

Use of Membranes as a Concentration Step Prior to Incineration of Toxic Wastes. Toxic and noxious aqueous waste streams are disposed of in a number of ways. Selection of disposal methods has been a matter of economics and suitability to the specific material involved. For many toxic (or potentially toxic) aqueous waste streams, incineration proves to be the safest disposal method.

Aqueous waste streams are usually well over 90% water; they often contain inorganic salts in concentrations ranging from less than 1% to more than 5%, and typically contain relatively small concentrations (in the range of 1000 ppm) of toxic organic substances. A typical aqueous-waste incinerator has a relatively large and long vertical or horizontal cylindrical combustion chamber. The aqueous waste is sprayed into the chamber with fuel and combustion air. The heat from the fuel vaporizes the water to steam and the mixture of steam, combustion products, and excess air is heated to the appropriate pyrolysis temperature, which is usually 180°F or above. Combustion chamber design provides sufficient retention time at such a temperature to ensure that all of the toxic organic material is completely destroyed. The hot combustion gases and superheated water vapor then are quenched in a quench chamber, and the gases further cleaned in a series of contact-scrubbing steps. Heat recovery is sometimes feasible, but at best less than one-third of the heat released can be recovered. In addition, heat recovery presents technical problems from fouling of heat-transfer surfaces, system corrosion, etc. Many operators simply prefer not to complicate the installation with heat recovery devices because of the extremely sensitive nature of toxic waste disposal.

A aqueous-waste incinerator using natural gas for fuel and operating with 20% excess air to destroy 30 gpm of typical toxic aqueous waste will require at least 45.6×10^6 Btu per hour of fuel input to hold the temperature at 1800°F. This consists of 15.0×10^6 Btu per hour of latent heat to vaporize the water; 12.8×10^6 Btu per hour to raise the temperature of the water vapor to 1800°F; and 17.8×10^6 Btu per hour to heat the combustion products and excess air to 1800°F. The fuel input required to incinerate the waste amounts to 65,524 equivalent barrels of oil per year, which at \$58 per barrel amounts to \$3,800,000.

Substantial energy savings could be realized by reducing the amount of water to be incinerated. Removal of one-half of the water, for instance, would reduce the incineration energy requirement by roughly one-half. It is envisioned that reverse osmosis could be used to remove some of it as a clean water stream, thus concentrating the inorganic and organic contaminants and reducing the amount of material to be incinerated. Depending on the nature of the aqueous waste, it might be necessary as a first step to subject it to ultrafiltration to remove suspended particles, emulsified water-insoluble materials, and the like.

Contacts with DuPont Company representatives (manufacturers of Permasep® reverse-osmosis permeators), review of their technical product information, and discussion with others indicates that the technology is

basically feasible but may have certain important limitations in this application. Concentration of aqueous waste by reverse osmosis prior to incineration has been investigated but, at the time, cost incentives were not sufficient to prompt serious efforts to overcome the initially perceived problems. Most notably, these are:

- Very high osmotic pressures, requiring even higher operating pressures (more than 1000 psig), if salt concentrations in the solution are on the order of 5% or more. The structural strength of permeators currently available is the limiting factor.
- Extensive pretreatment may be required to prevent or retard damage to the membranes by plugging or chemical deterioration.
- Permeator efficiencies of less than 100% may permit passage of some of the toxic material, particularly when operating pressures are high, necessitating second-stage permeators.

The consensus is that these limitations can be overcome with an intensive development program, given anticipated energy-conservation incentives. For instance, DuPont's first Permasep® permeators were developed for desalination of brackish water containing up to 1500 ppm of sodium chloride, operated at a feed pressure of 400 psi. A stronger permeator design is now used for desalination of seawater. One of the primary incentives for this advance was conservation of energy. It should be noted here that much of the literature examined on the subject of toxic or dangerous waste disposal indicated that incineration is by far the preferred method, and that the use of incineration is expected to increase markedly in the future. Nearly all other disposal methods do not destroy the material, but store or dilute it without completely removing the potential hazard. Conceivably, the amount of aqueous waste requiring incineration could increase many-fold beyond the above current estimate in spite of the high cost in energy.

A rough estimate of the reverse osmosis facilities required for treating 30 gpm of aqueous waste to remove one-half of the water is included in Table 2.6 on the following page. The indicated investment is about \$10⁶, plus an estimated \$500,000 in development cost for the first installation.²²

The typical facility for 30 gpm would save 33,288 equivalent barrels of fuel oil per year, which, at \$58 per barrel, would be a savings of \$1,664,000 per year. A liberal allowance for the operating cost of the facility leaves approximately \$1,200,000 per year in net savings to offset the estimated \$1,000,000 investment.

It is believed that the impact of the government in the development of this technology through a full-scale demonstration project would be very

Table 2.6 Estimate of Investment Cost for Membrane Technology^a

Cost Component	Cost (\$10 ³)
Membrane modules (installed)	216
Prefiltration facilities	100
Pumps, controls, heat exchangers, etc.	75
Foundations, structure, piping material, etc.	50
Total Equipment and Material	441
Installation @ 60% (including a heated/ventilated building housing all critical installation components)	265
Engineering and contingency @ 40%	282
Total Investment	988
Estimated Development Cost for 1st Copy	500
Approximate Total for Demonstration Project	1,488

^aFacilities for treating 30 gpm of aqueous waste to remove one-half of the water.

substantial. Our best judgment is that development of the technology to the status of commercialization without government assistance would require more than 15 years, even with the same relative energy-cost incentives that now exist. With a substantial degree of support, this could be accelerated to commercialization within roughly five or six years.

Electrocoat Paint Rejuvenation and Rinse Water Recovery. Electroplating is a method of painting and coating metallic parts. The paint is a colloidal suspension of charged pigment particles in high concentration, which migrate to the metal part of the surface under an electrical potential applied between the part and the paint tank wall. After periods of use, impurities build up in the paint which render it useless, and it must be discarded. It cannot be effectively treated in a sewage treatment plant, so it contaminates the treatment plant effluent with organics and color. In addition, water from rinsing the excess paint from the coated part is also discharged in very high volumes, and it similarly represents an untreatable hazard.

Ultrafiltration is used in most electrocoat painting plants in two ways. First, ultrafiltration can often remove dissolved impurities from the paint, which extends the life of the paint bath and drastically reduces the

pollution caused by paint bath discharge. Second, ultrafiltration can recover the colloidal paint from rinse water, thereby eliminating pollution from the effluent and recovering paint for return to the paint bath. This combined process has been the most successful application of ultrafiltration in industry to date. It is invariably the process of choice, and the market is near saturation.

Treating Machining-Oil Emulsions. Metal cutting, rolling, and drawing oils are used as dilute emulsions to lubricate metal-working machines. The spent lubricant is heavily contaminated with metal fines and dirt. In the past, the spent emulsion has either been trucked away for disposal or discharged into sewers at the plant.

Ultrafiltration can concentrate the dirty spent emulsion, increasing the oil and solids content from several tenths of a percent to higher than 50%. Thus over 95% of the water can be removed and discharged or reused safely, and a small-volume concentrate can be disposed of by other means. The cost of incineration drops dramatically as the oil concentration is increased to the point where the solution will support combustion.

Problems can arise, however, when the oil is kept in suspension by a lower-molecular-weight emulsifying agent. This agent may permeate the membrane (increasing the BOD of the permeate) and its absence from the concentrate permits the oil to agglomerate and block the membrane. For this reason "tighter" membranes, more like reverse osmosis membranes, may be needed to reject the agent.

2.5 DISTILLATION, STEAM DISTILLATION, AND STEAM STRIPPING

2.5.1 Description of Technology

2.5.1.1 Basic Concepts

Distillation. Distillation is the boiling of a liquid solution and condensation of the vapor for the purpose of separating the components. In the distillation process there are two phases, the liquid phase and the vapor phase. The components to be separated by distillation are present in both phases, but in different concentrations. If there are only two components in the liquid, one concentrates in the condensed vapor (condensate) and the other in the residual liquid. If there are more than two components, the less volatile components concentrate in the residual liquid and the more volatile in the vapor or condensate.

Although the term distillation is sometimes employed for those processes in which a single constituent is vaporized from a solution, e.g., in "distilling" water, this term is properly applied only to those operations in which vaporization of a liquid mixture yields a vapor phase containing more than one component, and it is desired to recover one or more of the components in a nearly pure state or to obtain a mixture different from that of the original mixture.

Steam Distillation. Steam distillation is similar to conventional distillation, except that steam is bubbled through the material being distilled. Steam distillation solves several difficult industrial distillation problems: distilling compounds with relatively high boiling points, compounds that may decompose at their atmospheric boiling points, or chemicals that are hazardous when distilled without water vapor.

Steam Stripping. Steam stripping is essentially a distillation of volatile compounds from a wastewater stream. The volatile component may be a gas or volatile organic compound dissolved in the wastewater stream. In most instances, the volatile component, such as methanol or ammonia, is quite water soluble.

2.5.1.2 Process Descriptions

Distillation. Simple distillation is the partial vaporization of a solution of liquid components with separate recovery of vapor and liquid residue. The concentration of the more-volatile components (sometimes termed the "lighter" components) is greatest in the condensed vapor, while the concentration of the less-volatile components ("heavier" components) is greatest in the liquid residue. The degree of separation in a simple distillation process depends on the relative volatility of the components, which in turn depends on the thermodynamic properties of the mixture. Simple distillation may be carried out as a batch operation or as a continuous operation. A variation on simple distillation is flash distillation, in which an appreciable proportion of a liquid is quickly converted to vapor in such a way that the final vapor is in equilibrium with the final liquid.

Rectification is continuous countercurrent contact of the vapor resulting from a simple distillation with a condensed portion of the vapor product. This countercurrent contact results in greater enrichment of the vapor (often termed "overhead") product with the more volatile components than is possible with a single stage of simple distillation. The condensed vapor returned to accomplish this is termed "reflux." In rectification the feed is to the simple distillation stage (bottom) and the more important product is removed as vapor (top).

Stripping is continuous countercurrent contacting of the liquid feed with the vapor resulting from a simple distillation. This countercurrent contact results in a more complete removal of the more volatile components from the liquid ("bottom") product than could be accomplished by a single stage of simple distillation. In stripping, the liquid feed is introduced at the top of the column and the vapor is supplied by partial vaporization of the liquid stream at the bottom of the column in a "reboiler."

Commonly, rectification is carried out on the vapor product leaving a stripping operation. This is termed "fractional distillation," or "fractionation." In a fractional distillation column, feed is introduced at a feed stage within the column. Above the feed stage is the rectification section, and below it is the stripping section. Overhead product is condensed and a portion returned as reflux. Bottom product is partially vaporized, and the vapor returns to the column as boilup. The stripping section is for recovery of overhead product and purification of bottom product, while the rectification section is for purification of top product and recovery of bottom product. The important factors controlling separation are the number of stages in each section, the vapor/liquid flow ratios, and the relative volatilities of the components.

Figure 2.5 shows a schematic diagram of a continuous fractional distillation column. A steady feed stream enters the column. The column contains plates or packing that provides additional vapor/liquid contact stages. Overhead vapors and bottoms are continuously withdrawn. Vapor from the top plate is condensed and collected in a vessel known as an accumulator. Some of the liquid in the accumulator is continuously returned to the top plate of the column as reflux, while the remainder of the liquid is continuously withdrawn as the overhead product stream. At the bottom of the column, the liquid collects in the reboiler, where it is heated by steam coils or a steam jacket. The function of the reboiler is to receive the liquid overflow from the lowest plate and return a portion of this as a vapor stream, while the remainder is withdrawn continuously as a liquid bottom product.

Steam Distillation. In steam distillation the presence of water lowers the boiling point, allowing lower temperatures to be used in the distillation. This lowering of boiling point becomes very important in the case of heat-sensitive materials, or where there is a large amount of inert material present, or where a high concentration of nonvolatile liquid is present.

The equipment used for steam distillation in waste treatment is usually a batch distillation system with provision for bubbling steam through the material in the batch still. The still may be heated by heating coils in the still, a steam jacket around the still, or the live steam being bubbled through the charge in the still. The heat supplied in this manner is in addition to the live steam used as carrier steam, and is required to raise the charge to the distillation temperature, supply heat for vaporization of the

Fig. 2.5 Continuous Fractional Distillation Column

volatile organic, and make up for any heat losses. Feed pumps and tanks are also required, as well as a condenser, gravity settling tanks, and product receiver tanks.

When steam distillation is used to reduce the concentration of a volatile component to very low levels, as in the case of waste treatment, it is normally conducted as a batch or semibatch operation. In the case of a batch steam distillation, the still is charged, the charge heated to temperature, and the distillation conducted by bubbling steam through the liquid phase. In semibatch operation, the charge, containing a high ratio of volatiles to non-volatiles, is fed to the still continuously for a given period of time while the volatile component is steam-distilled from the mixture. After the last of

the feed is introduced, the steam distillation is continued until the volatiles are reduced to the desired residual concentration.

This process initially generates two output streams, the stripped waste (generally containing 100 ppm or less of residual volatile component) and a vapor stream of volatile component and water vapor. This second stream is usually condensed, and in the case of a water-immiscible organic, the immiscible liquids are separated by gravity to generate a second and third stream; a liquid stream of nearly pure volatile component and a wastewater stream containing traces of the immiscible volatile component. In the case of a water-soluble organic such as glycerine, the organic material may be recovered in a concentrated form by partially condensing the vapors, and then the pure product is recovered by evaporation, distillation, or other means.

Steam Stripping. Steam stripping is used to remove gases or volatile organics from a dilute wastewater stream. The input to the process is a wastewater stream containing dissolved gases or volatile organic compounds and the outputs are a concentrated vapor or liquid solution containing most of the gases or volatile organics and a very dilute treated wastewater stream containing only very small amounts of dissolved gases or volatile organics.

The equipment required for steam stripping is nearly the same as that required for conventional fractional distillation. In steam stripping, however, there are several differences. A heat exchanger is used for heating the feed entering the column and cooling the stripped wastewater leaving the column. Also, the reboiler is often an integral part of the tower body rather than a separate vessel.

Steam stripping is usually conducted as a continuous operation, with more than one stage of vapor/liquid contact. The preheated wastewater from the heat exchanger enters near the top of the distillation column and then flows by gravity countercurrent to the steam and organic vapors (or gas) rising up from the bottom of the column. As the wastewater passes down through the column, it contacts the vapors rising from the bottom of the column, which contain progressively less volatile organic compound or gas, until it reaches the bottom of the column, where the wastewater is finally heated by the incoming steam to reduce the concentration of volatile component(s) to their final concentration. Much of the heat in the wastewater discharged from the bottom of the column is recovered in preheating the feed to the column.

Although many of the steam strippers in industrial use introduce the wastewater at the top of the stripper, there are advantages to introducing the feed to a tray below the top tray when reflux is used. Introducing the feed at a lower tray (while still using the same number of trays in the stripper) will either reduce steam requirements (due to the need for less reflux) or will yield a vapor stream richer in the volatile component. In combination, using reflux and introducing the feed at a lower tray will increase the

concentration of the volatile organic component beyond that obtainable by reflux alone. Reflux may or may not be practiced, depending on the composition of the vapor stream that is desired.

2.5.1.3 Economic Characteristics

As a general rule, the capital cost of distillation equipment and the energy cost of its operation are both high. To some degree, design of the equipment can balance its cost against the amount of energy required for distillation. Theoretically, design possibilities range from minimum reflux with an infinite number of stages, to total reflux with a minimum number of stages. From an economic standpoint, the optimum design is one that does the job at the lowest cost. Both investment and operating costs are involved. However, since the relationship between those costs varies from company to company and from process to process, no single relationship between the two costs can be specified.

The operating costs depend on the difficulty in separating components of the liquid to be distilled. The difficulty of separation depends on such variables as the concentration of the feed, the degree of separation required, the relative volatility of the components of the feed, and the existence of contaminants. Capital investment is also affected by the operating variables. For example, higher purity requires larger equipment and possibly more sophisticated instrumentation.

Because of all of the variables that affect the capital investment, operating cost, and energy requirements for any particular distillation, it is difficult to cite a "typical" cost for distillation on a unit product or unit feed basis. This becomes even more evident when all of the different organic liquids and the range of possible concentrations and the feed conditions (i.e., temperature, whether or not there are contaminants, etc.), are taken into consideration. For illustrative purposes, however, one may cite the example of a steam distillation system for solvent recovery, the DYNA 1 system manufactured by the DCI Corporation.

In the DYNA 1 steam distillation system, injection of low-pressure live steam permits recovery of the solvents from contaminants such as adhesives, rubber, pigments, resins, heavy oils, etc. The total operating cost of the DYNA 1 is estimated to be \$0.05 to \$0.06 per gallon of recovered solvent (1980 costs). This system is currently being used in a wide variety of industrial applications, including paint and coatings manufacturing, degreasing, paper coating, blood processing, fiberglass processing, textile cleansing, contract waste reclamation, large appliance coating, tape manufacturing, printing, and nuclear waste recycling.

For those who generate relatively small volumes of distillable effluents, it may be more economical to enlist the services of a solvent-reclaiming contractor. A number of such firms exist that perform materials recovery for

small-volume clients. Such an operation may be economical for both the client and the contractor. The client may be able to buy back the reclaimed material at a price that is still lower than the cost of virgin material. The contractor, on the other hand, has the advantage of a lower capital recovery charge, because he can make better use of his equipment than can a single small waste producer.

2.5.2 Applications

2.5.2.1 Current Applications to Industrial Wastes

Distillation. Distillation is widely used in industry in the production of organic liquids. However, because of its expense and energy-intensiveness, its use in the treatment of wastes has not been so widespread. The only hazardous waste materials that can be feasibly and practicably treated are liquid organics, including organic solvents and halogenated compounds, that do not contain appreciable quantities of materials that would cause operational or equipment problems. Among industrial wastes to which distillation is applied are the following:²³

- Plating wastes containing an organic component;
- Organic effluents from printed circuit boards;
- Aqueous solutions of phenol;
- Contaminated methylene chloride;
- Polyurethane waste, for recovery of methylene chloride;
- Styrene, for the separation of ethylbenzene;
- Waste solvents (e.g., mixtures of ketones, alcohols, and aromatics);
- Offgas in plastic filter products, for recovery of acetone;
- Wastes from the production of penicillin, for recovery of butyl acetate; and
- Waste oil.

Flash distillation has been applied in a multistage mode to a fine chemical plant waste to allow recycling of 88% of the process water and 95% of the contained catalysts and salt.²⁴

Materials that cannot generally be treated by distillation are organic peroxides or pyrophoric organics and inorganic wastes. If waste streams that contain viscous, polymeric materials, tars, etc., must be treated by distillation, the streams should receive preliminary treatment, if possible, to remove these materials, as they may tend to foul the equipment severely. If such treatment is not possible, then special equipment or maintenance procedures may be required.

Steam Distillation. Steam distillation is used in waste treatment to remove volatile organic material from liquids, solids, slurries, or sludges. The volatile organic component is recovered for its value and its residual concentration is reduced sufficiently to allow the resulting liquid, solid, or sludge to be safely disposed of. Frequently, steam distillation is used for recovering a mixture of volatile hydrocarbons from a waste stream; the mixture of hydrocarbons is then further separated by conventional distillation.

Some examples of waste solvents treated by steam distillation include:²³

- Degreasing solvent waste;
- Printing ink waste;
- Paint waste;
- Shoe manufacturing waste;
- Electronics industry polymer masking;
- Halogenated hydrocarbon wastes.

Reactivity of the process or waste stream with water or steam is a limitation of this process. It is not possible to recover some chlorinated hydrocarbons from organic waste streams, for example, since the water (or steam) removes the stabilizer required to protect the chlorinated hydrocarbon from decomposition through peroxide formation.²⁵ Nevertheless, some stabilizer systems are so designed that as the chlorinated solvent is steam distilled, the stabilizers are also steam distilled and are retained in the chlorinated solvent.

Steam Stripping. Steam stripping has long been used in industrial chemical production for recovery and recycling of product. More recently, it has been applied to industrial waste treatment. Among the waste treatment applications of steam stripping are:

- Reduction of phenol content in phenol plant effluent;²³

- Removal of vinyl chloride monomer from suspensions of polyvinyl chloride;²⁵
- Removal of methanol and sulfur compounds from kraft mill condensate.²⁶

There are a number of independent operators and companies that specialize in solvent or chemical reclamation by distillation (including steam distillation and steam stripping). Historically, distillable solvents have been recovered primarily for economic reasons, but with imposition of more stringent government regulations for the disposal of hazardous wastes and increases in the cost of petrochemicals, the recovery of organic solvents should become even more prevalent. If by-product credits offset the higher cost of distillation as compared to other recovery methods, distillation will become a more competitive means of waste solvent recovery.

2.5.2.2 Potential Application to DOE Wastes

As seen in the preceding section, distillation, steam distillation, and steam stripping have been used by industry for recovery of several types of solvents and waste oils. These uses suggest that, in general, distillation should be applicable to the categories of "waste oils" and "spent solvents" in DOE's preliminary hazardous waste inventory. The technology for materials recovery via distillation is well established and commercially available now. However, the economic feasibility of applying distillation to DOE's waste oils and spent solvents is less certain. That feasibility is governed largely by the specific composition, as yet unknown, of the "waste oils" and "spent solvents" in the preliminary inventory.

Recall from the preceding discussion that the capital and operating costs of distillation depend on such operating variables as the concentration of the feed, the degree of the feed components, and the presence of contaminants. These characteristics of the wastes from DOE sites are not yet known. Further, it may be expected that these characteristics will vary among the sites. Thus, an evaluation of the economic feasibility of distillation will only be possible on a site-specific basis, and at such time as the specific composition of a given site's "waste oils" and "spent solvents" can be determined.

Perhaps the most serious potential drawback to the use of distillation on DOE wastes is the limited utility of the process for wastes containing contaminants. Such contaminants can greatly increase the equipment and maintenance costs, or even render the process virtually impossible. Also, the tars and sludges left as still bottoms may require disposal via landfill or incineration. Again, however, the existence of such problems will depend on the specific composition of waste streams from specific DOE sites.

It was noted previously that, in general, distillation equipment is expensive. Consequently, given the relatively small quantities of waste oils and spent solvents generated at several DOE sites, it may be worthwhile for DOE to consider centralized processing of these wastes. One possibility that merits further evaluation is the use of private contractors, who are able to use distillation equipment more effectively by servicing several small-volume clients.

2.6 EVAPORATION

2.6.1 Description of Technology

2.6.1.1 Basic Concept

Evaporation is the vaporization of a liquid from a solution or a slurry to separate it from a dissolved or suspended solid or a less volatile liquid. The term "evaporation" can only be applied to a unit operation in which heat energy is transferred to a solution or suspension in which one of the components is not appreciably volatile. The process and the equipment are similar to that for distillation, except that in evaporation no attempt is made to separate components of the vapor.

Most present-day evaporators are heated by steam tubes immersed in the material to be evaporated. Usually, the steam is at low pressure (i.e., below 40 psia). Often the boiling liquid is under a moderate vacuum (down to 28 in. Hg). Reducing the boiling temperature of a liquid by reducing the pressure increases the temperature difference between the steam and the boiling liquid and thereby increases the heat transfer rate in the evaporator.

The objective of evaporation is to concentrate a solution of a non-volatile solute and a volatile solvent, most often water. Evaporation is conducted by vaporizing a portion of the solvent to produce a concentrated solution or a thick liquor.

Evaporation differs from drying in that the residue is usually a highly viscous liquid, rather than a solid; it differs from distillation (Sec. 2.5) in that the vapor usually has only a single component, and even when the vapor is a mixture, no attempt is made in the evaporation step to separate the vapor into fractions; it differs from crystallization in that the emphasis is placed on concentrating a solution rather than forming and building crystals. In certain situations, for example, in the evaporation of brine to produce salt, the line between evaporation and crystallization is far from sharp. Evaporation sometimes produces a slurry of crystals in a saturated mother liquor.

2.6.2.1 Process Description

Heat transfer is the single most important factor in evaporator design. There are two other principal elements involved in evaporator design. These are vapor/liquid separation and energy utilization. Except in the cases where the materials to be evaporated are directly contacted by heated vapors or by submerged combustion units, the devices in which heat transfer takes place are called "heating elements" or "calandrias." The term calandria is also used to describe a certain type of evaporator. The flow diagram of a simple evaporation system is shown in Fig. 2.6. In the system shown, the vapor is cooled, condensed, and collected.

The vapor/liquid separators are variously called "bodies," or "flash chambers." The term body is also used to denote the minimum building block of an evaporator, comprising one heating element and one vapor head.

Types of evaporators to be discussed include tubular, wiped film, direct contact, natural energy, climbing film, atmospheric, and flash. Once a popular type, the coil or pot evaporator is seldom used today but is mentioned here since it is valuable in the treatment of radioactive wastes, especially for small installations. Coil type evaporators are simple evaporators that are used particularly in simple batch operations.

Fig. 2.6 Evaporator System (Source: Ref. 27)

Tubular Evaporators. The chief types of steam-heated tubular evaporators in use today are discussed in the following sections. Short-tube evaporators may be either horizontal or vertical. The horizontal tube evaporator (see Fig. 2.7) was once widely used in the chemical industry but is now almost obsolete. The main use today is for power plant steam makeup evaporators. Vapor purity is of prime importance and the shell, which is a horizontal cylinder, provides the largest possible vapor/liquid separation area, thus minimizing liquid entrainment.

The vertical tube evaporator (see Fig. 2.8) is popular throughout industry. The body is normally a vertical cylinder. The heating surface is provided by short tubes, usually 2-3 inches in diameter. This type of evaporator has high heat transfer rates, providing temperature differences are large. The standard vertical tube evaporator is versatile and relatively inexpensive.

Long-tube vertical evaporators use either natural circulation or forced circulation. The natural-circulation evaporator operates on somewhat the same principle as a smoke stack. It gives high fluid velocities, due to the velocity of the rising slugs of liquor and vapor. This, in effect, promotes higher heat transfer coefficients between the evaporating fluid and the tube wall.

Fig. 2.7 Horizontal-Tube Evaporator (Source: Ref. 27)

Fig. 2.8 Vertical-Tube Evaporator (Source: Ref. 27)

Forced circulation evaporators are suitable for the widest variety of applications, and are usually the most expensive. Forced circulation evaporators attain higher fluid velocities (8-12 ft/s) and higher heat transfer rates by pumping the circulating liquid around by mechanical means. They are especially useful for evaporating viscous liquids for which natural circulation rates would be too low. Heating elements in these evaporators can be either internal or external; the heat exchanger is connected to a flash chamber. Because of high fluid velocity, forced circulation evaporators are primarily applicable to feed liquors that do not contain abrasive solid particles in suspension; otherwise erosion could be a serious problem.

The downward-flow or falling-film evaporator is essentially a long-tube vertical evaporator turned upside down. Feed liquor flows down the tube walls as a thin film. Friction losses of the falling film are low, providing better economy of energy. Heat transfer rates in the falling-film evaporator are

quite high, higher in most cases than in the forced circulation evaporators. The principal difficulty in the falling-film evaporator is maintaining a uniformity of feed distribution at the top of the tubes.

Agitated or Wiped Film Evaporators. This type of evaporator might also be classified as a forced circulation evaporator, inasmuch as it uses mechanical energy to improve heat transfer. The heating surface consists of a single tapered cylinder of large diameter, with rotating blades that continuously wipe a thin liquid film on the surface of the heater. This continuous formation of a thin film permits the liquor to be evaporated to a higher concentration, i.e., greater viscosity, than can be handled by any other type of evaporator.

Direct-Contact Evaporators. In submerged combustion evaporators, an oil- or gas-fired burner is immersed in a tank of solution to be evaporated. Because there is no scale formation, these evaporators are well suited to handling scale-producing or highly corrosive solutions, providing that the product cannot be harmed by carbonization. Furthermore, the economics of energy utilization are greatly improved, since heat transfer by submerged combustion is about 92% efficient; whereas for steam heating efficiency is approximately 80%. A disadvantage, however, is that evolved vapors are contaminated by combustion gases and cannot generally be recovered for reuse.

Direct-contact evaporation is also possible with immersed electrodes, but the application is extremely limited because of the high cost of electrical energy. This technique is useful, however, where direct contact evaporation is required but combustion products would interfere with desired product quality.

Flue-gas contact evaporators are used in cyclone-type flues. Gas is admitted through a tangential inlet near the bottom of the evaporator, and flows in a helical path to the top, where it exits. The liquor droplets are mixed intimately with the high-velocity gas, thus providing high evaporation rates.

Natural Energy Evaporators. Sludge dewatering is generally done in outdoor drying beds, because the large volume of sludge involved creates serious difficulties concerning space for disposal. Liquid sludge is removed periodically from settling tanks, and because of its volume, it is uneconomical and inconvenient to transport it to landfill disposal areas. The sludge must, therefore, be further dewatered. The dewatering step takes place in shallow excavations called "drying beds." There are usually a number of drying beds in one location, separated from one another by concrete walls. The beds are flooded with sludge to a depth of 20 centimeters. The water is allowed to drain via collector pipes, and the sludge dries by solar energy for

a few days to a few weeks, depending upon initial solids concentration, local climate, and season of the year. In some instances, to promote faster evaporation rates, the drying beds are covered with a hood and hot air is blown across the surface of the sludge. When the solid content of the sludge is about 45%, drying is considered complete. A major disadvantage of this particular process is that relatively large areas of land are needed for the sludge drying beds.

Climbing Film Evaporators. The major elements of the climbing-film evaporator are the evaporator, the separator, the condenser, and the vacuum pump. As shown in Fig. 2.9, wastewater is drawn into the system by the vacuum so that a constant liquid level is maintained in the separator. Liquid enters the steam-jacketed evaporator tubes, and part of it evaporates so that a mixture of vapor and liquid enters the separator. The design of the separator is such that the liquid is continuously circulated from the separator to the evaporator. The vapor entering the separator flows out through a mesh entrainment separator to the condenser, where it is condensed as it flows down through the condenser tubes. The condensate, along with any entrained air, is pumped out of the bottom of the condenser by a liquid ring vacuum pump. Thus, the liquid seal provided by the condensate keeps the vacuum in the system from being broken.

Atmospheric Evaporation. Atmospheric evaporation could be accomplished simply by boiling the liquid. However, to lower the evaporation temperature, the heated liquid is sprayed on an evaporation surface, and air is blown over

Fig. 2.9 Climbing Film Evaporator (Source: Ref. 28)

this surface and then released to the atmosphere. Equipment for carrying out atmospheric evaporation is quite similar from one application to another. The major element is generally a packed column with an accumulator bottom, as shown in Fig. 2.10. Accumulated wastewater is pumped from the base of the column, where it is sprayed into the packing. At the same time, air drawn upward through the packing by a fan is heated as it contacts the hot liquid, which partially vaporizes and humidifies the air stream. The fan then blows the hot, humid air to the outside atmosphere. A scrubber is generally unnecessary because the packed column itself acts as a scrubber.

Double-Effect Flash Evaporator. The main elements of the flash evaporator system are the evaporator, the reboiler, and the condenser, as shown in Fig. 2.11. The evaporator is an empty tank maintained at a pressure below that in the reboiler. Wastewater fed to the base of the evaporator circulates through a thermosiphon reboiler. The liquid heated in the reboiler reenters the evaporator at a temperature above the boiling point corresponding to the evaporator pressure. Part of the liquid evaporates (flashes), and the resulting vapor goes out the top of the evaporator to the horizontal condenser, while the condensate runs into an accumulator from which it is pumped out of the system. A vacuum pump maintains the reduced pressure in the system by withdrawing noncondensable gases from the condenser. Concentrate is withdrawn from the bottom of the evaporator.

Fig. 2.10 Atmospheric Evaporator (Source: Ref. 28)

Fig. 2.11 Double-Effect Flash Evaporator (Source: Ref. 28)

2.6.2 Advantages and Limitations

Some advantages of the evaporation process are:

- It permits recovery of a wide variety of electroplating chemicals and other process chemicals.
- The water recovered from the evaporation process is of high purity. This process can be used to convert waste effluent to pure or process water where other water supplies are inadequate or nonexistent.
- The evaporation process may be applicable for removal and/or concentration of waste effluent that cannot be treated by any other means.

Some limitations or disadvantages of the evaporation process are:

- In general, the evaporation process consumes relatively large amounts of energy for the evaporation of water. However, the recovery of waste heat from many industrial processes (e.g., diesel generators, incinerators, boilers and furnaces) should be considered as a source of heat for a totally integrated evaporation system.
- For some applications, pretreatment may be required to remove solids and/or bacteria, which tend to cause fouling in the condenser or evaporator.

- The buildup of scale on the evaporator plates reduces the heat-transfer efficiency and may present a maintenance problem or increase operating cost. However, it has been demonstrated that fouling on the heat-transfer surfaces can be avoided or minimized for certain dissolved solids by maintaining a "seed" slurry, which provides preferential sites for precipitate deposition. In addition, low temperature differences in the evaporator will eliminate nucleate boiling and supersaturation effects.
- Steam-distillable impurities in the process stream are carried over with the product water and must be handled by pre- or post-treatment if they cannot be tolerated.

2.6.3 Special Characteristics

2.6.3.1 Energy Requirements

Energy requirements for evaporation will vary with process operating parameters and the heat-transfer characteristics of the equipment. The normal operating range of energy for evaporation is about 100-1,100 Btu/lb of liquid evaporated.

Steam economy not only varies with the number of evaporator effects but also with the quality of liquor, the solute content, and whether there is crystal formation upon evaporation. These all have an adverse effect on steam economy.

2.6.3.2 Environmental Effluents

There are usually no air pollution problems with evaporation, providing that any entrainment or foaming problems have been taken care of in equipment operation or design. If the vapors contain organics, they are generally condensed and either disposed of or recovered by some other process such as distillation.

Concentrated liquors are the usual products of evaporation; sometimes they must be further treated before disposal or recovery of components.

2.6.3.3 Process Economics

The recovery of chromic acid from electroplating is a good example of the economics of evaporation. Total installed investment, operating costs, and economics for installing a 20-gal/h evaporator are given in Table 2.7. The before-tax annual savings for this system are approximately \$1,800. The

Table 2.7 Economics of Evaporator System for Chromic Acid
Recovery, Operating 5,000 h/y^a

Item	Cost, \$
Installed Cost, 20 gal/h evaporator	
Equipment	
Evaporator.....	19,000
Tanks.....	1,660
Pumps.....	750
Cation exchanger.....	6,200
Piping.....	2,500
Miscellaneous.....	450
Subtotal.....	30,560
Installation, labor, and materials	
Site preparation.....	260
Plumbing.....	2,860
Electrical.....	1,230
Equipment erection.....	270
Miscellaneous.....	500
Subtotal.....	5,120
Total Installed Cost.....	35,680
Annual Operating Cost	
Labor, 100 h/y at \$7/h.....	700
Supervision.....	_b
Maintenance, 6% of investment.....	2,190
General plant overhead.....	880
Raw materials, cation exchanger	
H ₂ SO ₄ , 3,500 lb/y at \$0.28/lb.....	100
NaOH, 3,000 lb/y at \$0.08/lb.....	240
Utilities	
Electricity at \$0.045/kWh.....	1,400
Cooling water, at \$0.10/1,000 gal.....	500
Steam at \$3.00/10 ⁶ Btu.....	3,150
Total Operating Cost.....	9,160
Annual Fixed Costs	
Depreciation, 10% of investment.....	3,570
Taxes and insurances, 1% of investment.....	360
Total Fixed Cost.....	3,930

Table 2.7 (Cont'd)

Item	Cost, \$
Annual Savings	
Recovered plating chemicals (1,875 lb/h H_2CrO_4).....	7,310
Water treatment chemicals.....	4,500
Sludge disposal.....	3,000
Water use at \$1.10/1,000 gal.....	70
Total Annual Savings.....	14,880
Net savings = annual savings - (operating cost + fixed cost) (\$/yr).....	1,790
Net savings after taxes at 48% tax rate (\$/yr).....	930
Average ROI = (net savings after taxes/total investment) x 100(%).....	2.6
Cash flow from investment - net savings after taxes + depreciation (\$/yr).....	4,500
Payback period = total investment/cash flow (yr).....	7.9

^aSource: Ref. 29.

^bNone required.

cost for steam and fixed charges are the major costs of operation, approximately 55% of the total costs. The annual savings resulting from recovery of plating chemicals and reduction of wastewater treatment costs comes to \$14,880.

To minimize rinse rates, such methods as countercurrent rinse systems are usually cost effective. A 50% steam saving can be achieved with double-effect evaporators; however, the capital costs are much higher and operation is more complicated. As a rule, at evaporation rates below 150 gal/h, additional investment for double-effect evaporators is not justified.

Because of the high initial investment, the savings and economics for evaporative recovery depend to a great extent on the concentration of the rinse water being evaporated and the volume of drag-out. For example, if the 20-gal/h evaporator of Table 2.7 were fed a stream with 50% more plating chemicals, the annual savings for treatment and recovery would increase by 50%

to approximately \$22,300. The net savings would increase to \$19,100, and the payback period would decrease to 4.3 years.²⁹

If the concentration of the plating chemicals shown in Table 2.7 were to remain constant, but the volume of drag-out were to double, a 40-gal/h evaporator would be required. As Fig. 2.12 shows, the installed cost would be approximately \$45,000. Because the installed cost increased by only \$19,000, the net annual savings would be \$10,300, which yields a payback period of 4.6 years after taxes.

The results of a 1979 survey of evaporative recovery systems in 16 plating companies are shown in Table 2.8.

The data in Table 2.8 do not reflect any credit attributable to the elimination of costs for chemical treatment to meet waste discharge requirements, nor is credit given for eliminating the disposal of solid waste. Yet the reported data for the recovery of chromium plating solution drag-out (Table 2.7) show that the equipment investment has been or will be paid off in 2.0 to 5.6 years by the net saving accrued from the chemicals recycled to the plating operations.

Fig. 2.12 Installed Costs for Evaporative Recovery Systems (Source: Ref. 29)

Table 2.8 Evaporative Recovery Systems

Plant	Plating Operation	Recovery Unit		Operational Cost, \$/mo	Chemical Saving, \$/mo	Approx. Payback, yr	Cost Ratio ^b
		Cost, \$	Type of Unit				
A	Chromium	20,000	Atmospheric	300	600	5.6	0.025
B	Chromium	48,000	Vacuum	350	1,400	3.8	0.05
C	Chromium and etch	225,000	1 Atmospheric 3 Vacuum	4,500	6,600	8.9	0.05
D	Chromium	72,000	Vacuum	900	No data	-	0.025
E	Chromium, nickel & etch	260,000	3 Vacuum	1,500	6,000	4.8	0.09
F	Chromium and nickel	128,000	2 Vacuum	3,000	5,250	4.8	0.09
G	Chromium	58,000	Vacuum	1,400	3,900	2.0	0.10
H	Chromium	100,000	Vacuum	100	4,000	2.2	0.15
I	Chromium	175,000	2 Vacuum	1,200	6,000	3.0	<0.15
J	Chromium	70,000	Vacuum	160	2,900	2.1	-
K	Lead-tin	45,000	Vacuum	800	16,000	0.25	0.08
L	Lead-tin	85,000	Vacuum	600	33,000	0.2	0.05
M	Nickel	25,000	Vacuum	300	1,500	1.7	0.02
N	Nickel	4,000	Vacuum	No data	2,100	-	-
O	Zinc (CN)	55,000	Vacuum	4,000	2,000	None	0.04
P	Zinc (CN)	55,000	Vacuum	915	450	None	-

^aSource: Ref. 30.^bCost of recovery equipment divided by the value of plating equipment.

2.6.4 Applications to Waste Recovery

2.6.4.1 Principal Current Applications

Almost every industry utilizes evaporation equipment of one type or another. In the treatment of hazardous wastes there are three basic potential uses for evaporation:

- Where no other treatment is currently practical; e.g., concentration of TNT for simultaneous incineration.
- Where evaporation is preferable to other methods; e.g., the concentration of radioactive wastes for disposal.
- Where evaporation is used as pretreatment, as an integral part of a process, or as a polishing step; e.g., in processing molasses, mash, and dyestuff wastes.

Some of these applications are described below.

Radioactive Wastes. Evaporators handling liquid radioactive waste require special precautionary modifications. These might include special de-entrainment devices, antisplash impingement baffles, foam abatement baffles (foam abatement is also aided by chemical additives such as surfactants).

Low-activity radioactive wastes such as storm-drain runoff are handled by evaporating in a pot or coil evaporator with an extremely large vapor head and special devices to prevent foaming and entrainment.

In other radioactive waste-treatment schemes such as precipitation, a sludge is the product or by-product. The processing and dewatering of the sludge obtained during the decontamination process poses special problems. Sludge resulting from physicochemical treatment is dewatered by evaporation or by vacuum filters. The dried sludge is stored in buried tanks similar to those used for other radioactive waste.

Electroplating Industry. Evaporators are used primarily to concentrate and recover plating solutions, as shown in Fig. 2.13. Many of these evaporators also recover water for rinsing.

Table 2.9 summarizes the application of evaporation to electroplating. The tabulated values are based mainly on an EPA survey of evaporator manufacturers. The first flash evaporation unit was installed in 1949, and it is now the most common type.

Fig. 2.13 Evaporators Used to Concentrate and Recover Plating Solutions (Source: Ref. 28)

There is no fundamental limitation on the applicability of evaporation. There are, however, certain practical limitations for most types. For example, climbing film evaporation is used for acid copper-plating solutions but not for cyanide copper-plating, because cyanide corrodes the materials. However, both atmospheric and submerged-tube evaporators are used for cyanide solutions, and there is no reason why climbing-film evaporation could not be used if the equipment was made of suitable materials.

Explosives Industry. The destruction of trinitrotoluene waste is possible with evaporation and simultaneous combustion. Two evaporation schemes are currently being employed: evaporation and combustion of wastes in spray form, and multistage vacuum evaporation within an immersion burner.

Nitro explosives are sometimes treated by preliminary reduction to amines using waste sulfuric acid and iron chips, but a distinct advantage for evaporation is that the evaporation and combustion steps can be carried out more conveniently and safely.

Table 2.9 Types of Evaporators Used in the Electroplating Industry^a

Application	Number in Operation (Additional Units Ordered)				
	Atmos- spheric	Submerged Tube	Climbing Film	Flash	Wiped Film
Chromium Plating	21 (3)	14	8	7 ^b	-
Nickel Plating	6 (1)	9	-	-	-
Copper Plating	2 (2)	5	1	-	-
Cadmium Plating	-	4	-	56 ^b	-
Zinc Plating	1	6	-	-	-
Silver Plating	-	7	-	-	-
Other Cyanide Plating	-	3	-	-	-
Chromic Acid Etching	- (1)	-	4 (1)	-	-
End-of-Pipe	-	-	-	-	2
Other, Unknown	-	1 (1)	-	14 ^b	-

^aSource: Ref. 28.

^bEstimated by manufacturer.

Paper and Pulp Industry. Seventy-eight percent of the pulp in the United States is produced by the Kraft sulfate process illustrated in Fig. 2.14. After the wood chips have been digested, they are separated from the spent cooking liquor and washed. The dilute "black liquor" from the washers is concentrated in a multiple-effect evaporator. The black liquor is further concentrated by heat from the flue gas of the steam recovery furnace prior to incineration for heat and recovery of chemicals.

The sulfite process produces about 21% of U.S. pulp and paper. In some sulfite pulp mills direct-contact evaporators are used for concentrating wastes prior to incineration.

Photographic Chemicals. In some photographic chemical processing plants, waste dye materials are treated by precipitation and flocculation. The residue is centrifuged and dried by evaporation for volume reduction.

Independent Contract Waste Processors. In addition to the industries that use evaporation for the handling of their own liquid or wet hazardous wastes, there are a number of independent operators who contract to handle

Fig. 2.14 Waste Liquor Treatment and Recovery for Kraft Pulp and Paper Process (Source: Ref. 27)

hazardous wastes for reclamation or concentration by evaporation. One major function of these contractors is the evaporation of spent pickling liquors by solar evaporation; sometimes the dried residue is sold to municipal sewage plants as water treatment chemicals.

2.6.5 Potential Applications for DOE Facilities

Table 2.10 illustrates the types of DOE waste that could be handled by evaporation. Selection of evaporation instead of another method should be guided by site-specific considerations. Major factors are economics (does the value of the reusable residue outweigh the cost of fuel for evaporation?); dissolved solids content (are there enough solids in the waste to warrant evaporation?); foreign matter content (is there foreign matter present that could cause scale formation or corrosion, or interfere with heat transfer?); and environmental (how will the concentrated liquor or dried residue be disposed?).

Table 2.10 DOE Waste Types that Can Be Handled by Evaporation

DOE Waste Type	Remarks
Inorganic	
Heavy metals	Ionic in sludges and slurries. Nonionic in residues.
Radioactive materials Fluorides and chlorides	Ionic-salt of light and intermediate metals
Organic (in nonaqueous media)	
Hydrocarbons	As solvents containing suspended or dissolved solids
Halogenated	
Oxygenated	
Amines	Some specific types
Nitro compounds	
Explosives	Some specific types
Sulfur-containing organics	Dye stuffs, etc.
Phosphorus-containing organics	
Lead-containing organics	
Metal-organics	

Evaporation is a well-defined, well-established process, almost universally used in industry. It is currently used for the treatment of hazardous waste, and can handle liquids, slurries, and sometimes sludges, both organic and inorganic, containing suspended or dissolved solids or dissolved liquids where one of the components is essentially nonvolatile (Tables 2.11 and 2.12). It can be used to reduce waste volume prior to landfill disposal or incineration.

Table 2.11 Waste Forms that Can Be Handled by Evaporation

Waste Forms ^a	Yes	No	Remarks
Aqueous	•		
Nonaqueous	•		
Liquid	•		
Slurries	•		
Sludges	•		
Tars	•		Special equipment (such as a dryer) is required
Solids	•		
Dry powders		•	
Gases		•	

^aSource: Ref. 27.

Table 2.12 Physical Forms after Evaporation^a

Products	Physical Form
Overhead	Aqueous liquid Nonaqueous liquid
Bottoms ^b	Aqueous liquid Nonaqueous liquid Sludges Tars Slurries Dry solids in cake, powder or crystalline form

^aSource: Ref. 27.

^bUsually evaporator bottoms are wet but there are exceptions.

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3 CHEMICAL TREATMENT PROCESSES AND INCINERATION FOR RECYCLING, DETOXIFICATION, OR VOLUME REDUCTION

This section presents the characterization of eight treatment processes that involve chemical reaction or thermal destruction and are potentially capable of detoxifying, recycling, or reducing the volume of specific components in hazardous waste streams. These processes include chlorinolysis, electrolysis, precipitation, flocculation, sedimentation, chemical reduction, ion exchange, neutralization, chemical oxidation, and incineration. They are selected because they are technologically well developed and potentially applicable for hazardous waste management at DOE sites.

3.1 CHLORINOLYSIS

3.1.1 Description of Technology

3.1.1.1 Basic Concepts

In the presence of excess chlorine the carbon-carbon bonds of hydrocarbons can be broken and the molecular fragments can react with chlorine to form chlorinated hydrocarbons of shorter chain length. This process is termed "chlorinolysis." It is essentially a pyrolysis process carried out in the presence of chlorine, which can be used to convert chlorocarbon waste streams to salable carbon tetrachloride.

The reaction of chlorine with chlorinated hydrocarbons or benzene to form carbon tetrachloride (CCl_4) is thermodynamically and kinetically favored at pressures above 50 atm and temperatures above 500°C .^{1,2} The reactions, for the most part, are sufficiently exothermic to permit an adiabatic mode of operation. The ratio of hydrochloric acid to salable CCl_4 product varies from 0 to 2, compared to about 4 in the conventional production of CCl_4 by chlorination of methane.

Hoechst-Uhde has patented a chlorinolysis process to manufacture CCl_4 from chlorinated wastes and residues. A semicommercial plant producing 6000-8000 tons/yr of CCl_4 has been in operation in Frankfurt since November 1970.

3.1.1.2 Process Description

Most liquid chlorinated hydrocarbon mixtures can be used as feedstock for the basic chlorinolysis process if the feed streams are free of solids. To avoid corrosion problems, the sulfur content should not exceed 25 ppm.

A schematic diagram of the Hoechst-Uhde chlorinolysis process is shown in Fig. 3.1.¹ Chlorine is cooled, compressed, and passed through a preheater into the lower end of the reaction chamber. A chlorine pressure of 4 atm is needed on the lower-pressure side. Organic feed is stored at 4 atm, compressed with a diaphragm pump, and premixed with the chlorine before introduction into the reaction.³

The reactor is provided with external heat. When the temperature is raised to 500°C and the pressure adjusted to 240 atm, chlorinolysis is initiated. Because the reactions are exothermic, heat is turned off after the reaction begins, and the reaction is allowed to proceed at 240 atm with an adiabatic end temperature of 620°C. The final temperature is regulated with chlorine, which must be at least 20% (and normally should be at least 50%) in excess of theoretical.

At the end of the reaction, products are quenched to about 500°C with cold carbon tetrachloride bled from the output stream. The temperature is further reduced to about 420°C by decreasing the pressure to 21 atm, and an air cooler is then used to bring the temperature to about 210°C. The products of the reaction are generally a mixture of hydrochloric acid (HCl), unreacted chlorine (Cl₂), phosgene (COCl₂) from any oxygenated compounds present, CCl₄, and incompletely reacted hexachloroethane (C₂Cl₆) and hexachlorobenzene (C₆Cl₆), both of which must be recycled to the process.

The reaction products are separated by distillation in four columns. In the first column (high boiler/column), HCl, Cl₂, CCl₄, and COCl₂ go overhead, and C₂Cl₆ and C₆Cl₆ are recycled from the bottom of the column back to the reactor. The second column (crude CCl₄ column) separates a mixture of HCl, Cl₂, and COCl₂ as the head product from CCl₄ bottoms. The crude CCl₄ bottoms are then purified in an atmospheric distillation column and a side stream is taken for quenching the reaction products.

The head product from the crude CCl₄ column, consisting of HCl, Cl₂, and COCl₂, is separated in the HCl column. Chlorine is recycled to the reactor; HCl and COCl₂ might have value as by-products but instead are normally disposed of after passage through a caustic scrubber.

3.1.1.3 Special Characteristics

Environmental Impacts. The HCl and COCl₂ effluents produced by the chlorinolysis process must be recycled to the process, sold, or disposed of in an environmentally acceptable manner.

Energy Requirements. Electricity and fuel requirements per ton of CCl₄ produced are relatively small: 135 kWh and 794 Btu, respectively.

Fig. 3.1 Hoechst - Uhde Chlorinolysis Process

Barriers to Implementation. Provided that a reasonable market for the product CCl_4 exists, there must be chlorocarbon wastes of sufficient volume to support an operating chlorinolysis plant. The HCl and COCl_2 wastes produced as by-products of this plant are toxic and must be recycled, sold, or treated in an environmentally acceptable manner.

Cost. Capital and operating costs will depend on the volume and concentration of waste, utility costs, and a variety of other factors. However, the estimated capital investment for a plant to treat 25,000 metric tons/yr of mixed chlorinated hydrocarbon feedstock will be approximately $\$8 \times 10^6$ (1981 basis).

3.1.2 Applications

3.1.2.1 General Discussion of the Application of Chlorinolysis to Waste Streams

The chlorinolysis process was not developed as a waste disposal process, but as a production process for CCl_4 from waste or residues rather than virgin materials. The process has excellent resource recovery potential, provided that there is a sufficient market for the CCl_4 produced. The waste streams that can be treated with chlorinolysis are typically those found in the production of vinylchloride, propylene oxide, allyl chloride, perchloroethylene, and mono- and di-chlorobenzenes.

3.1.2.2 Potential Application to DOE Waste Streams

Conversion of Chlorinated Hydrocarbon Wastes to Salable Carbon Tetrachloride. The chlorinolysis process seems to provide an efficient, cost-effective means for recovering a salable CCl_4 product from chlorinated hydrocarbon waste streams, assuming that the demand for CCl_4 remains stable. One factor that must be addressed is the difficulty in securing the necessary volume of waste streams. There may also be a problem in obtaining long-term commitments for waste feed streams. Changes in processing are not at all uncommon, and such changes usually affect the wastes available.

The recovery of Cl_2 from the HCl effluent of the chlorinolysis process and sale of the phosgene would improve the environmental acceptability of the process. Hoechst has a patent for production of Cl_2 from HCl_4 ; the COCl_2 by-product, however, may not be produced in sufficient quantity to be worth marketing.

3.2 ELECTROLYSIS

3.2.1 Description of Technology

3.2.1.1 Basic Concepts

The terms "electrolysis" and "electrolyte reaction" are applied to those reactions of oxidation or reduction that take place under the influence of an applied potential at the surface of conductive electrodes immersed in a chemical medium. At the negative electrode, or cathode, the reactions may include the reduction of a positively charged metal ion to the metal itself, or in aqueous media the reduction of the hydrogen ion or water to hydrogen gas. At the positive electrode, or anode, the reactions may involve the oxidation of negatively charged ions, leaving the discharged neutral atoms or group of atoms. The applied voltage necessary to promote a desired electrode reaction depends not only on the theoretical cell voltages, but also on concentration changes in the neighborhood of the electrodes and simple current losses resulting from the electrolytic resistance of the solution. Commercial electrochemical cells generally contain some stirring mechanism to decrease such concentration changes, and narrow electrode spacing to minimize resistance.

3.2.1.2 Process Description

Probably the most common use of electrolysis in waste treatment is the partial removal of concentrated metals from waste streams for recycling. An excellent example is the electrolytic regeneration of spent copper-pickling solutions. In the copper industry, scale and oxide are removed from freshly cast and hot-worked copper metal by "pickling" in concentrated sulfuric acid. As it is used, the pickling bath becomes loaded with copper; as a result, the bath becomes less acid and loses its effectiveness. It is now fairly routine to employ a small electrolytic cell to plate the excess copper out of the solution, thus maintaining the bath at an effective acid concentration.

When it is necessary to recover metals from dilute (less than 1% metal) streams, the rate of removal becomes very dependent upon the rate of diffusion of the metal ions to the cathode surface. Two general approaches have been used to overcome this inherent limitation. To decrease the reliance on diffusion, vigorous pumping or stirring is used to circulate the electrolyte through narrow slits or passageways between electrodes, to supply new metal ions to the cathode. This not only brings the electrolyte into close contact with the electrodes, but also, under certain conditions, allows the metal to be deposited as a nonadhering powder that can be washed from the electrode surface and filtered out downstream. Such a system has been reported to operate at 10% cathodic efficiency on a liquid containing 100 ppm of copper.⁴

The second approach is one in which electrolyte is pumped through a narrow gap over the surface of a rotating cylindrical cathode. For example, when copper is deposited on a stainless steel cathode, the adherence of the deposited film is minimal; the film can be mechanically stripped and reused as anode material in plating. Such systems have been shown to work at low levels of metal, down to about 10 ppm.

Anodic oxidation is generally used to destroy specific organic chemicals or oxidize cyanide wastes. Cyanide waste destruction in the presence of alkali probably occurs as follows:

The cyanide then reacts further with excess caustic to yield ammonium hydroxide, ammonium bicarbonate, and sodium carbonate. However, some of the cyanide, such as that tied up as ferricyanide, may not be amenable to treatment, and thus the process may not result in complete destruction of cyanide.^{5,6}

In an alternative to this reaction, sodium chloride may be added to the electrolyte, resulting in the production of hypochlorite upon electrolysis. The hypochlorite then reacts with the cyanide to yield carbon dioxide, nitrogen, and sodium hydroxide. The electrolysis may use conventional planar electrodes; recently fluidized-bed electrodes have been found to perform well also.

Combining some of the attributes of the two systems mentioned above is a recently developed system in which a rotating cylindrical cathode is separated from a stationary anode by an ion exchange membrane. As dendritic metal crystals are formed on the cathode, they are stripped away by high liquid flow rates and subsequently removed from the electrolyte (see Fig. 3.2). The system is reported able to decrease metal concentrations of 100-100,000 ppm to levels of 2-10 ppm; thus this system may have applications in both metal recovery and water cleanup.

3.2.1.3 Special Characteristics

Environmental Impacts. Gaseous emissions from electrolysis may frequently be significant; these emissions may consist of oxygen, hydrogen, chlorine, and other gases produced either by inefficient reactions at the working electrode or expected reactions at the counterelectrode. Some gases such as hydrogen and oxygen may be vented to the atmosphere, provided that

certain safety precautions are taken; others may have to be scrubbed or otherwise treated.

Although it is the goal of most metal-deposition schemes to render the process stream disposable or reusable, other systems, such as the destruction of cyanide or the reduction of chromium, simply change the contaminant to a less harmful or more easily treated form, which must then be processed by a separate process. This fact, however, should not be a primary reason for eliminating electrolytic processes from consideration. Use of electrolysis to reduce metal ion concentrations to a sufficiently low level to permit reverse osmosis or to do the final polishing of the product of ion exchange treatment may, under the appropriate circumstances, result in a feasible cost for the total treatment process.

Barriers to Implementation. Common to all electrolytic processes is the problem of maintenance of a high-performance electrode surface. Anodes, especially, are prone to oxidation -- especially carbon anodes where significant wastage may change the dimensional tolerance of the electrolytic cell. Obviously, anode consumption and replacement should be considered among the economic factors when such a system is evaluated.

Although dimensional changes in the cathode due to metal deposition are the most predictable, other more subtle changes may take place. For example, a cathode substrate chosen to have a high overvoltage for hydrogen evolution in order to permit operation at higher voltages and thus higher currents will, when plated with a particular metal, begin to exhibit the characteristics of an electrode made of that metal. Cathode efficiency may thus fall.

Fig. 3.2 Electrolysis with a Rotating Cylindrical Cathode

The most common, least predictable, and most difficult to control form of electrode deterioration is fouling. Fouling means the accumulation at the electrode surface of a coating of insoluble salts, oxides, organic materials, and biological films, which interpose a high resistance barrier to the desired electrolytic reactions. For example, an inefficient cathode evolving hydrogen according to the equation

is also developing a region of high pH, which may cause precipitation of species that are in solution at the pH of the feed. Likewise, organic films or slimes may deposit. These films and slimes may be present in the feed only in minute quantities but may be slowly accumulated. Also variations in feed may be enough to push the chemistry at an electrode surface from a nominally nonfouling condition to a fouling one.

Cost. Electrolysis is one of that set of processes in which material is removed from the solvent, rather than vice versa. Thus, the cost of treatment is very dependent upon the concentration and nature of the material to be removed. As a point of reference, a partial cyanide destruction system has been reported to have direct operating costs of about \$1.80 per pound of cyanide destroyed. Capital cost was \$31,000 for a capacity of 20,000 gpd. With a feed stream concentration of about 110 ppm total cyanide, this represents a cost of \$1.60 per thousand gallons of wastewater.⁶

It is worth noting here an interesting and simple trade-off between operating and capital cost. Increasing the electrode current will generally permit a greater throughput of feed in a given system (effectively a reduction in capital cost) but at reduced current efficiency (and increase in direct costs). Generally, systems operating on concentrated solutions produce high current efficiency (thus at reduced direct cost), whereas systems operating on dilute streams tend to be designed for lower capital costs, although each situation has to be evaluated in light of all factors.

3.2.2 Applications

3.2.2.1 General Discussion of Applications

Electrolysis, including electroplating and anodizing, is currently in wide industrial use, as the following examples indicate.

Chlorine/Caustic Production. The bulk of the U.S. production of chlorine, amounting to many millions of tons per year, is achieved through the electrolysis of concentrated aqueous solutions of sodium chloride (NaCl). In

one type of system, Cl_2 and hydrogen (H_2) are evolved at inert anodes and cathodes, respectively, to give the overall cell reaction:

In an alternative method of chlorine/caustic production, the cathode may consist of a bed of metallic mercury, which makes possible the reaction:

The amalgam is subsequently removed and reacted with pure water to give NaOH free of chloride contamination.

Metal Refining. Many commercial metals are routinely refined by electrolytic processes in order to remove impurities. Bismuth, copper, gold, indium, lead, nickel, silver, and tin are generally treated in this manner. In practice, the anode is a bar of the impure metal and the cathode a plate of pure metal or an inert conductor. The electrolyte may be strongly acidic, alkaline, or neutral, depending upon the metal being refined and the nature of the impurities. The electrolyte is frequently chosen to be at or near the concentration of maximum electrolytic conductivity in order to minimize power losses.

Electrowinning. In contrast to the electrefining of impure metals, electrowinning may be employed to obtain metals from electrolytes derived from the primary metal ores. Such a process is frequently used to obtain copper, zinc, cadmium, cobalt, gallium, and other metals. For example, cadmium is generally present in significant quantities in the sludges and residues from zinc refining. The source materials are dissolved in sulfuric acid, pretreated as necessary to remove copper and certain other impurities, and the cadmium plated out onto aluminum cathodes. Oxygen is generated at the anodes, which are usually composed of lead sheet. For cadmium, and in fact for most metals, electrowinning is carried out at current efficiencies often exceeding 90%.

Molten Salt-Bath Electrometallurgy. The most important industrial nonaqueous electrochemical processes are probably the electrowinning of aluminum and magnesium from molten salt baths. In the case of aluminum, a bath of molten cryolite (Na_3AlF_6) is used to dissolve a feed of purified alumina (Al_2O_3), which is electrolyzed on carbon electrodes to yield molten aluminum and oxygen. Careful adjustment of voltages and current can eliminate the need for external heating, once the system is in operation at about 1000°C . Current efficiency ranges from 85-90%. The oxygen generated at the carbon or graphite anode reacts with it to a significant degree to form CO_2 ,

which, although it diminishes anode life, also helps to generate heat internally and to keep exposing a fresh anode surface.

Electroplating. The electroplating industry (including anodizing) is a widespread user of industrial electrochemistry for the preparation of decorative, functional, or protective surface finishes. Literally thousands of plating shops are in existence, some captive to parent manufacturing plants but most independent and small (with less than 15 employees). Among the metals commercially plated are antimony, arsenic, brass, bronze, cadmium, chromium, copper, gold, indium, iridium, iron, lead, nickel, palladium, platinum, rhodium, ruthenium, silver, tin, zinc, and lead-tin solder alloys. Most plating is from aqueous electrolyte baths with the work piece used as the cathode and the plating metal used as an anode. During plating, the anode is consumed and maintains the metal ion concentration of the bath at a constant level. Plating may also be done using an inert anode such as carbon, at which oxygen is evolved. In such cases, the bath concentration changes with use; generally such baths are prepared at higher metal concentrations than the baths in which consumable anodes are used. The concentration and composition of plating baths and the current density are generally determined by the type of finish required, the metal being deposited, and the material and geometry of the substrate. Current efficiency may range from about 10% for some chrome plating to virtually 100% for silver and copper.

3.2.2.2 Potential Applications to DOE Waste Streams

Electrolytic processes, although limited in their applications to waste streams, may be considered (1) for reclaiming heavy metals, including toxic metals, from concentrated aqueous solutions and (2) for polishing dilute metal streams. These processes are not generally useful for treating dissolved organics, organic waste streams, or viscous and tarry liquids.

Removal of Concentrated Metals for Recycling. Probably the most promising application for the electrolytic processes discussed above is in the partial removal of concentrated metals from waste streams for recycling or reuse. An excellent example is the electrolytic regeneration of spent copper pickling solutions as was described earlier.

Removal of Chromium from Industrial Wastewaters. Industrial electrolytic units are being marketed for the removal of chromium from industrial wastewaters. Hexavalent chromium is electrolytically reduced to trivalent chromium, which precipitates out as chromic hydroxide; chromium can be recovered from the hydroxide, purified, and recycled.

Recovery of Chlorine from Waste HCl. It has also been reported in the literature that waste HCl streams may be at least partially reclaimed by electrolysis to yield usable chlorine gas. However, as the system works only for streams containing in excess of 20-25% HCl, this application appears quite limited.⁷

3.3 PRECIPITATION, FLOCCULATION, AND SEDIMENTATION

3.3.1 Description of Technology

3.3.1.1 Basic Concept

Precipitation, flocculation, and sedimentation are consecutive processes used for reacting, solidifying, and settling out various waste constituents in the same stream. Precipitation transforms a substance in solution into an insoluble form thus producing a second phase consisting of small solid particles or colloids. Flocculation then transforms these solids into larger suspended particles so that they can be removed by gravity settling in a sedimentation basin.

Precipitation is a physicochemical process whereby waste constituents (often inorganic ions) are changed into a solid phase and thereby removed from solution. Precipitation involves an alteration of the chemical equilibrium relationships affecting the solubility of the component(s). This alteration can be achieved by one or a combination of the following steps:

- Adding a substance that will react directly with the substance in solution to form a sparingly soluble compound.
- Adding a substance that will cause a shift in the solubility equilibrium to a point that the continued solubility of the substance originally in solution is no longer favored; most often this is accomplished through changes in pH.
- Changing the temperature of a saturated or nearly saturated solution in the direction of decreased solubility; because solubility is a function of temperature, this change can cause ionic species to come out of solution and form a solid phase.*

*This technique, however, has very limited applications for waste treatment/recovery purposes, mainly because solubility of most slightly soluble compounds used in precipitation schemes is a weak function of temperature, and therefore very large differences in concentration cannot usually be achieved.

The most common precipitation reactions involve the removal of inorganic ionic species from various aqueous media.

Flocculation is the process by which the suspended particles generated by precipitation agglomerate into larger particles. It is accomplished chemically through a variety of mechanisms involving surface-chemistry and particle-charge phenomena. These phenomena, in general, can be grouped into two sequential mechanisms: (1) destabilization of the surface-related repulsive forces, thus allowing particles to stick together when contact between particles is made and (2) chemical bridging and physical enmeshment between the now nonrepelling particles, thus allowing the formation of larger particles.

Inorganic chemicals used to cause flocculation include alum, lime, various iron salts (e.g., ferric chloride, ferrous sulfate). Organic flocculating agents, often referred to as "polyelectrolytes," have come into widespread use relatively recently. These materials generally consist of long-chain water-soluble polymers such as polyacrylamides. They are used either in conjunction with the inorganic flocculants such as alum or as a primary flocculating agent.

Once suspended particles have been flocculated into larger particles, they are removed from the liquid stream by sedimentation. Sedimentation is a purely physical process whereby particles suspended in a liquid are made to settle by means of gravitational or inertial forces (e.g., as in centrifuges) acting on both the particles suspended in the liquid and the liquid itself.

3.3.1.2 Process Description

Precipitation is achieved by adding and rapidly mixing the appropriate amount of chemicals with the incoming waste stream. Mixing is accomplished by a stirring device mounted on the mixing tank. Sufficient retention time (usually less than one minute) is required to assure complete chemical contact. Flocculating agents may also be added in the rapid-mix tank.

Flocculation is usually achieved in a basin with gentle agitation provided by paddles or other stirring devices. Sufficient retention time is required to allow floc formation.

Sedimentation, essentially a liquid/solid separation process, can be carried out as either a batch or a continuous process. Continuous processes are by far the most common, particularly when large volumes of liquid are involved. Continuous sedimentation can be achieved in rudimentary settling ponds, conventional settling basins, or in more advanced clarifiers, which are often equipped with built-in flocculation zones and tube-like devices that enhance settling.

A representative configuration of waste treatment system employing precipitation, flocculation, and sedimentation is shown in Fig. 3.3.

Fig. 3.3 Representative Configuration Employing Precipitation, Flocculation, and Sedimentation (Source: Ref. 8)

3.3.1.3 Special Characteristics

Energy Requirements. The processes of precipitation, flocculation, and sedimentation are very low energy consumers compared with many other processes used to treat hazardous wastes. All of the energy consumed is mechanical energy required for pumping the liquid to and from the basins, mixing the chemicals with the liquid, and collecting the settled sludge. For any given size, clarifiers with recirculation of solids will have a slightly higher power requirement than will conventional settling basins. Usually, the energy required is a function of the volume of liquid treated rather than the composition of the liquid, and for a given type of equipment, the power required is reasonably linearly proportional to the volume treated. For example, the total power required for a complete system employing precipitation, flocculation, and sedimentation that is capable of treating 10 million gal/day of wastewater will typically be 40-200 hp, depending on the specific design. (This power estimate includes all pumping, mixing, and sludge-handling power requirements.)⁸

Environmental Effluents. Because the precipitation, flocculation, and sedimentation process is basically a liquid-solid separation process, two output streams will result: a high-volume purified liquid stream and a low-volume slurried solids stream. As a rule, there are no gaseous emissions from the process. The processes do employ equipment that exposes large open surfaces of liquid to the atmosphere; if that liquid is other than water and is highly volatile or contains highly volatile components, air pollution could result.

The liquid slurry or sludge produced from precipitation, flocculation, and sedimentation is usually treated to reduce its volume by some means of dewatering. The recovered solids can either be further processed for waste recovery or disposed of. It should be noted that precipitation, flocculation, and sedimentation are nondestructive processes. The precipitated substances may be less hazardous than the ions in solution, but they are by no means innocuous from an environmental point of view.

Cost. Treatment facilities using the processes of precipitation, flocculation, and sedimentation have been in full-scale operation for many years. As a result, the economics and operating parameters are relatively well defined. The process economics are mainly affected by the following parameters:

- The volume and contaminant levels of the waste stream to be treated,

- The degree to which a substance will precipitate, along with the reaction time and the required chemical dosages,
- The type of flocculating agents that must be used and the time required for flocculation, and
- The settling rate of the flocculated material.

The largest capital cost is likely to be for the sedimentation and sludge dewatering equipment (if required), whereas the types and dosages of chemical agents will, to a large degree, determine the direct operating costs.

To illustrate the economics of precipitation, flocculation, and sedimentation, Arthur D. Little (ADL) analyzed these processes for treatment of a representative wastewater stream from an automotive plating operation.⁸ The wastewater streams, after cyanide destruction steps, are treated with lime at a dosage approximately 50% greater than the stoichiometric amount required to convert all the soluble zinc to insoluble zinc hydroxide. A synthetic polyelectrolyte flocculant is added at a dosage of 2 mg/L. The precipitation, flocculation, and sedimentation processes are carried out in clarifiers. The wet sludge from the clarifiers is further dewatered in thickeners. Sulfuric acid is fed to the treated effluent in order to return the pH to the neutral range. For a system treating a waste stream at a 0.41×10^6 gal/day flow rate, containing a zinc concentration of 113 mg/L, the total annual cost (1976 dollars) was estimated to be \$144,000/yr, which translated to \$1.00/1000 gal treated. The same ADL study also indicates that, for a moderate size ($0.5\text{--}5 \times 10^6$ gal/day) system employing precipitation, flocculation, and sedimentation and using moderate dosages of normally used precipitating/flocculating agent, the unit treatment cost ranges from \$0.50 to \$3.00/1000 gal. For a small, specially designed system (less than 0.5×10^6 gal/day) using high dosages of precipitating/flocculating agents, the unit cost will be higher than that of the larger systems, but will rarely exceed \$6.00/1000 gal.

In a separate study by SCS Engineers,⁹ the total capital cost (mid-1978 dollars) of a Chicago-based precipitation, flocculation, sedimentation facility treating waste streams at 1.4×10^6 gal/day was calculated to be \$5.82/1000 gal. For a system treating waste flow at 7.2×10^6 gal/day, the total capital cost was \$3.71/1000 gal. The average cost over a 10-yr lifetime was estimated to be \$1.72/1000 gal for the 1.4×10^6 gal/day system, and \$1.22/1000 gal for the 7.2×10^6 gal/day system.

When used in hazardous waste treatment, precipitation, flocculation, and sedimentation are generally considered rather low-cost processes, especially when compared to other processes such as carbon adsorption or distillation.

3.3.2 Applications for Waste Recovery

3.3.2.1 Principal Current Applications

Precipitation, flocculation, and sedimentation have been in use since the 19th century for a wide variety of industrial applications. Today, the processes are used in the manufacture of chemicals, in treatment of industrial water supplies, and in treatment and/or recycling of waste and hazardous materials. The processes can be applied wherever it is necessary to remove precipitable soluble substances and/or suspended particles from liquid streams.

Some typical example of use of precipitation, flocculation, and sedimentation in treatment of recycling of hazardous waste are described below.

Silver. Silver is frequently removed from wastewater by precipitation as silver chloride (AgCl). Silver chloride is an extremely insoluble compound which will dissolve in water to a maximum concentration of approximately 1.4 mg silver ion per L water.¹⁰ This property places AgCl in contrast to most metal chlorides, which are relatively soluble. Thus, silver can be selectively recovered as AgCl from a mixed metal waste stream without initial waste stream segregation or concurrent precipitation of other metals. Concurrent precipitation of mixed metals can happen when the treatment conditions are alkaline. In this case, acid washing of the precipitated sludge will remove contaminant metal ions, leaving the insoluble AgCl .

Some waste streams, particularly those from plating shops, contain silver cyanide (AgCN), which interferes with precipitation of AgCl . Removal of cyanide is necessary before precipitation of silver as the chloride. It can be accomplished by oxidizing the CN with Cl_2 , releasing chloride ions into the solutions, which in turn react to form AgCl directly (see Sec. 5.3 on chemical oxidation). In the event that cyanide is present in great excess over silver, high chloride concentration resulting from cyanide oxidation may favor the formation of soluble AgCl complexes, thus reducing the effectiveness of this silver removal process.¹¹

Silver in waste streams can also be precipitated as silver sulfate-oxide salts. A process patented by Eastman Kodak Co.¹² recovers silver from waste photographic solutions containing high levels of organic acids by reacting the solutions with magnesium sulfate (MgSO_4) and lime. The silver precipitates as a mixed sulfate-oxide and is recovered from the sludge.

Another silver recovery process patented by Eastman Kodak Co.¹³ is for treatment of waste photographic processing solutions that contain silver thiosulfate (AgS_2O_3) complex. The waste solutions are chlorinated under alkaline conditions to precipitate a silver-bearing sludge from which the

silver can be separated and to destroy thiosulfate ion and thereby reduce the oxygen demand of the solution. Chlorination can be achieved by introduction of chlorine gas or by use of hypochlorite solution.

Copper. A commonly practiced method for treatment of copper-containing waste streams is precipitation of the relatively insoluble copper oxide at an alkaline pH. Full-scale treatment facilities for removing copper from wastewater by means of precipitation, flocculation, and sedimentation using lime, have been in operation over decades.^{14,15} Lime is the desired base for pH adjustment, because of its low cost and property of reacting to form the metal hydroxide.

Copper hydroxide solubility is minimal around pH 9.0 to 10.3.¹⁶ Jenkins et al.¹⁷ have reported a maximum solubility of 0.01 mg/L at pH 10. This value corresponds to the theoretical minimum effluent concentration that could be achieved by precipitation. Theoretical levels are seldom attained, however, due to poor settling of colloidal precipitates, slow reaction rates, pH fluctuations, and the influence of other ions in solution.

Tallmadge¹⁸ reports that the Scoville Brass Mill, of New Milford, Conn., disposes of its rinse waters and waste pickle liquors by lime precipitation. Rinse waters containing 10 to 20 mg of copper per L of waste are treated on a continuous basis, while the more concentrated waste pickle liquors are pumped into holding tanks and bled into the waste stream slowly, thus allowing continuous treatment of the high-concentrate solutions. Lime is used to neutralize the acid and precipitate copper. The resultant effluent, before further dilution, contains 1 to 2 mg of residual copper per L of effluent.

Nickel. Nickel can be removed from waste streams by means of precipitation, flocculation, and sedimentation using lime. Full-scale facilities for removal of nickel have been reported.¹⁴ Nickel forms insoluble nickel hydroxide upon addition of lime. The nickel hydroxide has a minimum theoretical solubility of 0.01 mg/L at pH 10.¹⁷ The precipitation is most effective at a high pH, although little efficiency is gained above pH 10. Kantawala and Tomlinson¹⁹ reported the precipitation of 100 mg of nickel per L at pH 9.9, by addition of 250 mg of lime per L of solution and resultant formation of nickel hydroxide. The use of lime, followed by conditioning of the nickel hydroxide sludge with ferric chloride (to improve dewatering), and filtration on sand reduced a combined waste effluent averaging 21 mg of nickel per L of effluent down to a concentration of 0.09 to 1.9 mg nickel/L effluent. Total waste flow was 200,000 gal/day. Hansen and Zabban²⁰ report that a lime treatment that employed the coagulant aid Separan NP-10 at a concentration of 1 to 2 mg/L was able to reduce nickel from a concentration of 39 mg/L waste to 0.17 mg/L of waste. Stone²¹ reported that nickel in the lime-treated effluent of a copper, brass, cupro-nickel metal processing plant was 0.1 mg nickel/L waste prior to

sand filtration of the treated wastewater. Filtration acts as a polishing process to remove small nonsettlable metal hydroxide particles.

Mercury. In pilot-scale facilities, mercury has been successfully removed from wastewater by means of precipitation, flocculation, and sedimentation using sulfide salts in conjunction with alum, lime, and coagulant aids.^{22,23} Deriaz²⁴ developed a process to recover mercury as mercuric sulfide (HgS) from waste brine generated from mercury cells. The waste brine coming from the mercury cells is acidic and hot. Mercury is removed from the waste brine through the following steps: A solution containing sulfide ions is added to brine until the redox potential relative to the saturated KCl-calomel electrode is in the range from 0.85 to 0.93 V. The pH is raised by the addition of alkali to a pH in the range of 7 to 9 (preferably 8). The introduction of sulfide ions into the brine is then continued until the redox potential is in the range from 0 to -0.2 V, and the precipitate is flocculated, settled, and separated from the substantially mercury-free brine.

Lead. Precipitation, flocculation, and sedimentation processes have been used to treat wastewaters that contain lead. In the precipitation processes, lead is normally precipitated as the carbonate or the hydroxide. The solubilities of both compounds are very low at alkaline pHs, and formation of either product is effective in reducing dissolved lead concentrations.

In forming insoluble lead hydroxide, lime is the most effective treatment chemical. Dean et al.²⁵ report the use of lime to remove dissolved lead from wastewater in full-scale treatment facilities. Treatment of a wastewater from a tetraethyl lead plant has also been described.²⁶ The effluent was alkaline and contained inorganic lead salts in solution and suspension, plus organic lead salts. The pH of the wastewater was adjusted to 8 to 9, and lead was precipitated by addition of lime. The addition of ferrous sulfate, which acted as a flocculating agent, enhanced the precipitation. The treated effluent flowed to a Dorr-Oliver Clariflocculator, in which the lead sludge was collected at the bottom. It was then dewatered in a filter and reclaimed by a lead slag refinery.

Chromium. Chromium is currently removed from wastewater by means of precipitation, flocculation, and sedimentation using lime in full-scale treatment facilities. It is necessary to reduce hexavalent chromium to trivalent chromium before effective precipitation can be carried out. Chemical reduction and precipitation for recovery of chromium is discussed separately in Sec. 3.4.

A process developed by Richards²⁷ involves chemically removing chromium ions from industrial waste solutions by direct precipitation with barium

carbonate (BaCO_3) after acidification with nitric or hydrochloric acid or their salts. G.J. Nieuwenhuis²⁸ developed a process in which hexavalent chromium contained in aqueous wastes from metal treating is substantially removed from the aqueous solution. This process involves metering the acid wastes into rinse water, and then metering stoichiometric amounts of a lead compound such as lead nitrate [$\text{Pb}(\text{NO}_3)_2$] into the rinse water containing the hexavalent chromium to form an insoluble lead chromate (PbCrO_4) precipitate. The remaining liquor is subsequently treated with a caustic cleaning solution to neutralize the acids and precipitate the remaining metal compounds; the residual aqueous solution is suitable for reuse.

3.3.2.1 Potential Application of the Technology to DOE Facilities

Precipitation, flocculation, and sedimentation are well-developed processes currently being applied to many industrial wastes. The most common applications of these processes have been for removal of colloidal hazardous substances and heavy metals, such as iron, zinc, chromium, silver, mercury, lead, and copper, from aqueous streams. Those processes should be applicable in DOE facilities for recovery of hazardous material from such waste streams as photographic solutions, spent pickle solutions, cooling tower blowdowns, and plating shop rinses.

Precipitation, flocculation, and sedimentation processes have been in use for many years. The necessary equipment is relatively simple, easy to operate, and readily available. These processes are relatively inexpensive, particularly when applied to large streams. Furthermore, energy requirements of these processes, mostly for mixing and pumping of aqueous solutions and collection of settled sludges, are generally low.

Precipitation, flocculation, and sedimentation processes are not without disadvantages, however. Nonselectivity is an obvious problem, particularly when these processes are used for waste recovery. Very often, many different substances, hazardous and nonhazardous, exist in a stream and are simultaneously removed in these treatment processes. For example, in the lime precipitation of heavy metals from wastewater, large quantities of nonhazardous calcium are precipitated along with the toxic metals. In this case, further treatment of settled solids is necessary in order to separate the metals from the calcium.

Application of precipitation, flocculation, and sedimentation processes for sites with small waste volumes (<10,000 gal/day) could be a problem. Most suppliers of equipment for precipitation, flocculation, and sedimentation are geared toward marketing their systems to customers with large wastewater streams, because small systems are usually homemade or specially constructed by suppliers. In addition, there are very few batch precipitation, flocculation, and sedimentation systems in operation.

3.4 CHEMICAL REDUCTION

3.4.1 Description of Technology

3.4.1.1 Basic Concept

Originally, the term "reduction" referred to the reduction of the amount of oxygen associated with an element. Reduction now has the broader meaning of loss of electrons. Thus, the reduction of the metal lithium is described by the following equation:

If the formula for lithium oxide is written in its ionic form, it is clear that lithium has gained electrons during reduction.

The above equation shows that, through the reduction process, the lithium ion, Li^+ , is converted to lithium metal, Li , by gaining electrons.

In waste treatment and recycling processes, reduction is used in such a way that the reducing agent lowers the oxidation state of a substance in order to reduce its toxicity, reduce its solubility, or transform it into a form that can be easily handled.

Chemical reduction is applied primarily to the removal of heavy metals from aqueous solutions. Many metals can be reduced to their elemental form for potential recycling or can be converted to less toxic oxidation states. For example, chromium (VI) is a very toxic material, but when reduced to chromium (III), it is less hazardous and can be precipitated for removal. In the following equation

the oxidation state of chromium changes from 6^+ to 3^+ (chromium is reduced) while the oxidation state of sulfur increases from 2^+ to 3^+ (sulfur is oxidized). This change of oxidation state implies that an electron was transferred from sulfur to chromium (VI). The decrease in the positive valence (or increase in the negative valence) with reduction takes place simultaneously with oxidation in chemically equivalent ratios. The resulting chromic sulfate has a relatively low solubility and can be removed in solid form.

3.4.1.2 Process Description

Operations. The first step of the chemical reduction process is usually the adjustment of the pH of the solution to be treated. With SO_2 treatment of chromium (VI), for instance, the reaction requires a pH in the range of 2 to 3. The pH adjustment is done with the appropriate acid, H_2SO_4 , for example. This is followed by the addition of the reducing agent. The solution is then mixed to improve contact between the reducing agent and the waste. The agent can be a gas (e.g., SO_2), a solution (e.g., NaBH_4), or even a finely divided powder (e.g., Fe) if there is adequate mixing. Reaction times vary for different wastes, reducing agents, temperatures, pHs, and concentrations. For commercial-scale operations for the treatment of chromium wastes, reaction times are on the order of minutes. Additional time is usually allowed to ensure complete mixing and reduction. Once reacted, the reduced solution is generally subjected to some form of treatment to settle or precipitate the reduced material. A treatment for the removal of what remains of the reducing agent may be included. This treatment may consist of applying unused reducing agent or the reducing agent in its oxidized state. Unused alkali metal hydrides are decomposed by the addition of a small quantity of acid. The pH of the reaction medium is typically increased so that the reduced material will precipitate out of solution. Filters or clarifiers are often used to improve separation. A flowsheet for the typical process for the chemical reduction of hexavalent chromium is shown in Fig. 3.4.

Equipment. Very simple equipment is required for chemical reduction: storage vessels for the reducing agents and perhaps for the wastes, metering equipment for both streams, and contact vessels with agitators to provide suitable contact of reducing agent and waste. Some instrumentation is required to determine the concentration and pH of the waste and the degree of completion of the reduction reaction. The reduction process may be monitored by an oxidation-reduction electrode. This electrode is generally a piece of noble metal (often platinum), which is exposed to the reaction medium and produces an emf output that can be empirically related to the reaction condition by revealing the ratio of the oxidized and reduced constituents.

Numerous companies have commercial units for the treatment of chromium (VI) in industrial effluents. All of these units offer the user a preengineered system for a specific waste or range of waste streams.

Chemicals. Chemical reduction is applied primarily to the control of hexavalent chromium in the plating and tanning industries and to the removal of mercury from caustic/chlorine electrolysis effluents, dissolved lead compounds in wastewater from the manufacturing of tetraalkyllead, and silver from photographic waste effluents. The chemical reducing agents that are used for these applications include SO_2 , NaHSO_3 , FeSO_4 , NaBH_4 , and base metals such

Fig. 3.4 Typical Process Flowsheet for Chemical Reduction (Source: Ref. 8)

as iron, aluminum, and zinc. These reducing agents and their identified applications are listed in Table 3.1.

Other chemicals (in addition to reducing agents) may be needed to adjust the pHs of influent and effluent. For a reaction to occur with SO_2 treatment of hexavalent chromium, for example, a pH between 2 and 3 is required. The pH adjustment is done with the appropriate acid, such as sulfuric acid. After chemical reduction, the effluent is typically acidic and must be neutralized prior to discharge. Adjustment of the pH in this case is usually done with materials such as hydrated lime, caustic soda, or soda ash.

3.4.1.3 Special Characteristics

Energy Requirements. Total energy consumption, not including the energy required to produce the chemicals, is low for chemical reduction. The only energy needed is for pumping the waste and the reducing agent and for mixing the two.

Environmental Implications. Air pollution from chemical reduction processes is not expected to be significant.

Table 3.1 Chemical Reducing Agents
and Their Applications

Waste	Reductant
Chromium (VI)	Sulfur dioxide (often flue gas)
	Sulfite salts
	sodium bisulfite
	sodium metabisulfite
	sodium hydrosulfite
	Ferrous sulfate
	Powdered waste iron
	Powdered waste aluminum
	Powdered metallic zinc
Mercury	Sodium borohydride
Tetraalkyllead	Sodium borohydride
Silver	Sodium borohydride

Chemical reduction processes may introduce new ions into the aqueous effluent. If the level of these new contaminants is high enough to exceed effluent regulations, additional treatment of the effluent may be required. For example, after chromium (VI) reduction, the treated solution will be acidic and will also contain the reduced chromium and any other metals present in the original waste stream. Because this solution is corrosive, it may require neutralization prior to discharge or further treatment. Precipitation will occur because of the chemical nature of the materials used, and therefore settling basins or clarifiers will be required to remove the solids.

Most chemical reductions will produce a residue for disposal, unless the residue is recovered or the concentration of the waste constituent is so low that the reducing agent and the reduced waste can be carried away with the effluent. Residues that eventually will be disposed of on land can be a problem with this treatment process. The sludges formed in follow-up treatment may cause disposal problems because the metal hydroxides they contain may be susceptible to acid leaching. Since the common alkalies used are sodium hydroxide and hydrated lime, a large portion of the sludge will be excess lime and calcium sulfate.

The equipment required for chemical reduction processes is relatively simple, needed only for storage, metering, mixing, pumping, and monitoring. The cost of treatment at individual plant locations and of individual wastes varies greatly. The capital cost will depend on such factors as type, volume, and composition of waste; degree of treatment required; treatment process selected; availability of required services; and recovery objective. The major portion of operating costs is for required chemical agents -- especially when more concentrated wastes are treated. A.D. Little⁸ has prepared a preliminary cost estimate for installation and operation of a facility for the chemical reduction of chromium (VI) waste from a plating operation using SO_2 treatment. The results, expressed in 1976 dollars, are given in Table 3.2. The unit cost was estimated to be nearly \$194/1000 gal waste treated.

3.4.2 Applications for Waste Recovery

3.4.2.1 Principal Current Applications

Reduction reactions are among the most common of chemical reactions. Experience with these reactions for waste treatment is primarily related to removal of trace contaminants in water effluents and for treatment of chromium (VI) from operations such as plating and metal finishing. The following paragraphs describe some selected examples of the application of chemical reduction to management of hazardous waste.

Table 3.2 Estimated Costs for Treatment of Chromium (VI)
Using Chemical Reduction^a

Cost Component	Annual Quantity	Cost Per Unit Quantity	Annual Cost
Capital Investment - \$230,000			
Variable Costs			
Operating Labor	2,500 man-hours	\$12.00/h	\$30,000
Chemicals			
Sulfur Dioxide	29 tons	\$170/ton	4,900
Lime	250 tons	\$ 35/ton	8,800
Total Chemical Costs			13,700
Utilities			
Electricity	35,000 kWh	\$0.02/kWh	700
Maintenance (3% Investment)			7,000
Total Variable Costs			51,400
Fixed Costs			
Taxes on Insurance (2% Investment)			4,600
Capital Recovery (10 yr @ 10%)			37,000
Total Annual Cost			\$93,000
Unit Cost (\$/10 ³ gal)			\$193.80

^aBasis: 1976 dollars; 240 days/y.

Stream Flow: 2,000 gal/day

Treatment: batch

Influent Concentration: 100,000 ppm CrO₃ (85% as Cr³⁺)
in 20% H₂SO₄

Effluent Concentrations: Cr⁶⁺ - undetectable

Source: Ref. 8.

Reduction of Chromium (VI) to Chromium (III) in Aqueous Solutions.

Numerous plating and metal finishing plants treat their chromium (VI) wastes using chemical reduction methods. Cyanides and chromium are often present together in plating industry wastes. The concentrations of these substances and their potential recovery value influence the selection of the treatment process. If the cyanide and chromium are not economically recoverable by a method such as ion exchange, the cyanide radical is first destroyed or converted to the less toxic cyanate by oxidation and the chromium (VI) is then reduced to chromium (III), which precipitates and is removed as a sludge.

The standard reduction-treatment technique is to lower the waste stream pH to 3 or below with acids and convert the chromium (VI) to chromium (III) with a chemical reducing agent. The chromium (III) is then removed, usually by precipitation. The reduction of chromium (VI) to chromium (III) is not 100% effective, and the amount of residual nonreduced chromium (VI) depends upon the allowed time of reaction, pH of the reaction mixture, and concentration and type of reducing agent employed. Chromic acid waste does not normally require pH adjustment, as the pH of the chromic acid itself is sufficiently low for the reduction to proceed.

Chromium (VI) can be reduced to chromium (III) by a variety of reducing agents including SO_2 , sulfite salts, and FeSO_4 . In industry, the most widely used reducing agent for this purpose is SO_2 . Chemical precipitation of chromium (III) is usually accomplished by using either lime or Na_2CO_3 . In the tanning and plating industries, sludges containing from 10-80% solids obtained from precipitation of chromates are often redissolved by acidification and then subjected to reduction followed by precipitation to obtain the chromium in an insoluble, concentrated form.

Reduction Using SO_2 . The reaction equations for chromium waste treatment using SO_2 are as follows:

Using hydrated lime, the neutralization is

Chromium (VI) can be reduced to the range of 0.7 to 1 mg/L in the effluent by using such a treatment.²⁹

Reduction with Sodium Metabisulfite (and Bisulfite). About 3 lb of sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) are required to reduce 1 lb of chromium (VI).

Reduction with Ferrous Sulfate. Because of the sludge volume produced, this use of ferrous sulfate is rare in larger-scale treatment facilities.

The treatment of a metal electroplating waste containing 140 mg/L of chromium (VI) has been reported.²⁹ Reduction was carried out at pH 2.5 to 2.8, employing sodium bisulfite as the reducing agent. The process was reported to reduce the chromium (VI) to concentrations of 0.7 to 1.0 mg/L. The Electric Autolite Company (Sharonville, Ohio) also attempted to use sodium bisulfite to reduce the waste from the process of chrome plating automobile bumpers.³⁰ They abandoned the use of sodium bisulfite as a reductant because of odors and corrosion hazards associated with its use, and instead, employed SO_2 .

Sulfur dioxide appears to be the most popular reducing agent used in treatment of chromium wastes. Hulse et al.³¹ have reported its use at a Boeing plant to treat chromium in metal finishing wastes. The waste was adjusted to pH 2.5 with H_2SO_4 before reduction. Schink³² also reports the use of SO_2 to treat chromic acid plating bath and chromic acid etch bath wastes. At an average waste flow of 40 gal/min, and for a 20-30 min treatment period, Schink reported that residual chromium (VI) was less than 1.0 mg/L. The chromium (VI) concentration in the raw waste was not reported.

Sulfur dioxide has also been used as a reductant at an IBM plant,²⁰ to treat a waste estimated to contain 1,300 mg/L of chromium (VI). The chromate wastes were treated with SO_2 at pH 2 for approximately 90 min with sulfuric acid added to the waste to maintain the proper pH. Chemical analyses by the state department of health revealed no chromium (VI) in the treated effluent.

An unusual source of SO_2 is employed by the Fisher Body Plant of Elyria, Ohio, to treat the chromium (VI) in its plating waste.³³ In this process, which has been in operation since 1959, sulfur dioxide is washed out of the power-house-stack gas, and used as the chemical reducing agent for converting chromium (VI) to chromium (III). On occasions when additional reduction was necessary, sodium bisulfite was employed as a supplement. No values for raw or treated waste chromium concentrations were reported, although it was claimed that the process was highly effective.³⁴

Removal of Mercury from Aqueous Solutions. Reduction/precipitation processes are being used increasingly to treat wastewater containing mercury when the flow rate is relatively small and intermittent. Because of its value, and because it is not amenable to disposal, the elemental mercury produced by reduction processes is usually recovered for recycling. Depending upon the process, a cyclone filter, or perhaps a furnace and mercury condenser may be used.

In a reduction/precipitation process that has recently been commercialized, a caustic solution of NaBH_4 is mixed with wastewater that contains mercury. The ionic mercury is reduced to metallic mercury, which precipitates out of solution. The following reaction occurs:

In theory, 1.0 lb of NaBH_4 can reduce 21 lb of mercury. In actual operation, closer to 10 lb of mercury is reduced.

If the mercury in the solution is in the form of an organic complex, the driving force of the reduction reaction may not be sufficient to break the complex. In that case, the wastewater must be chlorinated prior to the reduction step in order to break down the metal-organic bond.

This reduction process compares favorably with the sulfide precipitation treatment for mercury removal. It does not have a large volume of waste residue; however, the efficiency is slightly lower in lab-scale tests, and the NaBH_4 is more costly.³⁴ Ventron Corporation holds patents for the use of NaBH_4 for heavy-metal removal.³⁵⁻³⁷

Mercury can also be removed from aqueous solution by using base metals as reducing agents. Those metals that readily reduce or liberate mercury from solution as metallic mercury include iron, zinc, bismuth, tin, nickel, magnesium, manganese, and copper. Of these, iron and zinc are preferred because of the lower cost, the generally lower solution losses, and the higher reaction rates when they are used in this process. Iron may be used for those solutions advantageously treated at a moderate pH, for example, to avoid or minimize precipitation of other solids, such as oxides and hydroxides, which precipitate at higher pH values.

Optimum mercury removal per pound of iron consumed is obtained when the pH of the solution is adjusted to a value between 6 and 9. At pH values below 6, solution losses of iron become increasingly larger. Below a pH of 5, hydrogen evolution reduces the effective surface area of the metal, and the competition of hydrogen ions with mercury ions becomes significant.

At a pH of 7-8, the consumption of iron in the form of steel turnings may be expected to be of the order of 0.1 lb/1000 imperial gal (1200 U.S. gal) of solution treated by this method. Zinc metal may be used for those solutions that are advantageously treated at a higher pH. Zinc is best used

with solutions brought to a pH between 9 and 11. Although zinc readily liberates mercury in less alkaline or in acidic solutions, zinc solution losses become increasingly larger at lower pH values.³⁸

Removal of Lead from Aqueous Solutions. Removal of dissolved lead compounds, including organo-lead salts, in wastewater from the manufacture of tetraalkyllead compounds is now being done on a commercial scale. The reduction process, using an alkali metal hydride as the reductant, lowers the lead content in the waste stream by altering the chemical form of the lead so that it can be precipitated. The concentration of lead in the wastewater thus treated is usually in the range 2-300 ppm. The lead is mostly in the form of soluble organo-lead compounds, which will not precipitate with pH adjustment alone, together with other soluble inorganic lead compounds.

After treatment with an alkali metal hydride (NaBH_4 is preferred in this reaction), insoluble lead products are formed. They include hexaalkyldi-lead compounds (which may with time decompose to elemental lead) that are formed from the soluble alkyl-lead compounds, and elemental lead from the soluble inorganic lead components.

Low concentrations of the borohydride are preferred because one of the characteristics of the material is that it hydrolyzes with evolution of hydrogen, with an accompanying loss in its reductive properties (particularly at higher temperatures). For this process, a pH of 8-11 is preferred.³⁷

Removal of Copper from Aqueous Solutions. A process developed by Saubestre³⁹ involves the removal of essentially all of the copper from a substantially cyanide-free alkaline waste solution containing ionic copper. A reducing agent (e.g., formaldehyde) for the ionic copper is added to the solution if it is not already present and usually a complexing agent for the ionic copper is added also. The process leads to the recovery of marketable metallic copper.

The alkaline waste solution is placed in contact with a material or metal catalyst in order to reduce the ionic copper to metallic copper; this process is continued until the desired amount of copper is precipitated as metallic copper. The metallic copper precipitate is then separated from the solution by filtration or other means. Catalytic metals used in the reduction of the ionic copper to zero-valent metallic copper are palladium, platinum, gold, and silver.

Removal of Silver from Aqueous Solutions. Alkali metal hydride (e.g., NaBH_4) is being used to recover silver from photographic-waste effluents.

Dissolved silver in aqueous solution can also be removed by reductive exchange. This method involves precipitation of silver onto another metal,

usually zinc or iron, which are relatively inexpensive. The net result is a substitution of iron or zinc ion for silver in solution. This process was used at the Oneida Silverware plant prior to the installation of a cyanide chlorination-silver chloride recovery system.⁴⁰ The reductive exchange process was replaced because of the necessity to install cyanide treatment facilities.

Schrieber⁴¹ indicates that by using zinc or steel wool under proper conditions to maintain exposure of sufficient metal surface, 95% removal of silver can be accomplished with column operation. Silver ions in the solution are replaced with equivalent quantities of zinc or iron ions, however.

3.4.2.2 Potential Application to DOE Facilities

Chemical reduction is being applied commercially for recovery or detoxification of dissolved metals in aqueous effluent. At present, chemical reduction is applied primarily to the control of chromium (VI) in the plating and tanning industries and to the removal of mercury from caustic/chlorine electrolytic cell effluents. This technology should be applicable to treatment of similar streams generated in DOE facilities. In addition, it can be employed to recover lead in wastewaters from the manufacture of tetraalkyllead compounds and to remove ionic copper from alkaline waste solutions and silver from photographic waste effluents.

Chemical reduction, in general, is suitable for treatment of aqueous streams containing materials that can be reduced. The following statements can be made about suitable waste streams:⁸

- Physical form of waste: Gases and aqueous solutions are acceptable. Chemical reduction would have limited applicability to slurries and sludges unless it were possible to dilute them for treatment. It might be that some waste streams could be placed in contact for the time necessary, with a sufficient excess of the reducing agent and sufficient mixing to effect treatment. Tars also would find limited applicability.
- Chemical nature of contaminants: Heavy metals such as chromium, mercury, lead, and antimony are removable from waste streams either as the metal hydroxide or the element.
- Concentration range: Most of the applications to date have been for dilute systems, generally for not more than a few thousand ppm.

Chemical reduction is likely to be cost effective for the less-concentrated hazardous wastes. Energy requirements for the technology, in

general, are not significant. The equipment used in the process is simple to obtain and use. There is limited use of instrumentation, and minimal heating and cooling requirements.

Chemical reductions, however, are not without disadvantages. One disadvantage of chemical reduction for waste treatment is that it may introduce new ions into the effluent. If the level of these new contaminants is high enough to exceed effluent regulations, additional treatment operations, such as precipitation, filtration, or sedimentation, will be required.

Another disadvantage of chemical reduction is that chemical reducing agents are, in general, relatively nonselective. All easily reducible materials present in the waste streams will be reduced simultaneously. As a result, the recovered material may be a mixture of many compounds, and further processing may be needed if a high-purity material is needed for reuse.

3.5 ION EXCHANGE

3.5.1 Description of Technology

3.5.1.1 Basic Concept

Ion exchange involves the removal of ionic species, principally inorganic, from aqueous or partially aqueous phases. In simplest terms, ion exchange may be thought of as the reversible interchange of ions between an insoluble, solid salt (the "ion exchanger") and a solution of electrolyte in contact with that solid. As an example, a cation exchange material (designated R^-) having a cation (N^+) associated with it can react with a solution of an electrolyte (M^+X^-) as shown below:

The direction (forward or reverse) and extent of the reaction are governed by the relative insolubilities of the insoluble salt(s) that can be formed (i.e., MX , NX , RM , RN) and by the equilibrium constant for the reaction,

$$K_{eq} = \frac{[RM] [N^+]}{[RN] [M^+]}$$

where $[RM]$ and $[RN]$ represent the concentrations of the cations in the ion exchange material, and $[N^+]$ and $[M^+]$ represent the concentrations of the cations in the solution. K_{eq} is constant for any given set of R^- , M^+ , and N^+

for solution concentrations up to approximately 0.1 mol/L, but may vary somewhat above that point. As with similar equilibrium reactions, changes in either $[M^+]$ or $[N^+]$ will result in a change in the equilibrium position, or extent, of reaction.

In the customary use, the ion exchanger is placed in contact with the solution containing the ion to be removed until the active sites in the exchanger are partially or completely used up ("exhausted") by that ion. The exchanger is then placed in contact with a sufficiently concentrated solution of the ion originally associated with it to convert ("regenerate") it back to its original form. Specific exchange reactions include

which occurs in the exhaustion step, and

which takes place in the regeneration step. As $[N^+]$ is higher in the regeneration step than in the service step, the solution volume used for regeneration can be smaller, and consequently $[M^+]$ will be higher in the regeneration solution.

An alternative route for regenerating the ion exchanger involves a third ion (frequently a hydrogen ion in cation exchange) to give the corresponding form of the exchanger, which can then be converted to the desired salt as shown below:

Such a sequence might be desirable in a case where H^+ was a much more effective regenerant than N^+ , but where the release of H^+ into the solution being purified would be undesirable.

Thus, ion exchange provides a mechanism for removing an undesirable (or, in some cases, desirable) ion from a stream, and for transferring that ion, at a higher concentration than before, to another aqueous stream.

3.5.1.2 Process Description

In carrying out ion-exchange reactions in a column or bed operation (as opposed to a stirred-batch operation, which is occasionally used in chemical processing), four operations are carried out in a complete cycle:

- Service (exhaustion)

- Backwash
- Regeneration
- Rinse

The service and regeneration steps were described by the third and fourth equations in the preceding section. The backwash step is one in which the bed is washed (generally with water) in the reverse direction to the service cycle in order to expand and resettle the resin bed. This step eliminates channeling, which might have occurred during service, and removes fines or other material that may be clogging the bed. The rinse step removes the excess regeneration solution prior to the next service step.

In the usual modes of operation, the ion-exchange process yields a large-volume, purified stream depleted in the species being removed, and a small-volume solution of spent regenerant containing a high concentration of the species removed. The purified streams from ion exchange in general are recycled, used in another process, or discharged without further treatment.

The spent regenerant is usually treated to remove or detoxify the ions it contains; because that species is at a much higher concentration than in the original stream, such treatment is frequently easier and/or more economical than it would have been prior to the ion-exchange treatment. In some cases, the spent regenerant containing the ions it has removed and concentrated can be recycled to a process without further treatment. This is done with chromium and nickel in some electroplating operations and with chromium in some recently developed processes for treating cooling-tower blowdown. Some of these processes will be described in Sec. 3.5.2.

Regeneration. There are three principal operating modes for regeneration in use today: cocurrent fixed-bed, countercurrent fixed-bed, and continuous countercurrent.⁸ A flow diagram for the continuous countercurrent mode is shown in Fig. 3.5 and a brief summary comparison is given in Table 3.3.

Most ion-exchange installations in use today are of the fixed-bed type, with countercurrent operation favored, especially for removal (polishing) of traces of hazardous species from the industrial wastewater prior to reuse or discharge.

In order to make most efficient use of regenerant, many fixed-bed installations use a technique termed "staged" (or "proportional") regeneration. The first part of the regeneration solution to exit from the ion exchange bed is the most enriched in the component being removed; the concentration of that component decreases in succeeding portions of the exiting regeneration solution. In staged regeneration, the solution is divided (generally in separate tanks) into two or more portions. The first

Fig. 3.5 Continuous Countercurrent Mode for Ion Exchange
(Source: Ref. 8)

portion through the bed is discarded or sent on for subsequent treatment, while the second and succeeding portions (less rich in the species being removed) are retained. On the next regeneration cycle, the second portion from the preceding cycle is passed through the bed first and then discarded, followed by the succeeding portions, the last of which is a portion of fresh regenerant. In this way, regenerant utilization can be maximized.

Continuous countercurrent-ion-exchange systems in a variety of configurations have been offered on the commercial market over the past few years. Included in these are the Higgins-type systems,⁴²⁻⁴⁴ the Permutit process,⁴⁵ and a fluidized moving-bed system.⁴⁶ Some of these systems have been discontinued and even replaced by fixed-bed units in some cases. Problems have included inefficiency stemming from the need for close flow control for upflow operation, high resin attrition, and the mechanical problems that might be expected from such complex systems.⁸

Another mode of ion exchange uses the so-called "powder resins." The ion-exchange resins are prepared as fine powders (generally less than 400 mesh) and are applied in relatively thin layers (because of the high impedance to flow) on a filter support (plate, tubular filter, etc.). The fine particles are extremely efficient for ion exchange (large surface area and little intraparticle diffusion), but are generally not regenerated because of the handling, flow, and pressure problems. Powder resins have found extensive use in disposable polishing units in the nuclear-power industry,⁴⁷ and may

Table 3.3 Comparison of Ion Exchange Operating Modes

Operation Parameters	Cocurrent Fixed Bed	Countercurrent Fixed Bed	Countercurrent Continuous
Capacity for high-feed flow and concentration	Least	Middle	Highest
Effluent Quality	Fluctuates with bed exhaustion	High with minor fluctuations	High
Regenerant and rinse requirements	Highest	Somewhat less than cocurrent	Least; yields most concentrated regenerant waste
Equipment complexity	Simplest; can use manual operation	More complex; automatic controls for regeneration	Completely automated
Equipment for continuous operation	Multiple beds; single regeneration equipment	Multiple beds; single regeneration equipment	Provides continuous service
Relative Costs (per unit volume)			
Investment	Least	Middle	Highest
Operating	Highest chemicals and labor; highest resin inventory	Less chemicals, water, and labor than cocurrent	Least chemicals and labor; lowest resin inventory

Source: Ref. 8.

have analogous application in polishing effluents resulting from the treatment of extremely hazardous wastes.

Equipment. Fixed-bed ion-exchange operations are straightforward systems, requiring a cylindrical ion-exchange bed, tanks for solution storage, and pumps. The choice of materials is governed by the chemical environment. Continuous ion-exchange systems are much more complex, requiring equipment for handling solids and more intricate control systems. Chemical Separations Corp. has been successful in the design and fabrication of continuous ion-exchange systems.⁸

Ion Exchange Materials

The classes of materials that are in use or that have been proposed for use as ion-exchange materials include inorganic crystals (both natural and synthetic) and synthetic organic resins, modified natural organic materials, and water insoluble liquids. Synthetic organic resins are by far the most important in general ion-exchange use.

Three important parameters for ion-exchange materials, by which the exchangers can be selected and compared and from which approximate exchanger and chemical requirements can be determined, are functionality, exchange capacity, and selectivity. Functionality refers to the kinds of ions (cations, anions, selected groups) that are exchanged. Exchange capacity is a measure (generally in meq/g or meq/ml of resin) of the total uptake of a specified ion. Selectivity refers to the preference of the material for one kind of exchangeable ion over another, expressed as a ratio of equilibrium constants.

Synthetic Ion-Exchange Resins. A variety of cation and anion exchangers have been prepared by adding appropriate functional groups (exchange sites) onto solid particles (usually beads) of polymeric materials. In some resins, the functional groups are introduced prior to or during the polymerization step. Most of the resins now offered commercially are either styrene-divinylbenzene copolymers or acrylate-methacrylate copolymers.

Earlier ion-exchange resins were prepared from phenol-formaldehyde ("Bakelite") and related polymers; however, these materials were inferior to the present ones in stability, variety, and capacity; and only a few specialized ones are now available.

In the past, styrene-divinylbenzene materials suffered from rather large volume changes ("swelling") when they were cycled between different ionic forms. Newer methods of preparation and materials have now resulted in a variety of "macroreticular" resins, which combine a rigid polymer framework with a high exchange capacity and suffer only minor swelling.

Some of the more common reactive groups offered are listed below:⁸

<u>Reactive Group</u>	<u>Exchangeable Ions</u>
strong acid (sulfonic)	cations in general
weak acid (carboxylic)	cations in general
weak acid (phenolic)	cesium and polyvalent cations
strong base (quaternary amine)	all anions, especially anions of weak acids (cyanide, carbonate, silicate, etc.)
weak base (tertiary and secondary amine)	anions of strong acids (sulfate, chloride, etc.)
chelating (varied, may be iminodiacetate or oxime groups)	cations, especially transition and heavy elements

Differences in the particular starting materials and preparation route frequently give rise to differences in handling properties, stability, and reaction kinetics between resins that have the same polymer backbone, functional groups, and exchange capacity. Hence, it is important to test a variety of resins for a particular application. A reasonably comprehensive listing of older types of resins is given in Perry's Handbook.⁴⁸ For more up-to-date information, the various resin manufacturers should be contacted directly.

The synthetic resins are generally stable to strong acids and bases, but suffer irreversible damage from oxidizing agents, high temperature, and radiation.

Inorganic Ion Exchangers. Both naturally occurring and synthetic zeolites (aluminum silicate minerals) have been used as cation exchangers. The majority of these materials are stable only over a narrow pH range (neutral) and are somewhat fragile. A major use of these materials is in water softening. Newer synthetic materials such as zirconium phosphates have improved physical and chemical properties, e.g., acid resistance. These materials are never used in continuous operation because their nonspherical geometry, density, and fragility preclude effective solids-handling operations. The inorganic exchangers are less affected by oxidants, heat, and radiation than are the synthetic resins, and, consequently, have found use in the processing and disposal of radioactive wastes.

Modified Natural Organic Materials. A variety of natural materials have been proposed and demonstrated for ion exchange, including sulfonated

coals, sulfonated nut shells, and modified cottons. For example, peanut hulls have been used to remove traces of heavy metals from solution. Although none of these materials has been used recently in a large-scale process, they may find some use in a single-pass, disposable system.

Ion Exchange Liquids. The so-called liquid ion-exchange process (often termed "solvent extraction") in which the ion exchanger is a water-insoluble liquid, resembles, in operation, a liquid/liquid extraction process rather than conventional ion exchange. Recently, there have been reports of impregnating beds of synthetic resin with liquid ion exchangers to produce an exchange material that can be handled via conventional ion-exchange operations and have some important advantages in selectivity.⁴⁹

3.5.1.2 Special Characteristics

Energy Requirements. The energy requirements for ion exchange are quite low, consisting primarily of electricity for pumping. The Arthur D. Little, Inc., study⁸ and a previous study of the deionization of water puts power costs at 2-5% of the total operating costs.

Environmental Effects. Ion exchange is a solution-phase (aqueous) process. The dilute, purified product stream can be suitable for discharge or reuse. The concentrated regeneration stream requires further treatment for recovery and/or safe disposal of its components.

Emissions to air from ion exchange units will be essentially zero. Effluents to water will be significant only if the regenerant solution is discharged inadvertently to ground or surface water. In normal operation, effluent quality will be within environmental discharge limits. Emissions to land will be insignificant, except for spills from process accidents, or improper disposal of solid exchangers loaded with hazardous substances that would be leachable under the landfill conditions. The above points address only the ion-exchange process itself, and not disposal of spent or degraded ion-exchange materials. These materials should be disposed of (after proper cleaning to remove the hazardous substances) with other solid industrial wastes of similar composition.

Process Economics. Capital costs are probably high. Materials must withstand service/regeneration requirements, and equipment generally must be rubber-lined or made of stainless steel. Systems vary in complexity. Instrumentation requirements are the usual types for wet chemical operations.

Costs for chemicals may be significant because ion exchange is a reagent-intensive process. The chemical stoichiometry requires that at least one chemical equivalent weight of regenerant be added for each one removed in the exchange. In practice, inefficiencies in operation often result in 1.5-2.0 equivalents being required per equivalent removed. In contrast, energy requirements are relatively low.

Resin replacement (generally 20-30%/yr) is also a significant cost element; resin costs run \$30-180/ft³ with commonly used ones costing \$40-\$100/ft³.

Labor and maintenance costs are the usual costs for chemical operations having typical equipment with pumps, valves, etc.

Waste-Treatment Costs. Costs for treatment and recovery of wastes using ion-exchange technologies appear to be reasonable; around \$5 per 1000 gal for separation of complex mixed wastes, and \$1 per 1000 gal for single-bed polishing.⁸ Credit for cleaned water and removed hazardous materials suitable for reuse will help the process economics.

3.5.2 Applications for Waste Treatment

3.5.2.1 Principal Current Applications

The earliest applications of ion exchange were for "water softening" -- the substitution of sodium for calcium and magnesium in water, and the reverse substitution in sugar solutions to promote better crystallization. These applications were initiated in the late 1800s and early 1900s, using natural and synthetic zeolites (aluminosilicate minerals). Synthetic ion-exchange resins were discovered in the late 1930s and were developed rapidly, particularly after World War II. Applications for the process were found rapidly in diverse areas. The deionization application, especially for high-quality process water (for nuclear power and conventional steam generators) is probably still the most widespread application.

Apart from deionization applications, ion exchange is used extensively in electroplating and metal finishing for removal of ionic species from process water and for further treatment of the removed ions prior to disposal or recycling. Other applications include recovery of valuable metals such as copper, molybdenum, cobalt and nickel from dilute leach liquor from tailing or dump piles; removal of radioactive species from solutions of various kinds; removal of organics from sour water from petroleum refineries; and recovery of chromium from cooling-tower blowdown. Some of these applications are described below.

Removal of Metals from Electroplating Wastewaters. Chromium (VI) is removed from plating rinses by contact with a strong base ion exchanger (hydroxide form) after neutralization of the rinse stream to pH 8-9. The chromium (as chromate) is removed, and the resin is regenerated with a sodium hydroxide solution. In most installations, the rinse water is also treated with a cation exchanger (acid form) to yield deionized water for recycling to the rinse tanks. The spent regeneration solution, which contains sodium chromate and sodium hydroxide, is neutralized with sulfuric acid and then treated with a cation exchanger to give chromic acid for recycling to the plating bath.^{8,50}

The countercurrent fixed-bed mode of operation is often used because the extra "polishing" achieved over cocurrent flow is needed to assure meeting the low limits for recycling or discharge of chromium.⁸

Treatment of metal-cyanide complexes is another application. Although these complexes are treated directly to destroy the cyanide, cyanide destruction is easier and more economical if most of the complexes have first been destroyed and the metals removed. To destroy the complexes, the solutions are treated sequentially, first with a cation exchanger to "break" the complexes and then with an anion exchanger to take up the liberated cyanide as shown below.

The potential for release of toxic HCN is minimized by directing the cation-exchange effluent immediately to the anion exchanger.

In order to isolate the cyanide completely for most economical destruction, and to avoid premature exhaustion of the anion resin by other anions such as chloride and sulfate, commercial systems utilize a second anion exchanger of the weak-base type interposed between the other two, which removes the chloride and sulfate but allows the cyanide to pass through.^{8,51}

Removal of Metals from Metal Finishing Streams. In the general metals finishing business, it is quite common to have a single-solution waste that can only be described as "mixed waste." Obviously, a variety of waste treatment schemes would be needed in order to be able to treat mixtures with

constituents including suspended metal particulates, oil and grease, chromium (III and VI), iron phosphate, cyanide, zinc, etc. A common thread among most treatment schemes is the frequent use of some sort of ion exchange step for final treatment before reuse or discharge.^{8,52} The largest part of materials in mixed wastes is removed or destroyed by precipitation, filtration, or membrane separation, with ion exchange used as the "polishing" step.

In addition to treating dilute aqueous streams, ion exchange is used to remove low concentrations of undesirable impurities from relatively highly concentrated aqueous streams. The object of treatment in most cases is to recycle or reclaim the active materials while ridding the bath of unwanted impurities. Frequently, ion exchange is the sole separation step, with other posttreatment steps being carried out on the spent regenerant solution.

Minor concentrations of cations such as iron, aluminum, and chromium (III) are removed from chromic acid plating-bath liquors via cation exchange, after dilution of the chromic acid content of the liquor from 250 g/L down to 100 g/L.^{53,54} The dilution is necessary in order to obtain efficient exchange and to minimize oxidative damage to the sulfonated styrene-divinyl benzene resins used.

Another large-scale application is for the removal of aluminum from the strong phosphoric acid/nitric acid solution that is used to clean ("bright dipping") aluminum metal.^{8,50,55} The phosphoric acid that has become contaminated with aluminum phosphate from dissolution of metal during the treatment is diluted with rinse-tank water to give a 40% phosphoric acid solution, which is then subjected to cation exchange to remove the aluminum. The purified phosphoric/nitric acid mixture is then evaporated to give concentrated acid for recycling to the process. The resin is regenerated with sulfuric acid to give aluminum sulfate. Both fixed-bed and continuous countercurrent installations are in operation.

In both of the above cases, neither of the main substances is a strong electrolyte -- i.e., both are only partly ionized; thus ion exchange is effective, since the minor components being removed are ionized.

Removal and Isolation of Radioactive Wastes. A great deal of work has been reported on removal of traces of radioactive species from solutions of various kinds. Of particular interest for waste treatment is a summary of the performance of ion-exchange systems in operational nuclear power plants, which indicates that the severe conditions of radiation and heat result in attrition rates higher than those expected in nonnuclear service. Even under these conditions, operating capacity varies from 50 to 75% of the theoretical.⁴⁹

Experience over long service lives in nuclear operations may provide some useful information on the long-term behavior of ion-exchange materials. Equipment reliability is normally extremely good in nuclear service, having been deliberately designed to deal with the extreme necessity to avoid trace-ion leakage and equipment downtime.

Treatment of Streams Containing Organic Materials. Ion-exchange processes have been employed at one time or another to remove or separate organic materials and inorganic salts from mixtures of industrial origin.

The DESAL (weak-base resin in bicarbonate form, followed by weak-acid resin in acid form) was used to treat "sour water" condensate from a petroleum refinery and achieved the results shown below.⁵⁶

Solute	Concentration (mg/L)	
	Before	After
Total dissolved solids	1310	210
H ₂ S	1150	<3
NH ₃	390	5
Phenol	365	<20

Recovery of Chromium from Cooling Tower Blowdown. Both continuous countercurrent and fixed-bed systems have been proposed for recovery of chromium from cooling-tower blowdown waters.

The Chem Seps continuous unit⁵⁷ uses a mixed-bed resin (cations and anions of unstated composition) to remove both chromium (VI) and chromium (III), as well as zinc. Chromates are eluted with sodium hydroxide and can be returned to the tower feed; chromium (III) and zinc are eluted with acid and removed.

The Rhom and Haas fixed-bed unit⁸ uses a weak-base resin operating in the acid form to load the chromate, sodium hydroxide to elute the bed for removal of the acid chromate, and sulfuric acid to regenerate the bed before the next cycle. If removal of chromium (III) and zinc are needed, then additional beds with a sodium-form weak-acid resin can be used.

Treatment of Metal Pickling Wastes. A recently-developed system for the removal of ferrous salts [iron (II)] from steel pickle liquors containing from 1% to 10% of the salts in 5% to 20% sulfuric or hydrochloric acid employs cation exchange (acid form) in a continuous countercurrent mode.⁵⁸ The cleaned acid, returned to full strength by the exchange, is recycled to the process. The resin is regenerated with warm 22% nitric acid, which results in complete oxidation of the iron to the ferric [iron (III)] state during removal. Hydrolysis of the resulting ferric nitrate solution yields ferric oxide (Fe₂O₃) and nitric acid for recycling for regeneration.

The pickling liquor application indicates that ion exchange can be used in selected high-concentration situations and may, in some cases, be an alternative to liquid ion-exchange separation processes.⁸

Removal of Cyanides from Aqueous Waste Streams. An approach to using ion exchange for the removal of cyanide from aqueous waste streams has been reported.⁵⁹ This approach involves conversion of cyanide to ferrocyanide and selective removal of ferrocyanide in the presence of other salts and organics using a weak-base resin in an acid form.

The waste stream is brought to a pH between 9 and 11, and excess ferrous [iron (II)] sulfate is added to produce ferrocyanide. Any excess ferrous ion precipitates as the hydroxide at this pH, and is removed by suitable means such as settling. The solution is acidified to a pH between 4 and 7 then is placed in contact with the ion exchanger, a macroreticular acrylic weak-base resin in the acid salt form. The resin is very selective for weak acids such as ferrocyanide and does not remove anions such as sulfate and chloride, metal cations, and most organics. Treatment of the loaded resin with dilute sodium hydroxide yields a concentrated solution of the ferrocyanide, which can be further treated for destruction or detoxification. The resin is treated with dilute acid to convert it to the acid form in preparation for the next cycle.

The cyanide complexes of copper, zinc, and nickel, which may be present in waste streams, are less stable than ferrocyanide and are expected to respond to the treatment process.

When tested on a waste stream containing 2% inorganic salts with a chemical oxygen demand of approximately 400 mg/L, the process reduced the total cyanide concentration from 1.0 mg/L to less than 0.1 mg/L.

The process is relatively straightforward and could be of significant value in removing and concentrating cyanides from streams that contain high concentrations of substances (particularly organic materials) that would interact with and result in excessive consumption of the reagents most commonly used for the destruction of cyanide, such as hypochlorite.

Removal of Mercury from Aqueous Waste Streams. Akzo Chemie of Holland has available a thiol (SH) resin (Imac TMR) that removes mercury from solution down to a level of 5 ppb.⁶⁰ If metallic mercury is present, it is first oxidized with chlorine; the solution is then filtered, dechlorinated with activated carbon, and passed through the exchanger. The total operating cost is \$0.80/1000 gal for a flow rate of 44 gal/min with an initial mercury concentration of 6 mg/L; if credit is given for the recovered mercury, the net cost for the process is \$0.60/1000 gal.

A resin (Srafion NMRR) produced by Ayalon Water Conditioning Co. of Israel removes both the mercuric ion and methyl mercury.⁶⁰ The resin has a capacity of 34 lb mercury/ft³ of resin. The removal capacity is strongly dependent on the pH of the solution. Inorganic mercury is removed best at pH 5, while at a higher pH (from 6-9) removal of methyl mercury is favored. In addition to removing mercury, this resin also is selective for noble metals. For example, the resin has a capacity for platinum of 30 lb/ft³ of resin. Again, the capacity depends on pH of the solution.

Nisso Soda Co. of Japan produces a mercury-selective adsorbent (ALM-125) for elimination of both ionic and organic mercury from wastewater and process solutions down to a level of 0.1 ppb.⁶⁰ When the mercury is dissolved in water, the adsorbent has a capacity of 680 lb Hg/1000 lb adsorbent, and when the mercury is dissolved in 10% sulfuric acid, the capacity is 340 lb mercury/1000 lb adsorbent. Regeneration of the resin is accomplished with sodium sulfide, after which the mercury can be obtained in the metal form by reduction with borohydride. The resin is then treated with dilute HCl and rinsed for reuse. Another method of recovering the mercury is to roast the mercury-containing resin and collect the condensed mercury vapor upon cooling. Of course, this method destroys the resin. This solid adsorbent is also made in paste form (ALM-126) for use in batch processes at controlled pHs. The mercury-containing sludge formed in the batch reactor is removed from the liquor by filtration.

3.5.2.2 Potential Applications for DOE Facilities

Ion exchange will remove (or recover) any ionic species from aqueous or partly aqueous solutions. Solutions must be free of oxidants and suspended matter. This ion removal has already been demonstrated on many aqueous streams such as those discussed in the previous section. For DOE facilities, ion exchange can be used to remove and/or concentrate the following classes of chemicals:

- Inorganic: All metallic elements, including mercury, chromium, nickel, copper, silver, lead, aluminum, iron, and zinc, when present as soluble species (either cationic or anionic) in streams such as electroplating wastes, metal finishing wastes, photographic solutions, and cooling tower blowdown; and anions such as halides, sulfate, nitrate, cyanide, etc.
- Organic (water soluble and, in general, ionic): Acids such as carboxylic, sulfonic, and some phenolic, at pHs sufficiently alkaline to cause ionization; amines, when the solution is sufficiently acidic to form the corresponding acid salt; and anionic and cationic species such as quaternary amines and alkylsulfates, which are frequently used as detergents.

In addition, ion exchange can remove radioactive species from solutions of various kinds.

Generally, if a species known to be exchangeable in aqueous solution can be scrubbed, dissolved, or otherwise extracted into water solution from another form or phase (gaseous, liquid, or solid), then ion exchange can be used to concentrate that species.

The upper concentration limit of the exchangeable ions, for efficient operation, is generally 2500 mg/L, expressed as calcium carbonate (or 0.05 equivalents/L). This upper limit is due primarily to the time requirements of the operation cycle. A high concentration of exchangeable ions results in rapid exhaustion of resin during the service cycle, with the result that regeneration requirements, both for equipment and in terms of the percentage of resin inventory undergoing regeneration at any time, become inordinately high.

Ion exchange is one of the options available for recovery of hazardous materials. Applicability of this technology to a specific site, naturally, should be evaluated on the basis of factors such as availability of ion-exchange materials for specific wastes, economics of the technology, the quantity of and demand for recycled material, and relative location of the site of waste generation, processing plants, and markets.

3.6 NEUTRALIZATION

This section provides information on the fundamentals and practical experience of neutralization -- a method that is applicable to detoxify hazardous wastes prior to ultimate disposal. The primary reference for the material in this section is Ref. 8.

3.6.1 Technology Description

Neutralization is an accepted technically and economically feasible technique by which certain hazardous wastes can be treated. It is in widespread use in various industries. The basic principle behind the process is simple -- an acid is combined with an alkali to adjust the pH of the product to an acceptable level. In the case of effluent wastes, either excess acidity or excess alkalinity is corrected, bringing the pH to a value between 6.0 and 9.0. There are numerous methods by which the admixture can be accomplished, and a multitude of waste streams with diverse chemical and physical characteristics that are treatable by this technique.

3.6.1.1 Unit Operations

As mentioned earlier, the basic principle behind neutralization is simple: neutralization occurs when acid is mixed with an alkali. Neutralization may be carried out in tanks, ponds, absorber columns, or a variety of other types of reaction equipment either in batch or continuous-flow operations, depending in part on the volume and rate of flow of the solution to be neutralized. Although many different chemicals can be neutralized, certain principles are common to most systems and are independent of specific designs.

The addition of appropriate quantities of neutralizing agent is monitored and adjusted by pH measurement and control. In batch treatment, an operator can take samples, measure the pH, and add the required dose of acid or alkali. In a continuous-flow system, automatic pH monitors check the acidity or alkalinity of the waste stream and control the feeding of neutralizing agent. The number of neutralization units and the location of pH sensors are determined by the stability of the waste stream pH. Where widely varying pH levels are experienced, several reaction units, plus additional monitoring equipment, may be required. A stream with large fluctuations in pH might also be preceded by an equalization basin, which would yield for treatment a more homogeneous effluent with a narrower pH range. A schematic diagram of continuous-flow lime neutralization of sulfuric acid is shown in Fig. 3.6.

The neutralization process, like most chemical reactions, is subject to the influence of temperature. Generally, increasing the temperature of the reactants increases the rate of reaction. In neutralization, the interaction of acid and alkali frequently evolves heat, with an accompanying rise in temperature. An average value for the heat released during the neutralization of dilute solutions of strong acids and bases is 13,360 cal/g-mol of water formed. Through control of the rate of addition of the neutralizing reagent, the heat produced may be dissipated and the temperature increase minimized. For each reaction, the final temperature depends on the initial reactant temperatures, the chemical species participating in the reaction (and their heats of solution and reaction), the concentrations of the reactants, and the relative quantities of the reactants. In general, concentrated solutions can produce large temperature increases as the relative quantities of the reactants approach stoichiometric proportions. These temperature increases can result in boiling and splashing of the solution and accelerated chemical attack on materials. In most cases, proper planning of the neutralization scheme with respect to concentration of neutralizing agent, rate of addition, reaction time, and equipment design can alleviate the heating problem.

Fig. 3.6 Lime Neutralization of Sulfuric Acid Waste (Source: Ref. 8)

3.6.1.2 Chemical Reagents

Acids. The selection of a neutralizing agent is dictated by a number of factors such as economics, availability, and process compatibility. Commonly, the choice of an acid for neutralizing alkaline wastes is between sulfuric acid and hydrochloric acid.⁵⁴ Because of its lower cost, sulfuric acid is usually preferred, but it has the disadvantage of forming relatively insoluble salts, e.g., calcium sulfate, with the attendant problems of scaling and solids handling. The products of neutralization with hydrochloric acid are usually soluble (as are the salts of nitric acid). However, legal limits on the amounts or concentrations of different anions that may be discharged in final waste effluents may sometimes restrict the choice of neutralizing agents.

Bases. The alkali used for neutralization of an acid generally contains sodium, calcium, or magnesium. In the selection of an alkali, an

important element is the "basicity factor," which is the number of grams of calcium oxide that is equivalent in neutralization capacity to 1 g of the particular alkali under consideration.⁶¹ Solid sodium hydroxide has a basicity factor of 0.687; thus, it is somewhat less effective (on a weight basis) than calcium oxide for neutralization. However, caustic soda (solid sodium hydroxide) has the advantage of being very soluble, thus allowing the use of concentrated solutions. In addition, the resulting salts of neutralization are also highly soluble, precluding any solids problems.

The disadvantage of caustic soda is the relatively high raw-material cost. The lime/limestone reagents, such as high-calcium hydrate, Ca(OH)_2 ; high-calcium quicklime, CaO ; and high-calcium limestone, CaCO_3 , have basicity factors of 0.710, 0.941, and 0.489, respectively. They are less expensive than sodium hydroxide, but because of their low solubility neutralization systems using these agents often require more capital investment. These solids are usually fed as slurries ($\approx 15\%$ solids). In the presence of sulfuric acid, insoluble calcium sulfate is formed, thus producing problems with sludge and scale disposal. It should be noted that limestone is the least effective neutralizing agent (on a weight basis) described thus far. Sodium carbonate (soda ash) also has a moderate basicity factor (0.507), but it is much more soluble -- as are the products.

The use of magnesium in the oxide or carbonate form as a reagent can be beneficial in many instances. In particular, the neutralization of sulfuric acid by a magnesium-based alkali produces a soluble magnesium sulfate (as opposed to the insoluble calcium salt). Magnesium oxide is more effective as a neutralizing agent than calcium oxide (on a weight basis), as is dolomitic quicklime $\text{CaO} \cdot \text{MgO}$ (basicity factor of 1.110). Also, dolomitic limestone, $\text{CaCO}_3 \cdot \text{MgCO}_3$, is an improvement (basicity factor of 0.564) over calcium limestone.

In appropriate situations, it may be feasible to use a plant's acid or alkaline waste stream as a neutralizing agent for other effluents. Economically, reuse of such waste materials as acid or alkali reagents is usually superior to other alternatives for their disposal. In industries producing both acidic and basic wastes, as in plating installations, pH adjustment is performed by proper mixing of streams. Carbon dioxide from flue gas is also used in pH treatment simply by bubbling the gas through an alkaline waste stream. Acetylene sludge (an impure lime formed in the manufacture of acetylene) is employed as an inexpensive alkali in treating acid wastes, e.g., pickling liquor from a steel mill.⁶²

3.6.1.3 Output Streams

The products of neutralization can be liquid, solid, gaseous, or a combination. The physical form of the product is not related to the form of the reactants, but to its own chemical composition and the composition of its environment. The chemical species present in the neutralized stream may

include the original components of the waste stream and those of the neutralizing agent. The concentrations of the individual species will depend on the solubility of the products formed during reaction. For example, the neutralization of hydrochloric acid with lime yields dissolved calcium chloride as a product remaining in the stream; however, neutralizing sulfuric acid with lime produces solid calcium sulfate as a slurry or sludge that contains most of the calcium and sulfate originally in solution. In the case where a solid product is present, further treatment to separate the material will be necessary. Gaseous products can be toxic, as in the case of hydrogen sulfide gas formed during the acid neutralization of a basic stream containing sulfide salts. Provisions must be made for the containment and disposal of hazardous vapors if their formation cannot be avoided.

3.6.1.4 Special Characteristics

Energy Requirements. The energy required to operate a neutralization process depends on the particular chemicals involved and the size of the stream to be treated. In a small-scale operation, the energy requirement would be primarily for electricity to run mixers and pumps. Such would be the case in an electroplating shop, treating 10,000-100,000 gal/day of wastewater. An operation in this range might consume up to 100,000 kWh per year in neutralizing its waste streams. However, in other industries such as steel, pickling waste streams can be on the order of millions of gallons per day. Larger mixers and pumps, as well as additional pieces of equipment, such as feeders for lime, agitators for clarifiers, etc., are required. In all, such a system could consume well over a million kWh per year. Differences of one or two orders of magnitude would not be unexpected between various pH adjustment schemes. Thus, there is no simple means to predict the energy requirements of a neutralization process until the size of the waste stream and the design of the system are determined.

Environmental Impacts. After neutralization, a waste stream will usually show an increase in the total amount of dissolved solids due to addition of the chemical agent. There may be, however, an accompanying reduction in the concentration of heavy metals if the treatment proceeds to alkaline pHs. Conversely, in neutralizations involving the addition of acid to alkali, there is the possibility of solids dissolution. This may, on occasion, be disadvantageous, particularly if the suspended matter is slated for removal by filtration. The anions resulting from neutralization of sulfuric and hydrochloric acids are sulfate and chloride, respectively. These ions are not considered hazardous, but there are recommended limits for their discharge, based primarily on problems in drinking water. The common cations present after neutralization involving caustic soda and lime (or limestone) are sodium and calcium (possible magnesium), respectively. These ions are not toxic and there are no recommended limits; however, calcium and magnesium are

responsible for water hardness and produce a scaling problem. The carbonate produced during limestone neutralization is also harmless both in solution and as carbon dioxide gas.

With regard to atmospheric emissions, one must be cautious not to indiscriminately neutralize wastewater streams. Acidification of streams containing certain salts, such as sulfide, will produce toxic gases. If there is no satisfactory alternative, the gas must be removed through scrubbing or some other treatment. In cases where solid products are formed (as in the precipitation of calcium sulfate or heavy-metal hydroxides), clarifier/thickeners and filters must be provided. If the precipitate is of sufficient purity, it could be a salable product; otherwise, a disposal scheme must be devised.

Costs. The capital investment for neutralization depends on the specific treatment process selected and the size of the stream to be treated. In addition, construction materials and the need for sludge-handling equipment are factors that can drastically alter an economic analysis. It would be inappropriate to draw conclusions concerning investment capital for neutralization without some knowledge of the system to be used.

With regard to operating costs, similar specific considerations, such as sludge disposal costs, may be critical. For comparison purposes, prices for disposal of acid or alkali waste quoted in an EPA report⁶³ on waste management facilities were between \$60 and \$250/1000 gal.

In the design of a system, the selection of the neutralizing reagent is a decision that must be made not only on chemical, but also on economic, grounds. As an indicator of relative costs for alkaline chemicals, Table 3.4 presents a comparison. Note that basicity is expressed in terms of grams of CaO per gram of material. One can readily see that caustic soda is the most

Table 3.4 Costs of Alkaline Reagents

	\$/ton	Basicity Factor	\$/ton of Basicity	Relative Cost
Caustic soda (solid)	290	0.687	422.13	15.89
Quicklime	25	0.941	26.57	1.00
Limestone	19	0.489	38.85	1.46

Source: Ref. 8.

expensive alternative. However, because of its reactivity, solubility, and the lack of insoluble reaction products, it is often preferred. By an intelligent choice of neutralizing agent, savings in capital and operating costs can often be realized.

3.6.2 Applications for Waste Treatment

Neutralization is a treatment process of demonstrated technical and economic feasibility, which is in full-scale use in a wide spectrum of industries. Most industries can produce a wide range of pH in their wastewater, depending on the specific products produced and manufacturing processes used. The chemical industry alone accounts for the creation of such diverse wastewater products as those from the manufacture of TNT (pH = 2.6) and reclaimed rubber (pH = 11.5). Sample applications of neutralization of acidic and alkaline wastes are given below.

Petrochemical Waste Streams.⁶⁴ Neutralization is applied to (1) washwaters, acid or alkaline, (2) spent caustics, (3) acid sludges from alkylation, sulfonation, sulfation, and acid treatments, and (4) spent acid catalysts. Sulfuric acid and carbon dioxide from flue gases are both used to treat spent caustic wastes. Pits filled with lime, limestone, and even oyster shells (a source of calcium carbonate) are utilized to neutralize spent acid sludges.

Sulfuric Acid Pickle Liquor.⁶¹ In small-scale operations (less than 5,000 gal/day) neutralization of pickle liquor from steel cleaning operations can be performed in a batch, usually with quicklime. Typically, pickle liquor contains on the order of 70 g of iron and 170 g of sulfate per liter (approximately 5% sulfuric acid by weight). Large waste streams can be handled in continuous-flow systems, and other suitable alkaline agents may be employed. If calcium-based materials are utilized in the neutralization, calcium sulfate will form a product sludge, which is usually dewatered by vacuum filtration or placed in a lagoon. The formation of a flocculated ferrous hydroxide precipitate (at neutral pH) can produce a solid with poor settling and filtering properties. Thus, an oxidation step is often employed since ferric hydroxide is very insoluble, and there is an optimum ratio of ferric to ferrous ions at which the sludge can be handled most readily.

Hydrochloric Acid Pickle Liquor.⁶⁵ Although hydrochloric acid was not as widely used in the past as sulfuric acid in steel pickling operations, today there is a trend toward its use. Up to 1500 gal/min of acid rinse waters, containing up to 0.5 g/L free hydrochloric acid and up to 0.87 g/L ferrous chloride, are treated. An aeration step is included in the process to oxidize the iron, which then precipitates as ferric hydroxide. This

precipitate and unreacted limestone are the only solids to be handled because the major product, calcium chloride, is quite soluble. Temperatures above 49°C and a 25% excess of limestone are employed to increase the system's efficiency.

Acids from Resin Manufacturing.⁶¹ Upflow limestone neutralization beds are used at a resin manufacturing plant in New York to treat wastewater containing hydrochloric acid and some sulfuric acid. The unit is capable of operating at flows of up to 13.6 gal/min/ft² with 1% hydrochloric acid. The limestone beds are 3 ft deep with a cross sectional area of 113 ft². Present design calls for substantially deeper beds.

Metal Finishing Operations.⁶¹ A plant in Ohio that manufactures automobile bumpers produces wastewater containing sulfuric, phosphoric, hydrochloric, and chromic acids, as well as metal ions. This wastewater is combined with alkaline wastes and produces a final waste stream with a pH between 1.5 and 3.0, and a flow rate of about 1000 gal/min. Neutralization is carried out in a series of three lead-lined reactors, each of almost 7,500 gal capacity. A slurry of dolomitic lime is added to the first and third reactors to produce an effluent with a pH of 8.0 to 8.5.

Neutralization can be used at DOE facilities to treat either inorganic or organic waste streams that are excessively acidic or alkaline. It can find its immediate application in the treatment of aqueous wastes that contain strong acids such as sulfuric or hydrochloric, or bases such as caustic soda or ammonium hydroxide. The process can also be used to treat nonaqueous waste streams. For example, slurries and sludges are amenable to neutralization, with due consideration for the nature of the suspended solid and its dissolution properties. In principal, even tars can be neutralized, although the problems of reagent mixing and contact are usually severe, making the process impractical in most instances. Solids and powders that are acidic or basic can also be neutralized if they are first dissolved.

3.7 CHEMICAL OXIDATION

Chemical oxidation is by far the most important method for destruction or degradation of toxic substances, especially organic chemicals. Chemical oxidation is a process in which the oxidation state of the substance of interest is raised. In case of inorganic compounds, oxidation is equivalent to a loss of electrons. For organic compounds, oxidation can mean the addition of oxygen, the withdrawal of hydrogen, or the withdrawal of electrons with or without the withdrawal of protons. The chemical oxidation processes discussed here should be differentiated from thermal oxidation (incineration) which is discussed separately in Sec. 3.8. The primary reference for the material presented in this section is Ref. 8.

3.7.1 Technology Description

The use of chemical oxidation for hazardous waste treatment is primarily related to the destruction of cyanide in wastewaters from plating and metal finishing, and detoxification of a variety of hazardous species in dilute waste streams, such as phenols, organic sulfur compounds, and pesticides. Examples of chemical oxidation for waste treatment are given in Table 3.5.

Liquids are the primary waste form treatable by chemical oxidation. The most powerful oxidants are relatively nonselective; therefore, any easily oxidizable material in the waste stream will be affected. If, for instance, the waste included an easily oxidizable organic solvent, it might use up most of the oxidant, leaving little to react with a hazardous solute in the waste. Therefore, the most commonly used oxidants are limited to aqueous wastes.

Gases have been treated by scrubbing with oxidizing solutions for the destruction of odorous substances, such as certain amines and sulfur compounds. Potassium permanganate, for instance, has been used in certain chemical processes, in the manufacture of kraft paper, and in the rendering industry. Oxidizing solutions are also used for small-scale disposal of certain reactive gases in laboratories.⁶⁶

Oxidation has limited application to slurries, tars, and sludges. Because other components of the sludge, as well as the material to be oxidized, may be attacked indiscriminately by oxidizing agents, careful control of the treatment via multistaging of the reaction, careful control of pH, etc. is required.

3.7.1.1 Unit Operations

The first step of the chemical oxidation process is the adjustment of the pH of the solution to be treated. When chlorine gas is used to treat cyanides, for instance, this adjustment is required because in a solution with an acid pH hydrogen cyanide and/or cyanogen chloride, both of which are poisonous gases, will be produced. The pH adjustment, which is done with an appropriate alkali (sodium hydroxide, for example), is followed by the addition of the oxidizing agent. Mixing is used to provide contact between the oxidizing agent and the waste. Because some heat is often liberated, more concentrated solutions will require cooling. The oxidizing agent can be a gas (e.g., chlorine), a liquid (e.g., hydrogen peroxide) or even a solid if there is adequate mixing. Reaction times vary, but are on the order of seconds or minutes for most commercial-scale installations. (Additional time is allowed to ensure complete mixing and oxidation.) At this point, additional oxidation may be desired and, in the case of cyanide destruction, this additional treatment often requires readjustment of the pH and the addition of more oxidant. Once the reaction has occurred, the final oxidized solution is

Table 3.5 Selected Wastes and Effective Oxidants

Waste	Oxidant
Benzidine	Nitrous acid
Cyanide	Chlorine and caustic, chlorine dioxide, sodium or calcium hypochlorite, potassium permanganate, hydrogen peroxide
Ferrous iron	Air (very slow)
Formaldehyde (trace quantities)	Potassium permanganate
Lead	Sodium hypochlorite, potassium permanganate (for trace quantities), hydrogen peroxide
Manganese	Potassium permanganate
Mercaptans	Chlorine
Pesticides (Diquat, Paraquat)	Chlorine dioxide, potassium permanganate (for trace quantities)
Phenols	Hydrogen peroxide, potassium permanganate (for trace quantities)
Rotenone	Potassium permanganate (for trace quantities)
Sulfides	Air, chlorine
Sulfites	Air
Sulfur compounds	Hydrogen peroxide
Sulfur-containing organics	Potassium permanganate (for trace quantities)

Source: Ref. 8.

generally subjected to some treatment to settle or precipitate any insoluble oxidation products and other residues. It may be necessary to remove what remains of the oxidizing agent, reacted and unreacted. For example, one product of oxidation with potassium permanganate is manganese dioxide (MnO_2), which is insoluble and can be settled or filtered for removal.

Figure 3.7 shows a process flow diagram for a typical chemical oxidation system.

3.7.1.2 Special Characteristics

Chemical oxidation is suitable for treatment of streams with low-to-moderate concentrations of oxidizable material; total energy requirements, not including that required to produce the chemicals, are low. Chemical oxidation can introduce new contaminants into the effluent, depending on what agent is used. Additional treatment will be required if the level of such new contaminants is high enough to exceed effluent regulations. The equipment used in the process is simple to obtain and use. Operating costs vary, depending mainly on the type and quantity of chemicals used.

3.7.2 Applications for Waste Treatment

The following paragraphs describe some selected examples of the application of chemical oxidation to hazardous waste management problems.

Oxidation of Cyanide Effluents. Numerous plating and metal-finishing plants use chemical oxidation to treat their cyanide wastes. Cyanides and heavy metals are often present together in plating-industry wastes. Their concentration and the potential value of recovered metal influence the selection of the treatment process. If the cyanide and heavy metals are not

Fig. 3.7 Process Diagram for Waste Treatment Using Chemical Oxidation (Source: Ref. 8)

economically recoverable by a method such as ion exchange, the cyanide radical is converted either to the less-toxic cyanate or to CO_2 and N_2 by oxidation, while the heavy metal is precipitated and removed as a sludge.

In treating cyanide waste by oxidation, hypochlorite or caustic plus chlorine (alkaline chlorination) may be used to oxidize the cyanide to cyanate or to oxidize it completely to N_2 and CO_2 . This reaction is fast and adaptable to either batch or continuous operation. Smaller volumes would be treated in a bath system for simplicity and safety.

The rate of the oxidation to N_2 and CO_2 is dependent on pH and proceeds rapidly at a pH of 11 or higher. About 8 parts chlorine and 7.3 parts sodium hydroxide are required per part of cyanide.⁶⁷ Neutralization is required after treatment, because the waste is generally alkaline.

Hypochlorite salts of calcium, magnesium, or sodium are frequently used as oxidants in place of gaseous chlorine, even though the chlorine reacts faster and costs about half as much as hypochlorites; the hypochlorites are easier and safer to use and do not require the addition of supplementary alkali. Calcium hypochlorite will produce more sludge than sodium hypochlorite if certain anions such as sulfate are present.

There are problems associated with alkaline chlorination of cyanide if soluble iron or certain other transition-metal ions are present. The iron forms very stable ferrocyanide complexes, which prevents the cyanide from being oxidized. Potassium permanganate and hydrogen peroxide are also used to oxidize cyanide wastes.^{67,68}

Oxidation of Phenols. Chemical oxidation has been used to destroy phenols in dilute waste streams, usually with potassium permanganate as the oxidant; the phenol is oxidized to carbon dioxide and water.⁶⁹ The potassium permanganate was reduced to manganese dioxide (MnO_2), which is a filterable solid. In one application, the product MnO_2 has been found to act also as a coagulant, settling other material from the waste stream. Chlorine gas is not frequently used because of the high potential for formation of chlorophenols.

When phenol is present only in trace quantities, chemical oxidation is an economically favorable process for the treatment of waste. Oxidation with potassium permanganate has been used in the treatment of potable water. Removal of 1 ppm phenol in this application can be accomplished by the addition of 6 to 7 ppm potassium permanganate.⁷⁰

Oxidation of Other Organics. Chemical oxidizing agents have been used for the control of organic residues in wastewaters and for potable water treatment. The organics for which oxidative treatment has been reported include aldehydes, mercaptans, phenols, benzidine, and unsaturated acids. For these applications, sodium hypochlorite, calcium hypochlorite, potassium

permanganate and hydrogen peroxide have been reported as oxidants. In one application, nitrous acid was used.

Oxidation of Pesticides. Because of the resistance of pesticides to biodegradation, chemical oxidation has been investigated for removing pesticide residues from water. Goma and Faust⁷¹ experimented with potassium permanganate, chlorine, and chlorine dioxide to remove residual Diquat and Paraquat from water. With potassium permanganate oxidation, manganese dioxide was precipitated as expected. The application of KMnO_4 at a molar concentration 25 times that of the pesticides causes fairly complete oxidation to oxalate, ammonia, and water. The reaction is said to go through several intermediate reactions; the rates of these intermediate reactions are pH dependent, being faster above pH 8. When chlorine dioxide is used as the oxidizing agent on these substances in concentrations of 15 and 30 mg/L, the reactions are complete in less than one minute. (These reaction rates were observed at pH values above 8.) At pH 9.04, for example, a solution of 15 mg/L of Diquat treated with 6.75 mg/L chlorine dioxide had a residual Diquat concentration of less than 0.005 mg/L and residual chlorine dioxide at 2.61 mg/L.

3.8 INCINERATION

3.8.1 Background/Process Description

Incineration is a controlled combustion process in which organic wastes (including inorganic constituents) are reacted with oxygen at high temperature to produce water, carbon dioxide, and other partial or ultimate oxidation products. Gaseous, liquid, and solid wastes can all be disposed of by incineration, if they are combustible to some extent. Under proper operating conditions, organic wastes are converted to oxidized gases, and inorganic substances are converted to ash. Although incineration is capable of producing a less bulky, less toxic, or less noxious material, the combustion gases can contain excessive amounts of products of incomplete combustion (PIC) such as smoke, carbon monoxide, gaseous hydrocarbons, tars, and other compounds if proper operating conditions are not maintained. Ash will also contain unburned and partially converted organic products. The presence of PIC (or daughter products) and unburned waste constituents necessitates careful monitoring of these streams.

The effectiveness of incineration is dependent on three factors: (1) the residence time of the waste material in the incinerator in contact with air; (2) the amount of mixing that occurs between the air, which is the oxidant, and the waste material; and (3) the temperature at which the reaction takes place. These factors are very interdependent. If, for example, the amount of mixing in the incinerator were reduced, then it would be necessary

to increase the residence time and perhaps the temperature in order to achieve the same degree of combustion or combustion efficiency.⁷² Table 3.6 summarizes typical ranges for temperature and residence time for six incineration processes.

3.8.2 Incineration Technologies

Several different incineration technologies are applicable to destruction of hazardous wastes. Table 3.7 lists six incinerator types and the physical forms of waste for which each is most suitable. Rotary kiln and liquid injection incineration are the two major techniques used for hazardous waste destruction. Fluidized bed and multiple hearth incineration are less frequently used. Coincineration usually involves a variation of rotary kiln or multiple hearth applications. The following section will describe these technologies and their major advantages and disadvantages.

Table 3.6 Incineration Processes and Their
Typical Operating Ranges

Incineration Process	Temperature Range, °F (°C)	Residence Time
Rotary kiln	1,500 to 2,900 (820 to 1,600)	Liquids and gases, seconds; solids, hours
Liquid injection	1,200 to 2,900 (650 to 1,600)	0.1 to 2 seconds
Fluidized bed	840 to 1,800 (450 to 980)	Liquids and gases, seconds; solids, longer
Multiple hearth	Drying zone 600 to 1,000 (320 to 540) Incineration 1,400 to 1,800 (760 to 980)	0.25 to 1.5 hours
Coincineration	300 to 2,900 (150 to 1,600)	Seconds to hours
Starved air combustion/pyrolysis	900 to 1,500 (480 to 820)	0.1 second to several hours

Source: Ref. 73.

Table 3.7 Applicability of Available Incineration Processes to
Incineration of Hazardous Waste by Type

Waste Type	Rotary Kiln ^a	Liquid Injection	Fluidized Bed ^a	Multiple Hearth	Coincin- eration	Starved Air Combustion/ Pyrolysis
Solids						
Granular, homogeneous	X		X	X	X	X ^b
Irregular, bulky (pallets, etc.)	X				X	X ^b
Low melting point (tars, etc.)	X	X ^c	X		X	X
Organic compounds with fusible ash constituents	X			X	X	X
Unprepared, large, bulky material	X					
Gases						
Organic vapors	X ^d	X ^d	X ^d	X ^d	X ^d	X ^d
Liquids						
High-organic aqueous wastes	X ^e	X	X		X	
Organic liquids	X ^e	X	X		X	
Solids/Liquids						
Waste contains halogenated aromatic compounds (2,200°F minimum)	X	X ^f			X	
Aqueous organic sludges	X ^g		X	X	X	

^aSuitable for pyrolysis operation.

^bHandles large objects on a limited basis.

^cIf material can be melted and pumped.

^dIf properly presented to the incinerator.

Source: Ref. 73.

^eIf equipped with auxiliary liquid injection nozzles.

^fIf liquid.

^gProvided waste does not become sticky upon drying.

3.8.2.1 Rotary Kiln^{73,74}

Rotary kiln incinerators are generally refractory-lined cylindrical shells mounted at a slight incline from the horizontal. Figure 3.8 is a schematic diagram of a general rotary kiln system. This schematic represents typical rotary kilns, including small portable units currently being used in the restoration of hazardous waste disposal sites and demilitarization projects. Afterburners are commonly used to ensure complete combustion of flue gases prior to treatment for air pollutants.

Rotary kilns can generally be used for the destruction of any form of hazardous material (solid, liquid, gas) that is combustible. They have been used to dispose of polyvinyl chloride wastes, polychlorinated biphenyl wastes, obsolete munitions, and obsolete chemical warfare agents such as GB, VX, and mustard gas.

Advantages

- Will incinerate a wide variety of liquid and solid hazardous wastes.
- Can receive liquids and solids independently or in combination.
- Has feed capability for drums and bulk containers.
- Is adaptable to wide variety of feed mechanism designs.
- Contains no moving parts within the high temperature area of the kiln.

Fig. 3.8 Schematic Diagram of Rotary Kiln Incinerator

- Is adaptable for use with a wet gas-scrubbing system.
- Can handle waste fed directly into the kiln without any preparation such as preheating, mixing, etc.
- Can be operated at temperatures in excess of 2,500°F (1,400°C), making them well suited for the destruction of toxic compounds that are difficult to degrade thermally.

Disadvantages

- High capital cost for installation.
- Necessity for operating care to prevent refractory damage (thermal shock is a particularly damaging event).
- Possibility of airborne particles being carried out of kiln before complete combustion.
- Possibility that spherical or cylindrical items may roll through kiln before complete combustion.
- High particulate loadings.
- Relatively low thermal efficiency.
- Problems in maintaining seals at either end of the kiln, a significant operating difficulty.

3.8.2.2 Liquid Injection^{73,74}

Liquid injection incinerators are currently the most commonly used incinerators for hazardous waste disposal. They can be used to dispose of virtually any combustible liquid or slurry with a viscosity value of 10,000 SSU (Saybolt Seconds Units) or less. This type of incinerator is made in numerous configurations, but is generally classified as either vertical or horizontal. The vertical type, Fig. 3.9, has the advantage that the incinerator acts as its own stack. The stack, or a portion of it, may serve as a secondary combustion chamber. The horizontal incinerator, Fig. 3.10, is connected to a stack. Efficient and complete combustion is achieved only if the fuel droplet size is sufficiently small and adequately mixed with the combustion air. An ideal droplet size is about 40 μm or less and is attainable mechanically using rotary cup or pressure atomization, or via gas fluid nozzles and high-pressure air or steam.

Fig. 3.9 Vertically Fired Liquid Injection Incinerator Schematic

Advantages

- Capability for incinerating a wide range of liquid hazardous wastes.
- No requirement for a continuous ash removal system, other than for air-pollution control.
- Fast temperature response to changes in the waste fuel flowrate.
- Virtually no moving parts.
- Low maintenance costs.

Fig. 3.10 Horizontally Fired Liquid Injection Incinerator Schematic

Disadvantages

- Can only incinerate wastes that can be atomized through a burner nozzle.
- Burners susceptible to plugging. (Burners are designed to accept a certain particle size; therefore, particle size is a critical parameter for successful operation).
- Burners possibly not able to accept a material that dries and cakes as it passes through the nozzles.

3.8.2.3 Multiple Hearth^{73,74}

A typical multiple-hearth furnace consists of a refractory-lined steel shell, with refractory hearths mounted one above the other in the interior of the shell. An air-cooled central shaft rotates a series of rabble arms equipped with teeth across the hearths, plowing the burning solids. The solids fall through drop holes from the upper hearth to successive lower hearths and eventually to an ash hopper.

Advantages

- The retention time in multiple-hearth incinerators is usually higher for hazardous materials having low volatility than in other incinerator configurations.
- Large quantities of water can be evaporated.
- A wide variety of wastes with different chemical and physical properties can be handled.
- Multiple-hearth incinerators are able to use many fuels, including natural gas, reformer gas, propane, butane, oil, coal dust, waste oils, and solvents.
- Because of the multizone configuration, fuel efficiency is high and typically improves with the number of hearths used.

Disadvantages

- Due to the longer residence times of the waste materials, temperature response is usually very slow throughout the incinerator when the burners are adjusted.
- It is difficult to control the firing of supplementary fuels, as a result of this slow response.
- Maintenance costs are high, because the moving parts (rabble arms, main shaft, etc.) are subjected to combustion conditions.
- This process is not well suited for wastes containing fusible ash, wastes requiring extremely high temperature for destruction, or irregular bulky solids.

3.8.2.4 Fluidized Bed^{73,74}

Fluidized bed incinerators are vessels containing a bed of inert granular material, usually sand, which is kept at temperatures ranging from 450 to 850°C. Fluidizing air is passed through a distributor plate below the bed and agitates the heated granular material. Hazardous waste material and auxiliary fuel are injected and mixed with the bed material, which transfers heat to the waste. The waste, in turn, burns and returns heat to the bed.

Sludges and slurries are the waste forms most commonly reported to be burned in fluidized bed incinerators. A homogeneous combustible liquid may be immediately injected into the bed, but a nonhomogeneous sludge including large pieces of solid matter will require sorting, drying, shredding, and special arrangements for feed.

Advantages

- Generally applicable for the disposal of combustible hazardous solids, liquids, and gaseous wastes.
- Simple design concept, requiring no moving parts in the combustion zone.
- Relatively low gas temperatures and excess air requirements, which tend to minimize nitrogen oxide formation and contribute to smaller, lower-cost emission-control systems.
- Long incinerator life and low maintenance costs.
- Enhanced combustion efficiency resulting from large active surface area caused by fluidizing action.
- Fluctuation in the feed rate and composition are easily tolerated due to the large quantities of heat stored in the bed.
- Properly selected bed material suppresses acid gas formation and reduces emission controls required.

Disadvantages

- Difficult to remove residual materials from the bed.
- Requires bed preparation and maintenance.
- May require special operating procedures to avoid bed damage.

- Possesses relatively high operating costs, particularly power costs.
- May require more development of hazardous waste incineration practices.
- Not well suited for irregular, bulky wastes, tarry solids, or wastes that produce a fusible ash.

3.8.3 Waste Characterization and Applicability to DOE Wastes

A number of different types of hazardous wastes can be destroyed by incineration. The wastes must be basically organic, but may be either combustible (i.e., sustaining combustion without auxiliary fuel) or noncombustible (i.e., not sustaining combustion without auxiliary fuel).⁷⁵ In classifying wastes for destruction, it has been found useful to categorize them on the basis of their elemental composition.⁷⁶ Table 3.8 shows the four classes of waste most suitable for incineration.

Table 3.8 Chemical Waste Classifications

Waste Class	Elemental Composition	Example
1	C,H or C,H,O	Tars from production of styrene; off-specification phenol
2	C,H,N or C,H,N,O	Solid residue from manufacture of aromatic amines
3	C,H,Cl or C,H,Cl,O	Vinyl chloride monomer manufacturing wastes, phenolic tar from 2,4-D manufacture
4	C,H,N,Cl or C,H,N,Cl,O C,H,S or C,H,S,O C,H,F or C,H,F,O C,H,Br or C,H,Br,O C,H,P or C,H,P,O C,H,Si or C,H,Si,O C,H,Na or C,H,Na,O	Nitrochlorobenzene manufacturing wastes Petroleum refining sour waste Fluorinated herbicide wastes Ethylene bromide manufacturing wastes Malathion Tetraethyl orthosilicate wastes Refinery spent caustic

Source: Ref. 76.

Generally, it is easier to incinerate wastes in classes 1 and 2 than those in 3 and 4. Nitrated organics can create problems because oxides of nitrogen will be created under normal burning conditions. However, several approaches can be used to reduce the oxides to acceptable limits. The preferred method is to use a two-stage combustion system where the primary chamber is operated in a fuel-rich manner; the unburned hydrocarbons are then oxidized in the secondary chamber. The objective is to reduce the formation of NO_x in the high-temperature zone by removing the oxygen necessary for its formation.⁷⁵

Wastes in classes 3 and 4 are more difficult to incinerate due to their content of chlorine, bromine, fluorine, sulfur, phosphorus, silicon, or sodium. Because their decomposition generates acids and oxides, special air-pollution control techniques are required. For the organic halogen wastes, the halogen can be hydrolyzed to the acid gas and absorbed in water in a packed tower so that it is not discharged to the atmosphere. Both HCl and HF are much easier to absorb than HBr . If hydrolysis of the halogen does not occur in the incineration process, then caustic scrubbing is required to remove the halogen from the discharged gas stream, a more expensive process.

Sulfonated organic wastes present similar problems to those created by halogenated wastes. However, sulfur is easily oxidized to sulfur dioxide and, if sufficient excess air is present, to sulfur trioxide. Both of these materials can be absorbed by caustic or soda ash solution. Another means of removing sulfur has been to inject caustic or soda ash in aqueous form into the combustion zone with the sulfur, then remove it by scrubbing. Organo-phosphorus mixtures can be incinerated with subsequent scrubbing of phosphorus pentoxide by water or caustic solution to form weak phosphoric acid or sodium phosphate.⁷⁵

Organic/inorganic salts can be difficult to incinerate because the inorganic materials will form oxides or carbonates upon exit from the incineration zone. These materials must be trapped by some device such as a wet scrubber, wet electrostatic precipitator, or an ionized scrubber. Liquids, solids, slurries, and sludges may all be suitable for incineration. Usually the organic noncombustible wastes contain the larger amounts of water.

A recent EPA publication, *Engineering Handbook for Hazardous Waste Incineration*,⁷³ identifies hazardous wastes defined in Sec. 3001 of RCRA, and some other wastes, that are good, potential, or poor candidates for incineration and indicates which technology is appropriate. The waste categories are listed in a very extensive table that may be usefully compared with any particular DOE waste for which a disposal method is sought. However, that table must be considered only a suggestive guide; decisions in specific cases must be based on detailed information about the constituents of the waste stream in question.

3.8.4 Environmental Effects

Incineration possesses several environmental advantages as a hazardous waste disposal technology:

- Toxic components of hazardous wastes can be converted to harmless compounds or, at least, to less-harmful compounds.
- Incineration provides ultimate destruction of those hazardous wastes to which it is applicable, eliminating the possibility of problems resurfacing in the future.
- The volume of hazardous waste is greatly reduced by incineration.
- Heat recovery makes it possible to recover some of the energy produced by the combustion process.

It is likely that incineration will be a principal technology for the disposal of hazardous waste in the future because of these advantages.⁷³

Although problems are substantially reduced, incineration does not eliminate all of the disposal problems associated with hazardous waste. Most incinerators produce combustion products that must be properly removed prior to discharging gas products to the environment. These products include ash or inert residues from such things as silica, oxides, and/or metals. Captured gas products, such as HCl, when reacted with caustic solutions in the scrubber, can also produce dissolved and suspended solids. These solutions from the quench and scrubber processes must be carefully disposed of to ensure that the entire sequence of combustion is safe. In some cases, these secondary wastes can be hazardous themselves.

The control of air pollutants with off-gas cleaning systems is the subject of rapidly developing technologies. Organic pollutants, emitted as a result of incomplete combustion of waste material, present a different control problem. Proper design of the incineration system and controlled operating conditions can minimize this problem. Emission of these organic pollutants can be controlled by using high-temperature afterburners or secondary combustion chambers.

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4 WASTE EXCHANGE

4.1 BACKGROUND

The stringent pollution control regulations under the Resource Conservation and Recovery Act (RCRA) present technical problems and the prospect of increased costs for the handling and disposal of industrial wastes. In addition, many wastes represent potentially valuable raw materials and energy sources. As the costs of raw materials and energy continue to escalate, firms will find it increasingly attractive to substitute wastes for raw materials, whenever possible, in their manufacturing processes. Waste exchanges provide a means to transfer usable wastes to those who can utilize them, minimizing waste disposal expenses and maximizing the value of the waste.¹

4.2 DESCRIPTION OF TECHNOLOGY

The following section describes the types of waste exchanges currently in operation and the types of wastes handled, then evaluates the process from the standpoints of effectiveness, cost, impact of regulations, and applicability to DOE wastes.

4.2.1 Types of Waste Exchanges

There are two distinct types of waste exchanges in operation: these are "waste information" and "waste materials" exchanges or clearinghouses. Waste information exchanges are more common, but a few companies, both in Europe and the United States, actually receive and handle waste materials.²

The information exchange performs only limited functions. It is designed primarily to help generators advertise the existence of wastes with possible reuse value, to help users identify such scrap wastes, and to link potential trading partners. All the other steps in the transfer are executed by the waste generators and users themselves.

The services of material exchanges are more complex and expensive. The waste materials are physically, economically, and legally transferred through the exchange, which earns its income from commissions charged on completed transactions. These exchanges buy or accept wastes, analyze their properties, identify potential uses, reprocess them as needed, and sell the wastes at a profit. Whereas an information clearinghouse frequently needs only a part-time staff and office space, a materials exchange needs people with highly competent technical, managerial, and marketing skills, as well as storage and processing facilities.²

The 30 U.S. waste exchanges are listed in Table 4.1. Table A-1 (Appendix A) summarizes more detailed information on material categories listed, type of exchange, and listing fees for 22 of the exchanges.

4.2.2 Types of Waste Materials Transferred through Waste Exchanges

A wide variety of waste materials have the potential to be transferred through a waste exchange. Most valuable are raw or virgin materials from nature (e.g., iron and bauxite) and unused manufactured materials such as plastics. Processing residues are generally less pure and less valuable. Common examples include solvents from pharmaceutical and paint processing, slag from steel making, and rejected lead plates from lead-acid batteries. All have recognized value for their chemical or physical properties. However, their prices are set by supplies of and demands for competing raw materials, and by disposal costs.²

Table A-1 and A-2 (Appendix A) summarize the major material categories listed on the American and foreign exchanges and the principal types of transfers, insofar as information is available. The types of materials listed most frequently include the following categories:

- Organic chemicals and solvents
- Oils, fats, and waxes
- Textiles, leather, and rubber
- Wood and paper products
- Spent catalysts
- Acids
- Alkalis
- Inorganic chemicals
- Metals
- Plastics

Materials listed to a lesser, but significant, extent include the following:

- Glass
- Food processing wastes

Table 4.1 U.S. Waste Exchanges

Name and Region	Address	Contact
<u>Region I</u>		
World Assn. for Safe Transfer and Exchange (WASTE)	130 Freight St. Waterbury, CT 06702	Marcel Veroneau (203) 574-2463
The Exchange	104 Charles St., Box 394 Boston, MA 02114	Howell Hurst (617) 367-2334 or 367-0810
<u>Region II</u>		
The American Alliance of Resources Recovery Interests Inc.	111 Washington Ave. Albany, NY 12210	John Flandreau (518) 436-1557
Enkarn Research Corp.	P.O. Box 590 Albany, NY 12201	J.T. Engster (518) 436-9684
Industrial Waste Information Exchange	N.J. State Chamber of Commerce 5 Commerce St. Newark, NJ 07101	Mr. Ludlum (201) 623-7070
National Waste Exchange	P.O. Box 190 Silver Springs, PA 17575	Ron Schaible (717) 780-6189
Northeast Industrial Waste Exchange	700 East Water St. Room 711 Syracuse, NY 13210	Walker Banning (315) 422-8276
<u>Region III</u>		
Pennsylvania Waste Information Exchange	222 North Third St. Harrisburg, PA 17101	Janice Berlin (717) 255-3252
Union Carbide Corp. (In-house operation only)	P.O. Box 8361 Bldg. 3005 South Charleston, WV 25303	R.L. Floyd (304) 747-5362
<u>Region IV</u>		
Georgia Waste Exchange	Georgia Business & Industry Assn. 181 Washington St., SW Atlanta, GA 30303	Bert Fridlin (404) 659-4444
Iso-Chem Marketing Inc.	P.O. Box 1268 449 Kingsley Ave., Suite E Orange Park, FL 32073	Anthony L. Tripi (904) 264-0070
Mecklenburg County Waste Exchange	Resource Recovery Analyst Mecklenburg County Engineering Dept. 1501, I-85 North Charlotte, NC 28202	Roy Davis (704) 374-2770
Tennessee Waste Swap	Tennessee Mfrs. Assn. 708 Fidelity Bldg. Nashville, TN 37219	Nancy Niemeier (615) 256-5141
<u>Region V</u>		
American Chemical Exchange (ACE)	4849 Gold Rd. Skokie, IL 60076	Tom Hurvis (312) 677-2800
American Materials Exchange Network	19489 Lahser Rd. Detroit, MI 48219	Vewiser Dixon (313) 532-7900
Environmental Clearinghouse Organization (ECHO)	3426 Maple Lane Hazel Crest, IL 60429	William Petrich (312) 335-0754

Table 4.1 (Cont'd)

Name and Region	Address	Contact
<u>Region V (Cont'd)</u>		
Industrial Waste Information Exchange	Columbus Industrial Assn. 1646 West Lane Ave. Columbus, OH 43221	Newton A. Brokaw (614) 486-6741
Minnesota Assn. of Commerce and Industry (MACI)	200 Hanover Bldg. 480 Cedar St. St. Paul, MN 55101	James T. Shields (612) 227-9591
Ore Corp. ("The Ohio Resource Exchange")	2415 Woodmere Dr. Cleveland, OH 44106	R.L. Immerman (216) 371-4869
Waste Materials Clearinghouse, Environmental Quality Control Inc.	1220 Waterway Blvd. Indianapolis, IN 46202	Noble L. Beck (317) 634-2142
<u>Region VI</u>		
Chemical Recycle Information Program	Houston Chamber of Commerce 1100 Milam Bldg., 25th Floor Houston, TX 77002	Jack Westney (713) 651-1313
<u>Region VII</u>		
Chamber of Commerce of Greater Kansas City	920 Main St. Kansas City, MO 64105	Max Norman (816) 221-2424
Iowa Industrial Waste Information Exchange	Center for Industrial Research Service 201 Bldg. E. Ames, IA 50011	E.O. Sealine W.A. Kluckman (515) 294-3420
Midwest Industrial Waste Exchange	10 Broadway St. Louis, MO 63102	Oscar S. Richards (312) 231-5555
<u>Region IX</u>		
<u>West</u>		
California Waste Exchange	Dept. of Health Services Hazardous Materials Section 2151 Berkeley Way	Paul H. Williams (415) 540-2043
Zero Waste Systems Inc.	2928 Poplar St. Oakland, CA 94608	Paul Palmer (415) 893-8257
<u>Region X</u>		
Information Center for Waste Exchange	2112 Third Ave., Suite 303 Seattle, WA 98121	Judy Henry (206) 623-5235
Oregon Industrial Waste Information Exchange	Western Environmental Trade Assn. 333 SW 5th, Suite 618 Portland, OR 97204	David Clark (503) 221-0357
Resource Conservation Consultants	1615 NW 23rd, Suite One Portland, OR 97204	Delyn Kies (503) 227-1319

Source: Ref. 3.

- Minerals
- Waste containers
- Paints
- Salts

With the exception of specialized materials, available information indicates that the most successful transfers involve²

- Organic chemicals and solvents (for other than fuel use)
- Plastic residues
- Wood and paper products
- Acids and alkalis
- Inorganic chemicals
- Leather and rubber
- Spent catalysts
- Waste oils
- Metals
- Metal-containing residues (sludge)

4.2.3 Effectiveness of Exchanges

Information on waste transfers successfully completed is an important measure of the effectiveness of an exchange; however, data are often unavailable or misleading. Of 22 U.S. exchanges surveyed, only three have offered match-up figures: 28%, 23%, and 9% of their respective waste listings led to successful transfers. Of all the U.S. exchanges, the Oregon Industrial Waste Information Exchange was the only one to submit a list of the materials actually transferred (see Appendix A, Table A-3). Foreign exchanges have more data. Eleven of the 18 exchanges offered match-up data as a percentage of listings. These ranged from a low of 10% to a high of 44%.²

Major reasons for sparse match-up information on U.S. exchanges are

- Acquiring match-up information is not a goal of many exchanges.

- Private for-profit exchanges want to keep this information confidential, so that competitors will not profit from a successful transfer.
- The U.S. exchanges have relatively small numbers of listings.
- Some exchanges are just getting started and have not had the opportunity to record or report match ups.

In addition, match-up information can be misleading because the figures do not reflect such factors as tonnage or volume of material transferred, value of the material, frequency of transfer (one-time, continuing, or periodic), and whether generators list wastes that they have accumulated and have not been able to dispose of for years.

Nearly a decade of experience has demonstrated the usefulness of waste exchange. The United Kingdom Waste Material Exchange, during five years of operation, has successfully exchanged about 156,000 metric ton of waste material per year on a continuing basis, plus 196,000 metric ton of waste in single transactions.² The U.S. exchanges have not demonstrated the success rate of most European exchanges; however, the U.S. exchanges are relatively new and have not yet reached their potential.

4.2.4 Economics

Transferring a waste through a waste exchange provides a means of avoiding the high cost of disposal and possibly even making money if the unwanted waste can be sold. Costs include listing fees (usually \$5-\$25 per item) for information exchanges and some kind of charge or commission if a "for-profit" materials exchange is used.

4.2.5 Impact of Regulations

The RCRA has had a significant impact on the existence of waste exchanges in the U.S. The number of exchanges has increased from 4 in 1976 (when the Act was passed) to 30 in 1981. The growth in the number of exchanges is attributed to the regulations governing hazardous waste treatment and disposal, which significantly increase the costs for secure disposal. It is expected that recovery and recycling of certain wastes through waste exchanges may be more cost-effective for handling hazardous wastes than the traditional methods (landfilling and incineration) now under severe scrutiny and regulation.²

Nevertheless, RCRA has been a mixed blessing for waste-exchange firms. The Act does not cover recycling operations in a comprehensive manner, and some companies may want to avoid dealing with a waste exchange out of fear

that if the wastes are improperly handled, the waste generator will be held liable. The EPA is thinking of revising some of the regulations that cover resource recovery. It is not clear what changes will be made, but the feeling is that hazardous waste recyclers will be brought within the RCRA system, possibly through specific rules for recycling operations. In addition, procedures for obtaining permits for recycling may be eased.⁴

4.2.6 Applicability to DOE Wastes

A number of DOE wastes have the potential to be transferred through a waste exchange. DOE wastes similar to those wastes with the best record for successful transfer (see Sec. 4.2.2) are the most likely candidates at the present time. The condition of the waste (percent solids, percent metals, chemical composition, etc.), the quantity available, and the demand in a particular geographic area will all affect the transferability of the particular waste. A sample listing form and sample listings are presented in Figs. A-1, 2, and 3 in Appendix A.

4.3 REFERENCES

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5 WASTE FIXATION

5.1 BACKGROUND

Waste fixation is for the most part synonymous with stabilization/solidification. Chemical fixation and stabilization/solidification are general terms used to designate processes that can be used to immobilize, isolate, or contain industrial waste materials, especially semisolids or sludges. Fixation usually has as one of its goals the production of a solid material from a semiliquid waste. The terms solidification or stabilization are usually used interchangeably although they represent different ideas.

Solidification suggests the production of a solid, monolithic mass with sufficient structural integrity to be transported in conveniently sized pieces without requiring any secondary containers. The solidification aspect of fixation comes from a Department of Transportation (DOT) regulation that all liquid radioactive waste material be converted into solid form (by adsorption on solids, drying, etc.) prior to interstate transportation. Some fixation technology has as its goal only the solidification of wastes to comply with this DOT regulation.

Stabilization suggests immobilization of toxic substances by reacting them chemically to form insoluble compounds or by entrapping the toxic element or compound in a watertight, inert polymer or stable crystal lattice. The dissolution of wastes has always been a major problem in the containment of toxic material, so much of the emphasis in stabilization has been placed on preventing the waste from coming in contact with water or on creating pH and oxidation-reduction conditions that minimize the solubility of the toxic compounds in the waste. Many fixation systems combine these two ideas by producing an impermeable mass that isolates the wastes from any surrounding water and at the same time holds the chemical conditions of any water that permeates the solidified wastes in the region of minimum solubility for the toxic compounds in the wastes.¹

This section provides information on the available fixation methods and their range of applicability. The material presented is primarily based on Ref. 2.

5.2 DESCRIPTION OF TECHNOLOGY

A large number of fixation methods are now available or under development, all having as their goal the safe, ultimate disposal of hazardous wastes. Ultimate disposal implies the final disposition of persistent, nondegradable wastes. Three primary goals of fixation of hazardous waste for ultimate disposal generally are to improve the handling and physical characteristics of the waste, to decrease the surface area across which transfer and loss of contained pollutants can occur, and to limit the solubility of any

pollutants contained in the waste. These goals can be met in a variety of ways, but not all techniques attempt to meet all three goals. Thus, individual fixation techniques may solve one particular set of problems but be completely unsatisfactory for others.

The important attributes, advantages, and disadvantages of the following major categories of industrial waste fixation systems are discussed below:

- Cement-based techniques
- Lime-based techniques
- Thermoplastic techniques (including bitumen, paraffin and polyethylene)
- Organic polymer techniques
- Encapsulation techniques
- Self-cementing techniques
- Glassification

5.2.1 Cement-Based Techniques

Cement-based waste fixation techniques owe much of their development to the use of this system in disposal of low-level radioactive waste.³ Cement-fixed radioactive waste (with low levels of activity) has been ruled acceptable for permanent disposal by U.S. agencies and by the International Atomic Energy Agency.⁴

Common cement or "portland cement" is produced by firing a charge of limestone and clay or other silicates at a high temperature. The resulting clinker is ground to a fine powder to produce a cement that consists of about 50% tricalcium and 25% dicalcium silicates. (Also present are about 10% tricalcium aluminate and 10% calcium aluminoferrite.) The "cementation" process is brought about by the addition of water to the anhydrous cement powder. This first produces a colloidal calcium-silicate-hydrate gel of indefinite composition and structure. Hardening of the cement is a lengthy process brought about by the interlacing of thin, densely-packed, silicate fibrils growing from the individual cement particles. This fibrillar matrix incorporates the added aggregates and/or wastes into a monolithic, rock-like mass. The success of the hardening process is affected by compounds such as sulfates, borates, salts of some metals, and a variety of organic compounds. Five types of portland cement are classified by variations in their chemical composition and physical properties:⁵

- Type I is the "normal" cement of the building trade, and constitutes over 90% of the cement manufactured in the United States.
- Type II is effective in the presence of moderate sulfate concentrations (150-1500 mg/kg).
- Type III has a high early strength, and is used where rapid setting is required.
- Type IV develops a low heat of hydration, which is desirable for large-mass concrete work.
- Type V is a special low-alumina, sulfate-resistant cement effective with high sulfate concentrations (>1500 mg/kg).

The types that have been used for waste fixation are Type I and, to a much lesser extent, Types II and V.

Most hazardous wastes slurried in water can be mixed directly with the cement; suspended solids will be incorporated into the rigid matrix of the hardened concrete. This procedure is especially effective for wastes with high levels of toxic metals, because at the pH of the cement mixture most multivalent metal cations are converted to insoluble hydroxides or carbonates. Metal ions may also be taken into the crystal structure of the cement minerals that form. Materials in the waste such as sulfides, asbestos, latex, and solid plastic wastes may actually increase the strength and stability of the waste concrete. However, the presence of certain inorganic compounds in the hazardous waste and the mixing waters can be deleterious to the setting and curing of the waste-concrete mix.⁵ Impurities such as organic materials, silt, clay, coal, or lignite may slow the setting and curing of common portland cement to as long as several days. Any insoluble materials that will pass through a No. 200 sieve (<74 μ m particle size) are undesirable, as they may coat the larger particles and weaken the bond between the particles and the cement. Salts of zinc, copper, lead, manganese, and tin may cause large variations in setting time and significant reductions in physical strength, zinc, copper, and lead being the most detrimental. Other compounds that are especially active as retardants for the setting of portland cement include sodium salts of arsenate, borate, phosphate, iodate, and sulfide, even at concentrations as low as a few tenths of a percent of the weight of the cement used. Products containing large amounts of sulfate (such as flue gas cleaning sludge) not only retard the setting of concrete but also, by reacting to form calcium sulfoaluminate hydrate, cause swelling and spalling in the solidified concrete. The special low-alumina cement (Type V) was developed for use in circumstances where high sulfate is encountered.

A number of additives have been developed for use with cement to improve the physical characteristics and decrease the leaching losses from the

resulting fixed sludge. Many of the additives used in waste fixation are proprietary and cannot be discussed here, but experimental work on the fixation of radioactive waste has shown some improvement in cement-based fixation and retention of nuclear waste by adding clay or vermiculite as absorbents.¹ Sodium silicate has reportedly been used to bind contaminants in cement fixation processes, but this additive causes an increase in volume to occur during the setting of the cement-waste mixture.⁴

Recent testing done by Brookhaven National Laboratory (BNL) under the sponsorship of the Nuclear Regulatory Commission indicates that a mixture of sodium silicate and Type II portland cement sets rapidly with no retardation from metallic ions.⁶ Sodium silicate appeared to precipitate most interfering ions in a gelatinous mass and thus was able to remove interferences and speed setting. Of the radwastes tested, only boric acid wastes produced any inhibition of set in the cement mixture. The development of a gel is important in the setting of the cement-waste-silicate mixture. Excessive mixing after the gel forms seems to cause slower setting and lessen final strength.

BNL developed a polymer-impregnation process that can be used to decrease the permeability of concreted sludge.⁴ The pores of the waste-concrete are filled by soaking in styrene monomer, and the soaked material is heated to bring about polymerization. This process results in significant increase in the strength and durability of the concrete-waste mixture. Surface coatings on concrete-waste composites have been examined extensively. The major problems encountered have been poor adhesion of the coating to the waste or lack of strength in the concrete material containing the waste. Surface coating materials that have been investigated include asphalt, asphalt emulsion, and vinyl.⁶ No surface-coating system for cement-fixed waste is currently being advertised.

The following are advantages of the cement-based fixing systems:

- Raw materials are plentiful and inexpensive.
- The technology and management of cement mixing and handling is well known, and the equipment is commonplace. Specialized labor is not required.
- Extensive drying or dewatering of waste is not required, because cement mixtures require water, and the amount of cement added can be adapted to a wide range of water content.
- The system is very tolerant of chemical variation. The natural alkalinity of the cement used can neutralize acids. Cement is not affected by strong oxidizers such as nitrates or chlorates. Pretreatment is required only for materials that retard the setting reactions of cement.

- Leaching characteristics can be improved where necessary by coating the resulting product with sealant.
- Control of the amount of cement used can produce very high load-bearing capacities, making the waste concrete good subgrade and subfoundation material.

The following are disadvantages of cement-based systems:

- Relatively large amounts of cement are required for most fixing processes. However, this may, in part, be off-set by the low cost of material. The weight and volume of the final product is normally about double that of other solidification processes.
- Uncoated cement-based products may require a well-designed landfill for burial. Experience in radioactive waste disposal indicates that some wastes are leached from concrete, especially by mildly acidic leaching solutions.
- Extensive pretreatment, or higher-cost types of cement or additives, may be necessary for wastes containing large amounts of impurities such as borates or sulfates that affect the setting and curing of the waste-concrete.
- The alkalinity of cement drives off ammonium ion as ammonia gas.
- Cement is an energy-intensive material.

5.2.2 Lime Based Techniques

Waste fixation techniques based on lime products usually depend on the reaction of lime with a fine-grained siliceous (pozzolanic) material and water to produce a concrete-like material (sometimes referred to as a pozzolanic concrete). The most common pozzolanic-type materials used in waste treatment are fly ash, ground blast-furnace slag or cement-kiln dust. All of these materials are themselves waste products with little or no commercial value. The use of these waste products to consolidate another waste is often an advantage to the processor who can treat two waste streams at the same time. For example, the production of a pozzolanic reaction with power plant fly ash permits the flue gas cleaning sludge to be combined with the normal fly ash output and lime (along with other additives) to provide an easily handled solid.

Advantages of lime-based techniques that produce pozzolanic cements are several:

- The materials are often very low in cost and widely available.
- Little specialized equipment is required for processing, as lime is a common additive (to neutralize wastes) in other streams.
- The chemistry of lime-pozzolanic reactions is relatively well known.
- Extensive dewatering is not necessary because water is required in the setting reaction.

The lime-based systems have many of the same potential disadvantages as cement-based techniques:

- Lime and other additives add to the weight and bulk to be transported and/or landfilled.
- Uncoated lime-fixed materials may require specially designed landfills to guarantee that the material does not lose potential pollutants by leaching.

5.2.3 Thermoplastic Techniques Including Bitumen, Paraffin and Polyethylene

Development of thermoplastic fixation systems for use in radioactive waste disposal has led to a waste containment system that can be adapted to industrial wastes. In processing radioactive waste with bitumen or other thermoplastic material, the waste is dried, heated, and dispersed through a heated plastic matrix. The mixture is then cooled to solidify the mass and is usually buried in a secondary container such as a steel drum. Variations of this fixation system can use other thermoplastic organic materials such as paraffin or polyethylene.

The process requires some specialized equipment to heat and mix the waste and plastic matrix, but equipment for mixing and extruding waste and plastic is available. The ratio of matrix to waste is generally quite high (1:1 to 1:2 fixative to waste on a dry weight basis). The matrix and the dry waste must be mixed at temperatures ranging from 130°C to 230°C, depending on the melting characteristics of the material and the type of equipment used.

A variant of this process uses emulsified bitumen, which is miscible with wet sludge. With this process, the mixing can be done at any convenient temperature below the boiling point of the mixture. The overall mass must still be heated and dried before it is suitable for disposal. Ratios of emulsion to waste of 1:1 to 1:1.5 are necessary for adequate incorporation.⁴

In many cases, the type of waste to be disposed rules out the use of any organic-based fixation technique. Organic chemicals that are solvents for the matrix obviously cannot be disposed of directly by this disposal system. Strongly oxidizing salts such as nitrates, chlorates, or perchlorates will react with organic matrix materials and cause slow deterioration. At the elevated temperatures necessary for processing, matrix-oxidizer mixtures are extremely flammable.

Leach testing undertaken on anhydrous salts embedded in bitumen as a matrix indicates that rehydration of the embedded compound can occur when the sample is soaked in water, which can cause the asphalt or bitumen to split apart, greatly increasing the surface area and the rate of waste loss.⁶ Some salts (such as sodium sulfate) will naturally dehydrate at the temperatures required to make the bitumen plastic, so these easily dehydrated compounds must be avoided in thermoplastic stabilization.

The following are the major advantages of the thermoplastic-based disposal systems:

- The leaching loss rates are significantly lower than those observed with cement-based systems.
- By disposing of the wastes in a dry condition, the overall volume of the waste is greatly reduced.
- Most matrix materials are very resistant to attack by aqueous solutions. Microbial degradation is minimal.
- Most matrices adhere well to incorporated materials.
- Materials embedded in a thermoplastic matrix can be reclaimed if needed.

The following are the principal disadvantages of thermoplastic-based disposal systems:

- Expensive, complicated equipment requiring highly specialized labor is necessary for processing.
- These systems cannot be used with materials that decompose at high temperatures, especially citrates and certain types of plastics.
- There is a risk of fire in working with organic materials such as bitumen at elevated temperatures.
- During heating, some mixes can release objectionable oils and odors, causing secondary air pollution.

- The waste material to be incorporated must be dried, which requires large amounts of energy. Incorporating wet wastes greatly increases losses through leaching.
- The incorporation of tetraborates or iron and aluminum salts in bitumen matrices causes premature hardening and can clog and damage mixing equipment.
- Strong oxidizers usually cannot be incorporated into organic materials without the occurrence of oxidizing reactions. High concentrations of strong oxidizers at elevated processing temperatures can cause fires.
- Dehydrated salts incorporated in a thermoplastic matrix will slowly rehydrate if the mixture is soaked in water. The rehydrated salt will expand the mixture and cause the waste block to fragment.
- The plasticity of matrix-waste mixtures may require that containers be provided for transportation and disposal of the material.

5.2.4 Organic Polymer Techniques

Organic polymer techniques were developed as a response to the requirement for solidification of radioactive waste for transportation. The most thoroughly tested organic polymer solidification technique is the urea-formaldehyde (UF) system. The polymer is generally formed in a batch process in which the wet or dry wastes are blended with a prepolymer in a waste receptacle (steel drum) or in a specially designed mixer. When these two components are thoroughly mixed, a catalyst is added and mixing is continued until the catalyst is thoroughly dispersed. Mixing is terminated before the polymer has formed and the resin-waste mixture is transferred to a waste container if necessary. The polymerized material does not chemically combine with the waste; it forms, instead, a spongy mass that traps the solid particles. Any liquid associated with the waste will remain after polymerization, thus often requiring that the polymer mass be dried before disposal.

Several organic polymer systems are available that are not based on urea-formaldehyde resin. Dow Industrial Division is developing vinyl ester-styrene polymer systems (Nuclear Binder 101) for use with radioactive waste.⁷ Testing of this material is currently underway in the Nuclear Regulatory Commission's research programs.

The Polymeric Materials Section at Washington State University has developed a polyester resin system that is being used in solidification of

radioactive wastes. This system is currently in a pilot-plant stage in the processing of radwastes.^{8,9}

The following are the major advantages of the organic polymer systems (especially the UF-resin system):

- Less fixative is required for solidifying the same amount of waste. The waste-to-fixative ratio is usually about 30% greater for a UF organic polymer than for cement.
- The waste material treated is usually dewatered, but not necessarily dried. (The finished, solidified polymer, however, must be dried before ultimate disposal.)
- The organic resin used is consistently less dense (specific gravity is approximately 1.3) than cement. The low density reduces the transportation costs to a disposal site.
- The solidified resin is nonflammable, and high temperatures are not required for forming the resin.

The major disadvantages of the organic resin technique, especially the UF resin system, are the following:

- No chemical reactions that chemically bind the potential pollutants occur in the solidification system. The particles of waste material are trapped in an organic resin matrix.
- Catalysts used in the UF systems are strongly acidic: the waste-UF mixture must be maintained at $\text{pH } 1.5 \pm 0.5$ for solidification to occur rapidly. The low pH can put many waste materials into solution. If the pH is not lowered to 1.5, the polymerization is slow; solids will settle out, and the fixed material will not be trapped effectively.
- Waste-UF mixtures shrink as they age and will produce uncombined "weep water" during aging. This must be allowed to evaporate to produce a fully-cured polymer. The "weep water" may be strongly acid and may contain high levels of pollutants.
- Some catalysts used in polymerization are highly corrosive and require special mixing equipment and container liners.
- The reactions producing the resin may release fumes that can be harmful or disagreeable even in low concentrations.

- Some cured resins are biodegradable (especially UF-based systems), according to several manufacturers.
- Secondary containment in steel drums is common practice in organic resin-waste fixation. This raises costs for processing and transportation.

5.2.5 Encapsulation Techniques

All fixation systems depend on binding particles of waste material together. To the extent to which the binder coats the waste particles, the wastes are encapsulated. The systems addressed under encapsulation are those in which waste that has been bonded together is enclosed in a coating or jacket of inert material. A number of systems for coating solidified industrial wastes have been examined by TRW Corporation.¹⁰ In most cases coated materials have suffered from lack of adhesion between coatings and bound wastes and lack of long-term integrity in the coating materials. After investigating many alternative binding and coating systems, TRW Corporation produced detailed plans for what it considered the optimum encapsulation system. The TRW-developed system has been thoroughly tested and published data on the process are available.¹¹

The TRW encapsulation system requires that the waste material be thoroughly dried. The dried wastes are stirred into an acetone solution of modified 1,2 polybutadiene for five minutes. The mixture is allowed to set for two hours. The optimum amount of binder is 3% to 4% of the fixed material on a dry-weight basis. The coated material is placed in a mold, subjected to slight mechanical pressure, and heated to between 120°C (250°F) and 200°C (400°F) to produce fusion. The agglomerated material is a hard, tough, solid block. A 3.5-mm-thick polyethylene jacket is fused over the solid block and adheres to the polybutadiene binder. In a 360 to 450 kg block, the polyethylene would amount of 4% of the fused waste on a weight basis.

The major advantages of an encapsulation process is that the waste material never comes in contact with water, so very soluble materials such as sodium chloride can be successfully encapsulated. The impervious jacket eliminates all leaching into contacting water as long as the jacket remains intact.

The major disadvantages of encapsulation are the following:

- The resins required for encapsulating are expensive.
- The process requires large expenditures of energy in drying, fusing the binder, and forming the jacket.
- Polyethylene is combustible with a flash point of 250°C, making fires a hazard.

- The system requires extensive capital investments in equipment.
- Skilled labor is required to operate molding and fusing equipment.

5.2.6 Self-Cementing Techniques

Some industrial wastes, such as the sludges from flue gas cleaning or desulfurization, contain large amounts of calcium sulfate or calcium sulfite. A technology has been developed to treat these types of wastes so that they become self-cementing.¹² Usually a small portion (8-10% by weight) of the dewatered sulfite/sulfate sludge is calcined under carefully controlled conditions to produce a partially dehydrated, cementitious calcium sulfate or sulfite. This calcined waste is then reintroduced into the waste sludge along with proprietary additives. Fly ash is added to adjust moisture content. The finished product is a hard, plaster-like material with good handling characteristics and low permeability.

The major advantages of self-cementing systems are the following:

- No major additives have to be manufactured and shipped to the processing site.
- The process is reported to produce faster setting times and more rapid curing than comparable lime-based systems.
- The material produced is stable, nonflammable, and nonbio-degradable.
- There are reports of effective heavy metal retention, perhaps related to chemical bonding of potential pollutants.¹¹
- These systems do not require completely dry waste. The hydration reaction uses up water.

The major disadvantages of the self-cementing systems are the following:

- Only high-sulfate or high-sulfite sludges can be used.
- Self-cemented sludges have much the same leaching characteristics as cement and lime-based systems.
- Additional energy is required to produce the calcined cementitious material.

- The process requires skilled labor and expensive machinery in calcining waste and mixing the calcined waste with additives to produce the fixed waste.

5.2.7 Glassification

Where material is extremely dangerous or radioactive, it is possible to combine the waste with silica and fuse the mixture into glass.¹³ Glasses are only very slowly leached by naturally occurring water, so this approach is generally assumed to produce a safe material for disposal without secondary containment.

The major advantages of glassification are the following:

- The process is assumed to produce a high degree of containment of wastes.
- The additives used are relatively inexpensive (syenite and lime).

The major disadvantages of glassification are the following:

- The process is energy intensive. A charge must be heated to 1350°C to produce a satisfactory melt.
- Some constituents, especially metals, may be vaporized before they combine with the molten silica in the glass.
- Specialized equipment and trained personnel are required for this type of operation.

5.3 RANGE OF APPLICABILITY

Fixation usually is applied to semiliquid wastes for production of solid material. From the previous discussions in this chapter, it can be seen that a wide variety of possible fixation systems exist, and obviously not every system is applicable to every waste in every situation. Table 5.1 lists organizations that develop and/or market chemical fixation techniques, and the types of waste that can be treated by each specific technique. Many companies involved with waste solidification/stabilization refuse to accept organic-rich wastes for treatment by their techniques. Organics, especially oily materials, interfere with the polymerization of silicate materials, so the cement or pozzolan-based fixatives tend to lose cohesion and never produce a "set." Fixing techniques that depend on encapsulation with organic resins encounter problems due to the solvent effects of organic wastes. Any fixation techniques that require that the waste be heated (as in asphalt or plastic

Table 5.1 Available Chemical Fixation Systems

Vendor	Process Type/Fixation Agent	Wastes Treated	Wastes Excluded
Atcor Washington, Inc. Park Mall Peekskill, NY 10566	Masonry-based solidification/ cement	Nuclear wastes	Sludges that do not combine with cement
Environmental Technology Corp. 1517 Woodruff St., Ste. 200 Pittsburgh, PA 15220	Solidification/lime, etc.	Pickling acids; spent plating solutions; scrubber sludges, organic sludges; wastewater treatment sludges	None listed
Chemfix, Inc. 1675 Airline Highway Kenner, LA 70063	Cements and soluble silicates	Not specified	Wastes containing certain organic compounds and toxic constituents
Davo Lime Co. 650 Smithfield St. Pittsburgh, PA 15222	Pozzolanic or cementitious/ "Calcilox"	Calcium-based SO ₂ scrubber sludge	Sludges containing organics and sewage wastes
Stabatrol Corp. 1402 Conshohocken Rd. Norristown, PA 19401	Cementitious	Most industrial wastes	None specified
Stablex Corp. 1 Radnor Corporation Center Ste. 112 Radnor, PA 19087	Silicate	Inorganic wastes; some organic wastes	Oils; solvents; greases; and dilute liquid wastes
TJK, Inc. 7407 Fulton Ave. North Hollywood, CA 91605	Cementitious	Industrial waste sludges	Sludges containing high levels of fats and oil; paint wastes

Table 5.1 (Cont'd)

Vendor	Process Type/Fixation Agent	Wastes Treated	Wastes Excluded
Todd Shipyards Corp. P.O. Box 1600 Galveston, TX 77553	Organic polymer	Radioactive waste sludge	None specified
Protective Packaging, Inc. 328 Production Ct. Jeffersontown, KY 40299	Solidification/organic polymer	Nuclear wastes	None listed
Sandia Laboratories Albuquerque, NM 87115	Solidification/hydrous oxides of Ti, Zr, Nb, Ta	High-level radioactive wastes	Low-value, low- hazard waste (because of high cost of the process)
Sludge Fixation Technology, Inc. 227 Thorn Ave. Orchard Park, NY 14127	Cementitious/calcium sulfite and sulfate	Sulfite/sulfate sludges from SO ₂ scrubbing	Not specified
I.U. Conversion Systems, Inc. 115 Gibraltar Rd. Horsham, PA 19044	Pozzolanic/flyash, etc.	SO ₂ scrubber sludges; wastes from electro- plating, steel mills, and chemical processes	Some organic wastes
Ontario Liquid Waste Disposal, Ltd. 160 Torbay Rd. Markham, Ont. L3R 1G6 Canada	Silicate	Mine tailing wastes, sewage sludge; industrial inorganic wastes	Some organic wastes

Table 5.1 (Cont'd)

Vendor	Process Type/Fixation Agent	Wastes Treated	Wastes Excluded
Polymeric Materials Section Dept. of Materials Science and Engineering Washington State University Pullman, WA 99164 (developer)	Organic polymer	Low-level radioactive wastes; metal ion wastes; cyanides; arsenic waste; some organic wastes	Highly acidic sludges
Werner and Pfleiderer Corp. 160 Hopper Ave. Waldwick, NJ 07463	Bitumen encapsulation	Low- and intermediate- level radioactive wastes; hazardous industrial wastes	Sludges containing strong oxidizers
TRW System Group One Space Park Redondo Beach, CA 90278	Inorganic cement/ polybutadiene resins	Solid wastes and sludges	None given

Adapted from Ref. 2.

encapsulation procedures) often cannot be used with organic-rich wastes because of vaporization or danger of fire.

In addition to the composition of the waste material, other factors, such as the quantity of waste involved, the cost of the specific process, and the properties of the disposal site all play a role in a decision on the fixation procedures to be used. By careful evaluation of economics, the hazardous nature of the material, and the containment provided by geologic and hydrologic situations at surrounding landfills, it should be possible to work out a minimum cost for responsible disposal of a particular waste.

The costs for waste fixation processes are geared to the volume of the waste to be fixed; therefore, it may become cost-advantageous to concentrate hazardous waste materials into a minimum volume to reduce handling and additive requirements. When hazardous wastes are concentrated, the precautions involved in handling and transportation are necessarily increased, so on-site stabilization (or at least solidification) would be desirable. In fact, solidification (stabilization) may simply become a unit operation to complete the waste treatment system, and the waste treatment operations could be tailored to produce the hazardous residue in a minimum volume with a pH and chemical composition compatible with the stabilization system that is required to insure safe containment under specified landfill conditions.

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6 ULTIMATE DISPOSAL

6.1 SECURE LANDFILL

6.1.1 Background

Landfilling has historically been the preferred means of disposing of hazardous waste; however, recent experiences at Love Canal in New York and other burial operations have demonstrated the potential for severe human health and environmental impacts from improper landfilling. Many argue that because many of these wastes remain hazardous for very long periods, they should not be landfilled. Although destruction or recycling of hazardous wastes is preferable to landfilling, the fact remains that, for the foreseeable future, land disposal will be necessary because it is technically not possible to recycle, treat, or destroy all hazardous wastes.

Over the past decade, research and investigations of good and bad practices have advanced the state of the art of landfilling significantly, making landfilling much more than just burial of wastes. New regulations require that landfills provide long-term protection of groundwater, surface water, air, and human health. Although the state of the art is still developing, a number of techniques are now available for effectively reducing the adverse health and environmental effects from landfills.

6.1.2 Process Description^{1,2}

Hazardous waste landfills are required to meet a stringent environmental performance standard coupled with design and operating criteria. The performance standard is a standard designed to prevent groundwater contamination and includes groundwater monitoring and response requirements applicable to all land disposal (i.e., landfills, surface impoundments, waste piles, and waste treatment facilities). However, the rules allow owners and operators of land disposal facilities the flexibility to use alternative design and operating procedures if it can be demonstrated that they provide as much groundwater protection as those criteria and procedures set forth in the regulations.

The design and operating standards require that landfills have liners to prevent migration of wastes to the subsurface soil or to groundwater or surface water. EPA has suggested that synthetic liners be at least 30 mils thick, chemically resistant to the wastes managed at the landfill, and protected by at least six inches of bedding material both above and below it. The bedding material should consist of materials no coarser than sand (SP) as defined by the Uniform Soil Classification System. Secondary soil liners are suggested by EPA as a backup to synthetic liners and for landfills that will not be capped for at least 30 years. EPA recommends that the soil

liners normally be made of clay, be at least two feet thick, and have a saturated hydraulic conductivity of not more than 1×10^{-7} cm/sec. The soil liner should be compacted as tightly as possible to minimize the transmission of leachate.

Landfills are also required to have leachate collection and removal systems (such as drains to collect leachate and pumps to remove it). The system must be designed and maintained so that the leachate depth over the liner does not exceed one foot. The liner must be constructed of materials that can withstand chemical attack and pressures from the leachate. To meet these standards, EPA suggests a drainage layer at least 12 in. thick with a minimum slope of 2% and a hydraulic conductivity of not less than 1×10^{-3} cm/sec. Drainage tiles approximately 4 in. in diameter and set 50 to 200 feet apart should effectively minimize leachate collection on the liner. A variance from the liner and leachate requirements is available to units where owners or operators can demonstrate that wastes from their units will never migrate to groundwater or surface water. Existing landfills are exempt from these requirements.

A landfill must have a run-on and run-off management system to control at least the water volume from a 25-year storm. In addition, at closure, landfills must be provided with a final cover (capped) to minimize the infiltration of precipitation. EPA suggests that a three-layer cap consisting of a vegetative top cover, a middle drainage layer, and a bottom layer of low permeability will achieve this goal.

The groundwater protection requirements are designed to insure that owners or operators detect any groundwater contamination, and perform corrective action, if necessary, during the active life of the unit plus a compliance period designated in the permit. The groundwater monitoring and response program requires the installation of a groundwater monitoring system at the waste boundary (including both upgradient and downgradient sampling wells). If migration is detected, a compliance monitoring program, to track the migration of hazardous constituents that are reasonably expected to be in waste from the facility, must be established. The standard requires that hazardous constituents not exceed certain concentration limits. If any of these limits are violated then corrective action is required. Corrective action consists of the removal of the contamination (by pumping or other means) or in-situ treatment of the hazardous constituents.

The regulations provide an option whereby owners or operators may comply with a more stringent set of design and operating standards and thereby obtain a waiver of the groundwater monitoring and response requirements. These special standards include two bottom liners (instead of the single liner generally required) and a leak detection system between liners (in addition to the leachate collection and removal system). If a leak is discovered, the leaking liner must be repaired or replaced, or else the owner or operator becomes subject to the groundwater monitoring and response requirements.

6.1.3 Types of Wastes/Applicability to DOE Wastes

Land disposal (in a permitted hazardous waste landfill) is an approved method for disposal of most types of hazardous wastes. Landfills continue to be the least expensive, in comparison with other technologies, and may account for up to 80% of the hazardous waste disposed of.³

Despite the ongoing development in sophisticated hazardous waste management methods (e.g., high-temperature incineration, physical/chemical treatment and resource recovery), some materials cannot be treated by any of these more modern methods. Some wastes may be too contaminated with heavy metals and other noncombustible materials to incinerate, too thick to inject in deep wells, too difficult (or impossible) to degrade chemically for harmless discharge into the air or surface waters, or unsuitable for processes involving recovery of reusable materials or energy. A secure landfill is also a method for disposal of contaminated residues from recycling, resource recovery, and incineration, which always have something left over.⁴

There are some limitations on the wastes that can be disposed of by landfilling. Landfill disposal of mineral oil dielectric fluids or other PCB liquid wastes is permitted (in an Annex II Chemical Waste Landfill, specified in the Toxic Substances Control ACT, TSCA) only if the PCB concentration is less than 500 ppm. Liquids with a PCB concentration greater than 500 ppm, and PCB capacitors, must be disposed of in an approved TSCA Annex I incinerator. PCB transformers, containers, and hydraulic machines may be disposed of in an Annex II Chemical Waste Landfill, provided they are properly drained and rinsed.

Certain restrictions also exist for landfilling ignitable or reactive waste. These wastes may not be placed in a landfill unless the waste is treated, rendered, or mixed before or immediately after placement in the landfill so that the material no longer meets the definition of an ignitable or reactive waste. Ignitable wastes in containers may be landfilled without meeting the above requirements, provided that the wastes are protected from any material or conditions which may cause them to ignite. At a minimum, ignitable wastes must be disposed of in nonleaking containers which are handled and placed so as to avoid heat or sparks; must be covered daily with soil or other noncombustible material to minimize the potential for ignition of the wastes, and must not be disposed of in landfill cells that contain or will contain other wastes which may generate heat sufficient to cause ignition of the wastes.

Landfill disposal of liquid wastes is also subject to special requirements. Bulk liquids may not be placed in a landfill unless the landfill has a liner which is chemically and physically resistant to the added liquid, and a functioning leachate collection and removal system. However, liquids may be placed in a landfill if all free-standing liquid has been removed by decanting or other methods (i.e., mixed with absorbent or solidified) so that free-standing liquid is no longer observed; the container is small, such as an

ampule; or the container is designed to hold free liquids for use other than storage, such as a battery.

6.1.4 Environmental Impacts

Landfill disposal of hazardous wastes presents two major environmental problems: the waste and its hazardous constituents may remain hazardous for a long period of time, and the waste or its constituents and by-products may migrate from the confines of the landfill into the broader environment.

Many hazardous wastes (e.g., heavy metals) placed in a landfill will not degrade to a point where they are no longer hazardous, or will do so only slowly. Toxic organics may degrade in the anaerobic condition of the landfill, but this can take 100 years or more and the degradation may not be complete, leaving toxic degradation products. Current scientific knowledge about the degradation of hazardous substances in landfills is incomplete.

Hazardous materials very likely will migrate from a landfill into the surrounding environment. This may occur several years or even decades after they are placed in the facility. Precipitation or groundwater may infiltrate the facility unless a water-tight containment system is constructed and perpetually maintained. Also, liquids within the wastes can generate leachates, which eventually leak out of the facility and migrate into the soil and groundwater, unless a liner and/or leachate collection system is perpetually maintained.⁴

6.2 DEEP-WELL INJECTION

6.2.1 Background

Deep-well injection is a process for disposing of wastes by pumping them into porous sandstone and limestone formations 3,000 to 10,000 ft below the earth's surface. The wastes are then permanently stored in the underground strata. The technique has been successfully used for many years in oil fields to return large volumes of brine removed during oil production. There are now about 70,000 wells used for brine disposal.⁵

Deep wells have received only limited use for industrial waste disposal, primarily due to legal and regulatory restraints and uncertainties, as well as to technical considerations.⁶ About 300 wells are used for such wastes: most of these are owned by companies that use them for their own wastes, but about a dozen are owned by waste disposal companies that use them for commercial waste disposal. The majority of both types of wells (brine and industrial) are located in the oil-producing states.⁶

Deep-well injection is permitted in about 20 states. In states where it is prohibited, the prohibition is usually due to a lack of suitable geologic formations rather than to opposition to the process.⁷ Suitable sedimentary formations are found under about half the land area of the U.S., and ideal conditions are found under about a quarter of it.⁵

6.2.2 Process Description

Injection strata generally are sandstone or limestone. Aquicludes (layers of impervious materials that maintain the isolation) may be clays, shale, marl, crystalline limestone, siltstones, impervious sandstone or gypsum. A test well or wells generally are necessary to provide verification of aquiclude formations, groundwater levels, and depths of potential injection strata. Pump-in tests to determine flow at various injection pressures can be performed. The compatibility of wastes with the stratum samples should be tested at the bottomhole temperature and pressure, because the formation of precipitates is a major concern.

More than one well casing is often necessary in deep wells to protect fresh water aquifers from contamination, to close off zones of soft rock and saltwater aquifers, and to protect gas and oil bearing strata. A typical injection well is diagrammed in Fig. 6.1. State and federal laws dictate the methods of sealing, cementing, and testing the wells.

6.2.3 Environmental Impacts

Considerable controversy exists about the potential environmental impacts associated with deep-well injection of hazardous wastes. Proponents argue that deep-well injection is safe as long as the wells are properly engineered and constructed because the injection sites have been separated from freshwater zones for millions of years by layers of impervious material that maintain the isolation. Generally, liquid movement within the injection formations is measured in inches per year, so migration is negligible.⁵

Opponents of deep-well injection point out that there is little precise knowledge about the actual fate of the injected wastes, and the thought of carcinogens, mutagens, and other potent chemicals wandering around below the earth's surface is profoundly disturbing.⁵ Critics cite such incidents as the earthquakes in the Denver area that were apparently triggered by injection of wastes at the Rocky Mountain Arsenal, and the 1968 eruption of an overpressurized waste injection well in Erie, Pa., as additional potential hazards associated with this waste disposal technique. However, advocates of the technique claim that the wastes in Colorado were injected into fractures in granite rock, the Erie well was poorly engineered, and construction techniques and new regulations should minimize any of these types of occurrences in the future.⁵

Fig. 6.1 Schematic Diagram of a Waste Injection Well Completed in Competent Sandstone (Source: adapted from Ref. 6)

The EPA has proposed specific requirements for disposal of hazardous wastes by underground injection under the RCRA. The regulations include requirements for general operating practices, waste analysis, monitoring and response, closure and post-closure care, financial responsibility, and special handling of reactive or incompatible waste. Underground injection of hazardous waste is under the jurisdiction of both RCRA and the Safe Drinking Water Act (SDWA), which created an Underground Injection Control (UIC) program. EPA has concluded that disposal of hazardous wastes by underground injection in each state will be regulated under RCRA until a UIC program has been established in that state.⁸

6.2.4 Economics

Initial capital costs for a deep well are high. A properly engineered well (5,000-10,000 ft below the surface) can cost about \$1,000,000 to build.⁷ However, once the well is drilled, the costs of operation are low. In some cases, pumping of wastes is not even required because negative pressure in the wells pulls the waste down into the underground strata.

6.2.5 Applicability to DOE Wastes

Deep-well injection probably is not a viable disposal option for most DOE wastes. Deep-well injection is most suited for large quantities of similar wastes, because different waste types may react with one another. For example, in Ohio, at the only permitted commercial injection well in Region V, mixing of wastes is strictly regulated by requiring the injection of a saltwater buffer between different wastes.⁷ Also, wastes suitable for deep-well injection must be fairly free from suspended solids: sometimes filtering of the wastes is required in order to protect the well from clogging.

Availability is another factor affecting the applicability of this option. There are extremely few commercial wells nationwide. Due to the high initial capital cost and the unsuitability for disposal of a wide mix of waste streams, this option is probably not a feasible one at DOE sites, even if the geology were suitable.

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APPENDIX

Table A-1 Characteristics of American Waste Exchanges

United States Exchange	Type of Exchange	Service Area	Material Categories Listed	Most Successful Transfers	Profit	Listing Fee	Subscription Fee	Government Funding	Confidential
MIWE (Midwest)	Information	National			No	\$10	No	Yes	(see A-1 No)
IIWIE (Iowa)	Information	Mixed ^a	Oils, wood products, metals, plastics, paper, chemicals	-	No	No	No	Yes	Yes
ACE (Amer. Chem.)	Broker	National	Surplus chemicals (inorg. + org.) acids, alkalies	Virgin chemicals	Yes	No	Yes ^b	No	Yes ^c
EKC (Enkarn)	Broker	National	Films, foils, laminates, equipment	Same as listed	Yes	No ^d	No ^d	No	Yes
ECHO (Ill.)	Broker Consulting	Int'natl	-	-	Yes	-	-	No	-
GWE (Georgia)	Information	Mixed ^a	-	-	No	\$25/item	\$25 ^f	No ^e	Yes
ICWE (WETA-Wash.)	Information	Interstate + Canada ^h	All materials except nuclear	-	No	No	No ^g	No	Yes
MACI (Minn.)	Information	State	All types of hazardous and nonhazardous materials	-	No	\$30/3 mo \$60/12 mo	No ⁱ	No	-
TE (The Exchange)	Broker	Int'natl Consulting	Hazardous and nonhazardous waste, secondary materials, excess inv.	Used equip, metals, electronics	Yes	Commissions and consulting fees		No	Yes
OIWIE (Oregon)	Information	State			No	No	No	No ^j	Yes
TWS ^k (Tennessee)	Information	State							
Waste (World)	Information	National			No	No ^m	\$150/yr	No	-
ZWSI (Zero)	Broker	Regional ⁿ	Surplus chemicals and other reprocessed materials	Same as listed	Yes	No regular listings	-	No	-
CWE (California)	Information	Regional ⁿ	-	-	No	No	No	Yes	-
WMC (Ind.)	Information	National	-	-	No	\$25/item/ 6 mo	No	No	Yes
IWIE (Columbus)	Information	National	-	-	No	\$5/item	No	No	Yes

Table A-1 (Cont'd)

United States Exchange	Type of Exchange	Service Area	Material Categories Listed	Most Successful Transfers	Profit	Listing Fee	Subscription Fee	Government Funding	Confidential
IWIE (Newark)	Information	State ^P		-		\$5/item	\$5/yr	No	Yes
MCWE (Mecklenburg)	Information	Regional	All types of wastes from all industries		No	No	No	Yes	Yes
UCC (Union Carbide)	Broker Material	National ^S	Damaged, off spec. or obsolete prod., slime, sludge, residues, catalysts, metallic waste, flue dust		Yes	Not Applicable ^F		No	No
HCC (Houston)	Information	Regional ^T			No	\$10/item	\$15/yr	No	Yes
AARRI (Amer. All.)	Information	State			-	\$6/item ^U	Yes ^U	No	Yes
ORE (Ohio)	Broker	Int'natl ^V	Emphasis on hazardous waste		Yes	No ^W	No	No	Yes

^AAvailable listings only in state-wanted listings from out-of-state.

^BA \$250 charge to become member with variable commissions upon transfer.

^CAnonymity is kept, but not considered important.

^DTen percent of purchase price charged for match-ups.

^EOriginally had government funding.

^FCharged to nonlisters.

^GFree to Western Environmental Trade Association of Washington members only.

^HServes State of Washington primarily, with some activity in Oregon, Idaho, and Western Canada. Plans to link with other exchanges.

^IService included as part of membership in Minnesota Association of Commerce and Industry.

^JOriginally received state funds, but not supported by Western Environmental Trade Association.

^KExchange is in process of being transferred from a government to a nongovernment agency.

^LFee is for commercial Associate Members, not for government, academic, or trade associations.

^MFees are charged for computer search of various wastes files.

^NSan Francisco-Oakland Bay area.

^OColumbus, Ohio area.

^PSome listings from New York, Pennsylvania.

^QFourteen counties in North Carolina.

^RInternal distribution of lists within Union Carbide Corp.

^SService is for all Union Carbide companies.

^THouston, Texas area.

^UAARRI members are not charged for listings, but membership costs vary from \$50 to 2,000 per year.

^VUnited States and Canada.

^WFee paid on completed transfers.

Source: Ref. 1.

Table A-2 Characteristics of European Waste Exchanges

Foreign Exchange	Type of Exchange	Service Area	Material Categories Listed	Most Successful Transfers	Profit	Listing Fee	Subscription Fee	Government Funding	Confidential
CWME (Canada)	Information	National	1a,b,2a,b,c,3a,b,4,5,6a,b,7, 8a,b,c,9,17	2a,b,6b,7	No	No	\$20/yr	Yes	-
UKWME (U.K.)	Information	National	1a,b,2a,c,3,4,5,6a,7,8a,b,c 9,11,12	1a,b,3,4,7,8c,10	No	No	\$45/yr	Yes ⁽¹⁾	Yes
NIMRA (U.K.)	Information	National	17 ⁽²⁾	17 ⁽²⁾	No	No	\$32/yr	No ⁽³⁾	No
SWE (Switzerland)	Information	National	-	-	No	-	-	No	Yes
CIAE (Austria)	Information	National	-	-	No	-	-	No	Yes
EWEE (Austria)	Information	National	-	-	-	-	-	-	No
NWE (Sweden)	Information	Int'l ⁽⁴⁾	1a,b,3a,b,5,6a,b,7,8a,b 9,13	1a,b,5,8a,9	No	No	Annual dues	No ⁽⁵⁾	Yes
TWME (Italy)	Information	National	1a,b,6a,7,8a,b,c,9,14	-	No	-	-	No	Yes
ANIC (Italy)	Information	National	17 ⁽⁶⁾	-	No	No	Yes ⁽⁷⁾	No	-
WEI (Israel)	Information	National	-	-	No	No	No	Yes	Yes
MWDA (Australia)	Information	Metropol-itan ⁽⁸⁾	1b,3a,4,5,7,8a,9,11,12 13,15	1b,3a,4,6c,14	No	\$5/item	No	Yes	Yes
IWES (Australia)	Information	Regional ⁽⁹⁾	1a,b,3,4,5,7,8a,9,13,16	1b,4,7,9,14	No	No	No	Yes	Yes
ANRED (France)	Information	National	-	-	No	-	-	Yes	-
VCI (Germany)	Information	Int'l ⁽¹⁰⁾	-	-	-	-	-	No	Yes
DIHT (Germany)	Information	National	-	-	No	No	Yes ⁽¹¹⁾	No	-

Table A-2 (Cont'd)

Foreign Exchange	Type of Exchange	Service Area	Material Categories Listed	Most Successful Transfers	Profit	Listing Fee	Subscription Fee	Government Funding	Confidential
VNCI (Netherlands)	Information	National	-	-	No	-	-	No	-
FICB (Belgium)	Information	National	-	-	No	\$25 ⁽¹²⁾	Yes ⁽¹²⁾	No	Yes
OBEA (Belgium)	Information	National	1a,b,5,6a,7,8a,b,c,9,11,12,14	1a,b,5,6a,7,8a,b,c,9	No	No	No	Yes ⁽¹³⁾	Yes

Materials Key:

- 1a - Organic Chemicals
- 1b - Solvents
- 2a - Oils
- 2b - Fats
- 2c - Waxes
- 3a - Acids
- 3b - Alkalies
- 4 - Inorganic Chemicals
- 5 - Metals
- 6a - Metal Containing Sludges
- 6b - Metal Containing Slugs
- 7 - Plastic
- 8a - Textile
- 8b - Leather
- 8c - Rubber
- 9 - Wood and Paper Products
- 11 - Catalysts
- 12 - Food Processing Wastes
- 13 - Minerals
- 14 - Waste Oil
- 15 - Glass
- 16 - Used Containers
- 17 - Used Plant and Equipment

- (1) UKWME was supported by government and directed to achieve 70% of costs from revenue by January 1980. This was not achieved and UKWME has been discontinued.
- (2) Used plant, reprocessed valves, old stores tanks, compressors, small amount of chemicals.
- (3) Originally received government funding.
- (4) Service area includes Denmark, Norway, Finland, Sweden.
- (5) Received government funding for first 3 years.
- (6) Chemical products, process equipment.
- (7) Included as part of membership in National Association of Chemical Industries.
- (8) Services New South Wales area.
- (9) Services Victoria region.
- (10) Service area includes Belgium, Netherlands, Norway, Switzerland, Italy.
- (11) Included as part of membership fees in Chamber of Commerce.
- (12) Cost of listing is included as part of Trade Association fee for members. Nonmembers pay \$25 for listing.
- (13) Government is providing financial support on a 2-year experimental basis.

Source: Ref. 1.

Table A-3 Successful Waste Transfers in Oregon:
Energy Savings Analysis

Waste Description	Amount	Estimated Savings (10 ⁶ Btu)
<u>April 1 - June 30, 1978</u>		
Metal racks	0.25 tons	2.3
Waxed sulphate board	45.50 tons	1,203.0
Polyethylene drums	0.60 tons	22.3
Paint	0.20 tons	1.4
Solvent	0.16 tons	1.1
Subtotal		1,230.1
<u>July 1 - September 30, 1978</u>		
Chlorine tablets	100 lb	11.7
Waste acid	500 gal	6.23
Beef by-products	600 cu yd/6 mo	-
Waxed paper labels	20 tons	487.8
Waste solvent	159 gal	4.45
Wood pallets	4,000 units	63.0
Voting booths	30 units	0.52
Subtotal		573.70
<u>October 1 - December 31, 1978</u>		
Broken plastic berry flats	2,500 units	27.8
Sheet aluminum	4,316 lb	610.7
Acetone	1,300 gal	78.2
Gasoline/oil mixture	5 gal	0.6
Gasoline (35%)/diesel (65% mix)	10,000 gal	1,422.0
Chlorinated solvent recovery waste	6,500 gal	152.0
Broken wood pallets/cardboard	200 units	3.15
Subtotal		2,294.45
<u>January 1 - April 15, 1979</u>		
5-gallon metal cans	100 units	5.67
Used lacquer thinner	200 gal	21.2
Full-twist glass gallon jars	1,440 units	3.42
Liquid waxes mixture	5,800 gal	84.9
Subtotal		115.19
Grand Total		4,213.44

Source: Ref. 1.

NORTHEAST INDUSTRIAL WASTE EXCHANGE

LISTINGS FORM

(Submit separate form for each listing.)

Exchange Use Only

Code # _____

Location _____

SIC _____

1. MATERIAL: ☐ Available ☐ Wanted
2. TYPE OF MATERIAL: ☐ Acids ☐ Alkalis ☐ Other Inorganic Chemicals
☐ Metals/Metal Containing Sludges ☐ Organic Chemicals/Solvents
☐ Oils/Fats/Waxes ☐ Plastics ☐ Textiles/Leather/Rubber
☐ Wood/Paper Products ☐ Miscellaneous
3. DESCRIPTION: Describe the material as you would like it listed in specific terms commonly used for such material. Specify condition, % solids, % metals, chemical composition, etc.: _____

4. QUANTITY: _____ lbs. _____ tons _____ gals. other _____
5. FREQUENCY: ☐ one time only ☐ daily ☐ weekly ☐ monthly ☐ quarterly ☐ yearly other _____
6. PACKAGING: ☐ loose ☐ bulk ☐ bag ☐ drum (size _____) ☐ carton ☐ bale other _____
7. GEOGRAPHIC LOCATION WHERE MATERIAL EXISTS OR IS WANTED: _____

8. FOR MATERIAL AVAILABLE: Give possible uses, if known: _____

9. FOR MATERIAL WANTED: Give possible sources, kinds of companies, if known: _____

Determining the nature and content of the subject material and its description or representation is not the Exchange's responsibility. The Exchange will not be involved in negotiations between our firm and potential customers or suppliers and will not make any determinations as to prices of materials or what may constitute hazardous substances or conditions. I agree to inform the Exchange when any negotiations have been successfully completed.

Company Name _____ Industry SIC # _____

Address _____ Telephone () _____
 (street) (area code)

_____ Zip _____
 (city) (state)

Your Name _____ Title _____

Signature _____ Date _____

Send completed form to: **NORTHEAST INDUSTRIAL WASTE EXCHANGE**
 700 E. Water St., Rm. 711, Syracuse, New York 13210

Fig. A-1 Listings Form (Source: Ref. 2)

MATERIAL AVAILABLE

Code Identification: A3-01

Item: Copper Chloride. CuCl_2 , HCL and H_2O with approx. one lb of Copper contained per gal

Availability: 3,500 gal per month

Location: Scranton, PA

MATERIALS WANTED

Code Identification: W5-01

Item: Waste Solvents -- Ketones, Esters, Aromatics, Aliphatics, Chlorinated and Blends

Quantity Desired 15,000 gal per week

Location: Albany, NY

Fig. A-2 Sample Listings - Northeast Industrial Waste Exchange
(Source: Ref. 2)

MATERIAL AVAILABLE

<u>Code</u> <u>No.</u>	<u>Classif.</u> <u>No.</u>	<u>Material</u>	<u>Quantity</u>	<u>Location</u>
A-1-2	1	Acid, 15% nitric, 5% hydro-fluoric, 5% metallic impurities, balance water	1,000 gals/mo	Northern New Jersey
A-1-14	2	Ammonia/water - approx. 12% NH ₃	3,000 gals/mo	Southern New Jersey
A-1-21	4	Miscellaneous clean solvents - toluene, xylene, benzene mix, etc.	3 drums/mo.	New York City
A-1-23	5	Waste hydraulic oil, water contaminated	6 drums/mo.	Philadelphia area

MATERIAL WANTED

W-1-5	5	Waste oil; no lacquers or thinners	10 drums/mo.	Northern New Jersey
W-1-8	10	Mixed nonferrous metals, miscellaneous sizes and forms	any amount	Central New Jersey
W-1-9	12	Sulfides, mixed composition	2 tons/wk	Southern New Jersey
W-1-15	14	Thermoplastic scrap waste	5 tons/mo.	Northern New Jersey
W-1-17	17	Waste materials; chemicals, residuals, metals, paper, wood, etc.	any amount	N.E. United States

Fig. A-3 Illustrative Listings of New Jersey Waste Information Service (Source: Ref. 1)

REFERENCES FOR APPENDIX

1. U.S. Environmental Protection Agency, *Waste Exchanges - Background Information*, SW-887.1 (Dec. 1980).
2. Northeast Industrial Waste Exchange, *Solicitation for Listings*, Syracuse, N.Y. (1981).