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Separations in Hazardous Waste Management

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Abstract

The innovative use of separation techniques can simplify the management of liquid and solid wastes. Valuable applications can include traditional unit operations as well as hybrid designs that exploit chemical, physical, and biological properties to achieve practical goals. Increasingly stringent release guidelines may dictate the use of separation technologies to recycle waste streams, rather than to decontaminate and discharge them. Process synthesis and design can be especially useful whenever separations are used to convert wastes into usable by-products. The most effective waste management schemes prevent pollution, increase by-product utilization, reduce capital investment, and eliminate unnecessary operating expenses.

Hazardous waste management problems have become more significant since the industrial revolution for at least two reasons. First, waste quantities have steadily increased due to population growth and because the waste generation rates per capita have increased. Second, the wastes have become more toxic. The manufacturers of televisions, automobiles, personal computers, and countless other consumer items also produce industrial wastes that must be managed. Disposable plastic objects, containers, and old newspapers are among the more obvious contributors to increasing municipal waste quantities, but hazardous wastes also result from their manufacture [1]. Automobile wastes, such as battery acids, paints and metal processing wastes, and residues from oil refining and mining operations, are both visible to public eyes and highly toxic, but only slightly biodegradable.

Once exotic, many toxic wastes are now commonplace. Radioactive wastes, for example, were virtually nonexistent prior to World War II. Many other industrial wastes (e.g., from solvent use, electrochemical applications, fertilizers, and pesticides, etc.), have come from relatively recent technological innovations. Waste management problems, however, are not insurmountable [2]. The best solutions are those that avoid future problems and reduce costs simultaneously [3]. Pollution prevention is one example.

Estimates of hazardous waste production rates in the U.S. were 680 million metric tons/y in 1986 [4]. Most of these are primary wastes, and wastewaters comprise about 90%. Baker and Warren provide a summary of waste management practices in 1986 (see Table 1). They estimate that about 1090 million metric tons of waste were processed in 1986; many of their listed management practices involve separation technologies. The total processed in Table 1 is 410 million metric ton/y greater than their annual production rate because many streams in Table 1 are processed and counted more than once.

Fischer presents a study using the data base generated by the Chemical Manufacturers Association [5]. Fischer estimates that in 1989 the U.S. chemical industry produced 6.17 million metric tons of hazardous solid wastes and 987 million metric tons of hazardous wastewaters. He also presents cumulative distributions of annual waste production for solids and wastewaters which are reproduced in Figure 1. They show that most of the waste generators produce relatively small amounts. About half produced less than 122 metric tons of solid wastes in 1989. Nearly 70% of the 617 chemical plants surveyed did not produce hazardous wastewaters that year, and the average solid waste production rate was 10,000 metric ton/y. On the other hand, the average wastewater rate was 1.6 million metric ton/y, but about 70% of the plants generated virtually no wastewater.

Thus, there are a few plants that generate relatively large waste streams while many more generate much smaller ones. Based upon Fischer's study for the 1980s (not shown), the incineration of hazardous solid wastes appeared to increase steadily over that decade while treatment and disposal decreased. Most of these effects were due to changes at a few plants with large waste streams.

Both studies find over 90 mass% of the wastes currently generated are aqueous, but neither study includes historical waste inventories. These latter

Table 1: Estimated U.S. waste quantities processed in 1986. [Adapted with permission from R. D. Baker and J. L. Warren, Generation and Management of hazardous waste in the United States, In *Preprints: AIChE 2nd Topical Pollutionc Prevention Conference, August 20–21, 1991, Pittsburgh, PA*, pages 163–166, American Institute of Chemical Engineers, New York (1991)].

Management Method	Number of Facilities	Quantity[a] M ton/y[b]
Disposal impoundment	70	4.19
Fuel blending	177	0.68
Incineration	197	0.99
Injection wells	63	26.1
Landfill	118	2.88
Land treatment	58	0.35
Metals Recovery	330	1.31
Other recycling	243	0.87
Other treatment	128	1.80
Reuse-as-fuel	295	1.31
Solidification	122	0.70
Solvent Recovery	1,470	1.07
Storage	1,785	172
Surface impoundment	298	211
Waste piles	71	0.62
Wastewater treatment	4,399	665
Totals[a]	9,824	1,090

[a] Some wastes processed and counted more than once
[b] Million metric tons/y

quantities include significant amounts of solids (e.g., contaminated soils and sediments), and there are clearly many opportunities for separations.

Manahan points out that hazardous wastes also arise from natural processes [6]. Many significant hazards result from various organisms found in nature [7]. The botulism toxin from *Clostridium botulinum*, for example, is one of the most acutely toxic substance known. Wastes from the food industry may include such hazards as aflatoxin B_1, produced by *Aspergillus niger*, a fungus which grows on moldy food, especially nuts and cereals. Hazardous

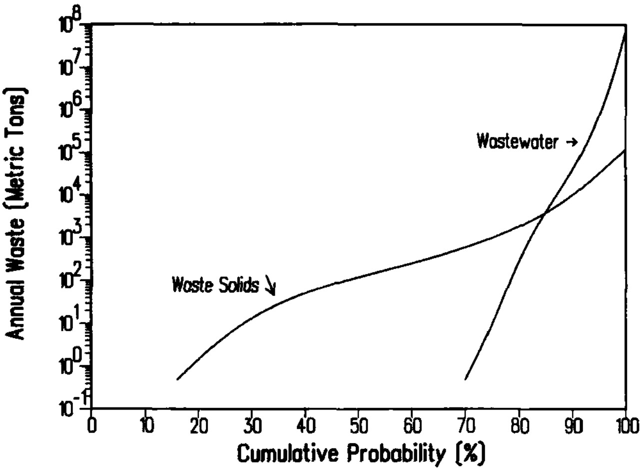

Figure 1: Cumulative distributions of wastewaters and solid hazardous wastes generated by the chemical manufacturing industry in 1989. All waste generators produced less than 0.1 million metric tons/y. [Adapted with permission from L. M. Fischer, The Chemical Manufacturers' Association hazardous waste database. In *Preprints: AIChE 2nd Topical Pollution Prevention Conference, August 20-21, 1991, Pittsburgh, PA*, pages 167–171. American Institute of Chemical Engineers, New York (1991)].

grain molds include *Cephalosporium*, *Fusarium*, *Trichoderma* and *Myrothecium* which produce trichothecenes [8]. Among the alkaloids, nicotine is particularly toxic and prevalent in many wastes [9].

Considerable research into biological warfare agents has focused on *Clostridium botulinum* and *Bacillus anthracis* which produce botulism and anthrax, respectively. Although not strictly natural products, biomedical wastes are significant both in the quantities and hazards they represent. They contain many infectious agents that occur naturally [10].

Separations and Waste Treatment

Separations exploit chemical, physical, or biological differences between species in a mixture. Chemical reaction may be used to induce phase changes or mass transfer between phases (e.g., electrolytic reduction and oxidation reactions and precipitation). Physical separations may include settling, decanting, centrifugation, filtration and flotation. Phase transitions may be used in separations through evaporation, sublimation, condensation, distillation, or precipitation. Mass transfer examples include liquid/liquid extraction, adsorption, and ion exchange operations. Important membrane separations include reverse osmosis, electrodialysis, and ultrafiltration. Biological systems may be used to induce precipitation or liberate species, to concentrate pollutants, and to decontaminate streams.

Waste stream heterogeneity can also be use. Examples include sedimentation to remove solids from wastewaters, decantation to separate immiscible liquids, or filtration to separate particulates from gaseous streams.

If a waste mixture is homogeneous, then a separating agent is required. Such additives may be classified as either *biological separating agents* (BSAs), or *energy separating agents* (ESAs), or as *mass separating agents* (MSAs). In all cases, the additives result in modified physical or chemical behaviors that are exploited using an appropriate separation device. Examples include differences in bioaccumulation factors, thermodynamic equilibria, or mass transfer rates [11].

Typical BSA-driven processes involve biologically-induced species degradation or transformation as well as separation. They are distinct from MSA-driven processes because they exploit living organisms which must be cultured and maintained. This feature complicates BSA-driven separations, because pH, nutrient adjustment, and aeration are often required to maintain culture viability. On the other hand, such methods can be economical, especially when the microbes occur naturally in the primary waste matrix. In such cases, the treatment mainly consists of promoting microbial growth and biomass retention in the separator. Examples include conventional wastewater treatment (e.g., activated sludge and trickle-bed filters) and bioaccumulation processes for organics removal from air streams.

Heat- or ESA-driven separations are common in the chemical process industries. Examples include evaporation, distillation, and crystallization. In some cases, pressure is used to cause mass transfer (e.g., gas-phase separations using membranes and reverse osmosis for water treatment). ESA-driven processes are usually preferred whenever a solute is recovered and purified in high concentrations. In cases where trace impurities must be removed, such processes are less attractive because they are unable to exploit the heuristic, "remove the most plentiful component first."

Table 2: Technologies for removing volatile species from wastewater. [Adapted with permission from S. E. Manahan, *Hazardous Waste Chemistry, Toxicology and Treatment*, Lewis Publishers, Chelsea, MI (1990)].

Primary Treatment	
Dissolution	Blending
Slurrying	Phase Separation
Secondary Treatment	
Neutralization	Emulsion Breaking
Oxidation/Reduction	Coagulation
Precipitation	Sedimentation
Adsorption	Centrifugation
Extraction	Air Floatation
	Sludge Dewatering
Polishing	
Filtration	Activated Carbon Sorption
Reverse Osmosis	Ultrafiltration

Thermal separation processes are often too expensive for waste treatment, but they are used in some situations. Distillation or evaporation, for example, may be used to remove small concentrations of volatile organics. One key consideration is the solute-to-solvent relative volatility at infinite dilution. At low to moderate pressures, α_{ij}^{∞}, the infinite-dilution relative volatility for a binary mixture can be written as:

$$\alpha_{ij}^{\infty} = \frac{\gamma_i^{\infty} P_i^{sat}}{P_j^{sat}} \tag{1}$$

since γ_j approaches unity by the Lewis and Randall rule. Solutes with larger values for α_{ij}^{∞} are more easily separated and recovered. Rogers and Brant point out, however, that distillation has limited value for waste separations because it is relatively complex, large, energy demanding, and capital intensive [12]. Evaporation has similar limitations [13, 14].

MSA-based processes involve the addition of a species or mixture that results in separation through intimate contact of the primary waste stream with a second phase. As defined here, MSAs are not living, but may be either gaseous, liquid, or solid phases. Examples include liquid/liquid extraction and carbon adsorption. Separating devices may be devised around an MSA (e.g., liquid-membrane separators) where a solid support is used to immobilize a liquid phase and separate two miscible liquids while permitting selective mass transfer. MSA-based separations may also use multiple phases. One example is perstraction where a solid membrane separates two miscible liquid phases [15, 16].

Waste treatment technologies are commonly divided into three general categories or steps: (1) primary, (2) secondary, and (3) polishing. Manahan provides the additional breakdown shown in Table 2. Separations occur in all three. Rich lists 73 waste management practices [17]. At least 33 are separations.

Efficient separation systems are usually part of an overall system that may include waste recycle, reagent regeneration, and the generation of useful byproducts to eliminate waste residuals. Economical separation and waste management systems often incorporate well-established separation unit operations that are strategically configured, rather than radically new separation technologies.

Goals of Separation Processes

Increasing environmental concerns are forcing waste generators to significantly modify their waste management practices. The concentration limits in liquid and gaseous effluents are decreasing. Zero discharge is the goal for many priority pollutants, especially in aqueous wastes. Thus, there are clear needs for improved separation technologies to achieve these goals—either directly by decontamination or indirectly by recycle and process modification. Zero-liquid discharge may become a reality in many instances.

Eckenfelder discusses traditional separation technologies in some detail [18]. Table 3, for example, indicates typical effluent concentrations for several metals using the traditional separation methods. As can be seen, there is a real need to devise technologies that can achieve lower practical concentration limits. The proposed EPA maximum contaminant level for Hg is 2 μg/L [19], for example, and that goal is only marginally achievable with these technologies. Moreover, the achievable concentrations listed in Table 3 are subject to several caveats:

Table 3: Achievable and permitted concentrations for selected heavy metals. [Adapted with permission from J. W. Patterson, *Industrial Wastewater Treatment Technology*, Butterworth Publishers, Boston (1985) and the EPA [19, 21]].

Metal	Concentrations (μg/L)		pH	Technology
	MCLG[a]	Achievable		
Arsenic	zero[b]	50	6–7	Sodium Sulfide ppt
		60		Carbon adsorption
		6		$Fe_2(SO_4)_3$ ppt
Cadmium	5	50	10	Hydroxide ppt
		8	6.5	Sulfide ppt
Chromium	100			
Cr^{6+}		75		Metabisulfite ppt
		23		Ion exchange
Cr^{3+}		750		Hydroxide ppt
Copper	1300	20–70	9-10	Hydroxide ppt
		10–20	8.5	Sulfide ppt
Mercury	2	10–20		Sulfide ppt
		1–10		Alum co-ppt
		0.5–5		$Fe(OH)_3$ co-ppt
		1–5		Ion exchange
Nickel	100	120	10	Hydroxide ppt
Selenium	50	50	6.6	Sulfide ppt

[a] Maximum Contaminant Level Goal [19]

[b] Former value [19], under review

1. Inlet metal concentrations are also low. Typically, 80–90% removal is achieved.
2. Interference often occurs because of other ions and complexation agents.
3. Filtration is often required when precipitation is used as a polishing step.
4. Many of the precipitating agents are also toxic.
5. Requirements for pH adjustment can be high.

Table 4: Permitted concentrations for selected organics based on Drinking Water Standards and recommended air concentrations.

Chemical	Concentrations (μg/L)		
	MCLG[a]	MCL[b]	TLV[c]
Atrazine	3	3	5
Benzene	zero	5	32
Dichloroethylene (cis-1,2-)	70	70	793
Dichloroethylene (trans-1,2-)	100	100	793
Dichlorobenzene p-	75	75	301
Lindane	0.2	0.2	0.5
Polychlorinated biphenyls (PCBs)	zero	0.5	0.5
Tetrachloroethylene	zero	5	339
Toluene	1000	1000	377
Xylenes	10000	10000	434

[a] Maximum Contaminant Level Goal [21]
[b] Maximum Contaminant Level [21]
[c] Threshold Limit Value-Time Weighted Average [23]

Selected EPA Maximum Contaminant Levels (MCLs) and the Maximum Contaminant Level Goals (MCLGs) are summarized in Table 4 from EPA data [19]. Current values are compared with Time Weighted Average-Threshold Limit Values (TLVs) published by the American Conference of Governmental Industrial Hygienists [22]. The MCLs are either comparable or lower than the TLVs, reflecting the importance of achieving essentially complete removals of many toxins from wastewaters. The TLVs and MCLs are, of course, correlated.

The concentrations in Tables 3 and 4 represent design goals for separations, and they lead to several possible conclusions. If one believes these goals are economically achievable for a particular wastewater, then they represent goals prior to discharge. If one believes they are not achievable, then they represent criteria for waste stream recycle and reuse, or for pollutant retention and destruction operations. If waste stream decontamination and discharge are adopted as part of an operating philosophy, the waste generator should also recognize that the goals in Tables 3 and 4 are likely to be moving targets for the foreseeable future.

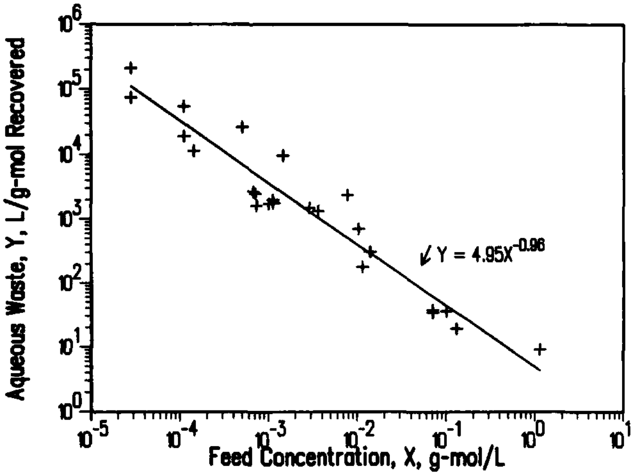

Figure 2: Typical dependence of secondary aqueous waste production on feed concentration using solvent extraction and ion exchange to recover heavy metals and fission products.

In either case, it is clear that improvements in separations technology will require accurate and detailed information concerning solute behavior at infinite dilution. In the case of liquid phase behavior, particularly aqueous phases, this challenge is significant.

Recovery becomes more difficult and expensive as feed concentrations decrease. This is partly due to the fact that secondary waste production per mol of product recovered is inversely related to the feed concentration. Figure 2 illustrates this effect. It shows data for aqueous secondary waste production using ion exchange and solvent extraction technologies to recover heavy metals and fission products [24–32]. Although the secondary aqueous wastes can usually be concentrated, Figure 2 clearly indicates why the practical returns, and the incentives for using decontamination technologies, rapidly diminish with feed concentrations.

Applications and Needs

The most obvious applications for separation technologies involve primary waste stream decontamination. As mentioned above, however, the benefits from stream decontamination rapidly decrease with pollutant concentrations. Thus, this approach is not necessarily the best one. Alternatives include using separations to reduce waste generation rates, to facilitate wastewater recycle and reuse, to permit the implementation of alternative manufacturing chemistry, and to enable sludge reduction and reuse. These latter approaches are sometimes less obvious, but may be preferred from the systems viewpoint.

Separations are important for virtually all aspects of hazardous waste management. They can be used to decontaminate and concentrate toxics, to retain hazardous species for their eventual destruction, or to convert them to more concentrated and immobile forms for final disposal. There are literally thousands of applications. Selected applications are discussed below.

Waste Reduction and Recycle

Brandt describes waste reduction in terms of the four *R*s—reduction, reuse, reclamation, and recycle [33]. The last three of these *R*s usually involve some type of separation.

Wastes may have value if they can be recycled or reused at the generation site, or if they are usable raw materials in another process. On-site recycle is particularly attractive if it also leads to higher product recoveries and waste concentration. In some cases, the waste has little intrinsic value, but recycle improves the overall process efficiency and the production of solid waste forms. Partly because of such complexities, several organizations have developed assistance programs [34, 35].

Off-site disposal necessarily incurs transportation costs, but may be advantageous if the waste can be used as a raw material by another process, promotes energy recovery, or assists in pollution abatement or waste treatment. This latter strategy is often more complex than the first because the supply-and-demand are less likely to match.

For many solid and liquid wastes, significant reductions are achievable in a variety of means. Simple accounting, inventory control, and more stringent disposal standards often yields significant reductions [36]. In some cases, less hazardous materials can be substituted. A current example includes the ongoing search for substitutes to chlorofluorocarbons for numerous dry-solvent applications. At the other extreme, process modifications may be implemented to reduce waste generation rates and, finally, alternative disposal technologies (e.g., incineration and compaction) may be adopted.

Constituents in municipal solids are among the more obvious candidates for recycle (e.g., tramp metals, glass, paper, plastics, and rubber). Some of these constituents are not hazardous, but they are often found in hazardous mixtures (i.e., in a contaminated state). Such wastes may be segregated manually or by using differences in physical properties such as density or magnetic susceptibilities.

Higher landfill costs are heightening interest in separating recyclables from solid wastes. Increasingly, residential generators are being encouraged to segregate their bottles and cans. Separation at the point of generation is less expensive, but still labor intensive. This approach can be effective, especially as an interim procedure, but a clear need exists for more efficient segregation technologies that are economical at centralized facilities.

Centralized segregation technologies remain both capital and labor intensive. Moreover, their economics of implementation are beset by unpredictable market prices for recycled materials, variable feed stream compositions, and significant recycled product decontamination requirements. Tramp metals, for example, are often contaminated with liquids (e.g., corrosive battery acids or food liquids). They must be washed before recycle and reuse, but such cleanup steps invariably generate secondary wastes that significantly increase waste management costs at centralized facilities [37]. Thus, improved dry cleaning technology is an important research need.

Water recycle can also be an important treatment technology that exploits separation. It is especially important in regions where water is in short supply [38–40]. It may also be important where water is abundant to minimize discharge costs. In manufacturing, water is mainly used to produce chemicals, paper, their allied products, and primary metals [41]. It is more widely used for cooling, processing, and boilers. Water recycle is already widely employed for cooling towers and boilers, but less so for process applications. Thus, improved strategies for reduced water use in process and waste cleanup applications are also important separation needs.

Soils, Sediments, and Residues

The widespread use of hydrocarbon fuels has resulted in significant contamination problems both in soils and sediments. Typically, waste oils are recovered by decantation, extraction, or evaporation with condensation. The most attractive means depends upon the waste matrix, oil concentrations, and its properties. However, the conventional means for oil recovery are generally not applicable for cleaning contaminated soils [42]. When petroleum products are released to the environment, they tend to become adsorbed and chemisorbed to soil particles. The primary factors are the relative permeabilities of the oil contaminants in the soil, their viscosities, and interfacial tensions. Secondary factors include the extent of oily contamination in the soil field and the areal distribution of oily pools.

Chawla et al. survey the interactions between soils, contaminants, and surfactants [43]. Mercer and Cohen provide an in-depth review [44]. This topic is particularly important whenever soil washing is contemplated [45]. Soil matter can bind with organic pollutants through various physical and chemical interactions. Adsorption, hydrogen bonding, and ion exchange can all be important. The interactions between a soil, the contaminant, and any surfactant that is considered for soil washing are of paramount importance. Pramauro and Pelizzetti also discuss the key role of surface active compounds [46]. McCarty and Zachara have studied subsurface transport of contaminants by colloids [47]. Chambers et al. [48] have compiled information on in situ treatment technologies, particularly contaminated soils. Pheiffer et al. [49] and Sims [50], have also compiled detailed studies of this topic. Young et al. [51] provides nine case studies.

Testa [42] describes conventional technologies for removing light nonaqueous liquid hydrocarbons (LNAPL) from soils and groundwater. Many contaminated sites resulted from underground storage tanks and petroleum facilities, and others from above-ground storage tanks and pipeline corridors. Petroleum chemicals are either adsorbed in the soil, dissolved in an aquifer, or free-floating.

Conventional technologies for recovering LNAPL often involve one or more separation methods. Simple linear interception (i.e., ditches, trenches, etc.) may be constructed on the down-gradient side of a contaminated area. As groundwater flows into or across the interceptor trench, LNAPL product may be collected and contaminated waters treated. Passive systems rely on the natural hydraulic gradient to transport LNAPL product. Normally they are slow, but rates depend upon soil permeabilities as well as the hydraulic gradient. Active systems increase the flowrates using wells to increase the hydraulic gradient. Typically, treated water is pumped into some wells while contaminated water is withdrawn from others. In this way an artificial hydraulic pattern is established over the contaminated site that is used to move LNAPL to the surface.

The effectiveness of aqueous soil washing depends upon the relative permeabilities of the water-immiscible solvent and the aqueous wash. Both permeabilities depend upon the percentages of water and solvent saturations in

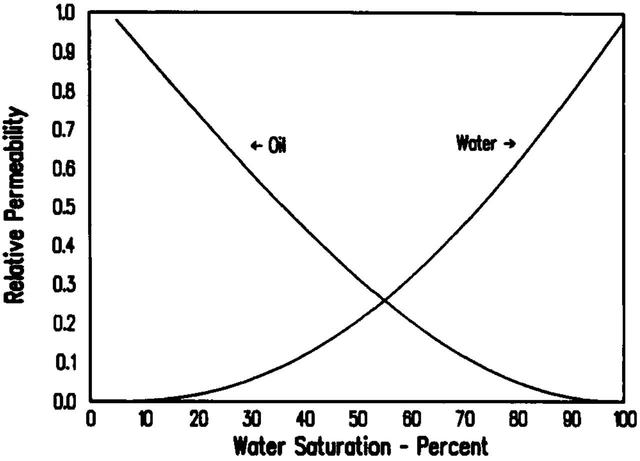

Figure 3: Relative permeabilities of water and immiscible solvents as a function of water saturation concentrations. [Adapted with permission from A. I. Levorsen, *Geology of Petroleum*, W. H. Freeman and Company, New York (1967)].

the soil. Levorsen [52] illustrates a typical example which is shown as Figure 3. Solvents are more readily recovered from soils in high concentrations and with low aqueous saturation concentrations. At low water concentrations, the water is essentially immobile and the solvent (or oil) is permeable. At high water concentrations, the solvent or oil residual is immobile, and the soil effluent is a solvent-contaminated wastewater. As much as 20% of the solvent may be essentially immobile and, therefore, not effectively removable by washing so a hybrid process is required to complete the decontamination.

Some fraction, particularly the light nonaqueous hydrocarbons, may be held loosely between soil particles, and this is more easily removed, say by soil venting. The residual, higher molecular weight hydrocarbons are, of course, more difficult to remove.

Soil venting is another important method for site remediation that is finding many applications. It is broadly accepted for soils contaminated with volatile or semivolatile species. It is complicated, however, by a need to understand the site hydrology and air flow in some detail; computer modeling can be helpful. Kuo et al., for example, describe a three-dimensional soil venting model that can be used to evaluate a site and develop venting strategies [53]. Their predictions are compared with experimental measurements at several remediation sites.

For many contaminated soils, high-temperature calcining is the most obvious treatment. While attractive for some relatively concentrated liquid wastes [54], other alternatives should be considered for soil remediation, especially when the pollutant concentrations or volatilities are low. Low-temperature technologies, either chemical or biological treatment, for example, can achieve similar results although at somewhat slower rates [55].

Wastewaters

Separations have always been important in wastewater treatment. Eckenfelder [18] describes the traditional methods which include: (1) sedimentation, oil separation and flotation, (2) coagulation and precipitation, (3) air stripping and aeration, (4) biological treatment, (5) adsorption and ion exchange, and (6) minor technologies (e.g., filtration and membrane processes).

Aquifer and Recovery Well Effluents

Aquifer and recovery well effluents may be subjected to various separation methods. Floating skimmers and decanters may be used to remove insoluble oil concentrations. Bennett reviews air flotation technology [56]. Volatile LNAPL may be evaporated from the contaminated water by vacuum stripping or countercurrent air-stripping at atmospheric pressure.

Ahlert and Kosson [57], Slater et al. [58–61], Syzdek and Ahlert [62], and Enzminger et al. [63] evaluated several alternative treatment technologies for managing hazardous landfill leachates and contaminated groundwaters. Biological, physical, and chemical treatments were evaluated. The latter included reverse osmosis, ultrafiltration, flocculation and sedimentation, membrane separations and adsorption. Pretreatment with ultra-high lime concentrations to pH 12 was effective in reducing turbidity and heavy-metals concentrations. This step was followed by a floc separation and recarbonation to pH 7. Membrane and biological treatments were ineffective without pretreatment to produce a homogeneous aqueous phase. Activated carbon adsorption was inefficient when dispersed oily phases were present. Ultrafiltration was of limited value because most solutes had molecular weights less than 500.

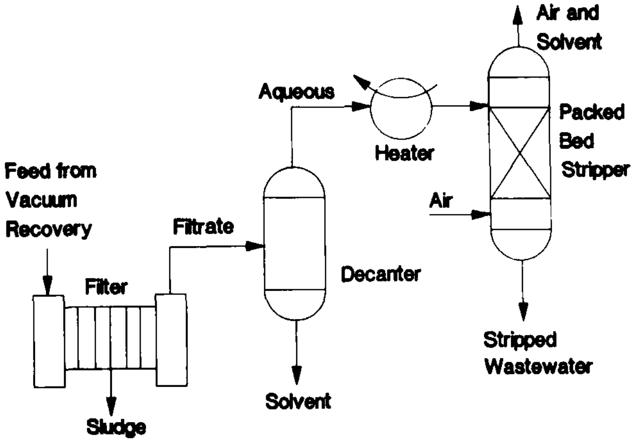

Figure 4: Typical air-stripping flowsheet for vapor removal from contaminated water.

A typical flowsheet is shown in Figure 4. Filtration is a common pretreatment followed by decantation. Other common pretreatment steps include coalescence to break down emulsions and enhance decantation. Volatile species can be removed by air-stripping as shown.

Air stripping or other physical separation methods may be used to decontaminate the aqueous stream from near saturation concentrations down to about 5 or 10% of saturation. This technology is widely used and studied [64–68]. Lower decontamination levels are possible, but become less cost effective. The usual goal is to remove the bulk of the contaminants so that a polishing step, such as activated carbon or biological treatment, can be used to decontaminate the water for discharge to a conventional water treatment facility.

Noonan and Curtis provide considerable detail for the design of remediation technologies for treating groundwater [69]. They provide engineering-related information regarding costs, removal efficiencies, and limitations to removing contaminants (primarily gasoline) from groundwater. Their focus is on widely applied and proven technologies.

Inorganics are commonly removed by precipitation [70]. Removal efficiencies depend on solubilities at a specific pH. Sulfide, carbonate, and hydroxide solubilities are typically exploited. Because most inorganic sulfides except arsenic have low solubilities, this is a fairly effective approach. There are some disadvantages, however, such as chemical handling problems and the tendency of sulfide sludges to oxide and form sulfates which have higher solubilities.

The carbonate system uses soda ash and pH, usually in the range from 8.2 to 8.5. It is more difficult to control because of this low pH operating range.

Hydroxide precipitation is widely used for the removal of inorganics and metals. It is based on either slaked lime or NaOH to increase pH and decrease solubilities. Hydroxide precipitation chemicals are easier to work with, but can form gelatinous sludges that are hard to dewater and difficult to work with. Testa and Winegardner further summarize the alternatives [42]. Table 5 is modified from their description.

Aqueous Phenolic Wastes

Phenolic wastes result from many industrial processes. Coal gasification and liquefaction operations, for example, produce phenolics in abundance. They also result from phenolic resin manufacturing and petroleum refining operations.

Phenolics may be recovered by solvent extraction [71] and by activated-carbon adsorption [72]. Some solvents used are hydrocarbons (e.g., benzene and toluene), chlorinated hydrocarbons, primary alcohols (e.g., 1-octanol), ethers (diisopropyl), esters like *n*-butyl acetate and tricresyl phosphate, and methyl isobutyl ketone. Phenol may be removed from extracts by forming the phenolate anion

$$C_6H_5OH(org) + NaOH \rightarrow C_6H_5O^-Na^+ + H_2O \qquad (2)$$

through reaction with an inorganic base such as NaOH. If sufficiently concentrated, phenol may be recovered from the aqueous stream by reacidification and physical separation.

Electrochemical Wastes

Acidic solutions containing dissolved metals result from various metal processing operations. Examples include Zn^{2+} and HCl from zinc stripping, Ni^{2+} and HNO_3 from nickel stripping, H_2SO_4 and Al^{3+} from aluminum anodizing, H_2SO_4, HCl, and Zn^{2+} from steel pickling, HNO_3, HF, Fe^{2+} and Cr^{3+}

Table 5: Aquifer and recovery well treatment options. [Adapted with permission from S. M. Testa and D. L. Winegardner, *Restoration of Petroleum-Contaminated Aquifers*, Lewis Publishers, Inc., Chelsea, MI (1991)].

Remediation Alternatives	Volatile Organics	Nonvolatile Organics	Inorganics
Air Stripping	Suitable for most cases	Not suitable	Not suitable
High-temperature air stripping	Effective removal technique	May be suitable	Not suitable
Steam stripping	Effective concentrated technique	May be suitable	Not suitable
Carbon adsorption	Effective removal technique	Effective removal technique	Not suitable
Biological	Effective removal technique	Effective removal technique	Effective at low concentrations
pH adjustment precipitation	Not applicable	Not applicable	Effective removal technique
Membrane processes	May be applicable	Effective removal technique	Effective removal technique
Electrodialysis	Not applicable	Not applicable	Inefficient operation, inadequate removal
Ion exchange	Not applicable	Not applicable	Inappropriate technology, difficult operation

from stainless steel pickling, and HNO_3, H_2SO_4, Cu^{2+} and Zn^{2+} from brass etching [6].

Such acidic wastes may be treated by lime precipitation, but this technique also produces a sludge waste from which it is difficult to recover the metals. Ion exchange can also be used [73]. Acetic acid may be extracted into organic solvents such as ethyl acetate and separated by distillation. Inorganic acids may be extracted into polar solvent systems containing basic moieties.

Precious metals in process streams or rinse waters are sometimes recovered electrolytically [74]. Metals may be recovered from electroplating wastes by reduction:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad (3)$$

Cyanide-bearing wastes can also be treated [75]. Ion exchange is also widely used for metals recovery from wastewaters. Usually, the H^+ form of the resin is loaded with metal and then regenerated using strong acid. Metals that form stable anions (e.g., $Cu(CN)_4^{3-}$ or CrO_4^{2-}) may be removed from wastewaters using anion exchange. They are eluted from the bed using a strong base.

Separation Technologies

The best separation technologies and systems satisfy multiple goals rather than simply meeting a single need. Energy conservation and secondary waste production, for example, are two common criteria that are used to evaluate separations alternatives. As with historical practice in separations, there are economic incentives to avoid the addition of new materials (MSAs) or biological agents (BSAs) to achieve the primary separation goals. If MSAs or BSAs are used, it is usually best to select them from materials already available at the waste-generation site.

In addition, there are usually severe economic constraints that apply to the treatment of hazardous wastes, and that preclude the use of many high-tech alternatives. Traditionally, waste technology has been kept as simple as possible. Thus, it may be more economical to market a waste solvent as a burnable fuel by-product, than to purify and recycle it on a plant site [76, 77]. Wastes with alternative applications, albeit low-grade uses, are often more economically managed by shipping them off-site than by utilizing separations technologies to purify and recycle. Researchers developing separations technologies for waste applications must recognize the severity of this constraint if they expect to realize commercial success in waste applications.

Solvent Extraction

Solvent extraction generally applies to liquid/liquid extraction and leaching. Most commonly, solvent extraction means liquid/liquid extraction when applied to hazardous waste treatment [71, 78, 79]. It has been studied for a number of applications. For wastewater treatment, studies include the separation of phenolics [80–92] and various priority pollutants [93], and the removal of carboxylic acids [94–98]. Napier [99] and Hancher [100] considered it for removing PCBs from transformer oils. Hall et al. present an overview of solvent extraction [101]. Valentinetti evaluated the CF systems organics extraction system [102, 103]. Sudell studied solvent extraction technology for sludge treatment [104].

Eyal et al. present a review of mixed ionic, or coupled, extractants and their use [105]. They focus on acid recovery from aqueous streams, a technology that offers recovery options with reduced dilution factors compared to ion exchange. Mixed solvents, comprised of amines and organic acids for example, can be used to recover inorganic acids and salts simultaneously. These authors emphasize a flowsheet they have developed for coextracting H_2SO_4 and $ZnSO_4$. Their solvent is a kerosene diluent blended with an extractant mixture of tricapryl amine, Alamine 336, and di(2-ethylhexyl) phosphoric acid. Hadi et al. provide results of further studies focusing on the removal of polar organics (e.g., phenol) from wastewaters [106].

Supercritical Extraction

Supercritical solvent extraction has been studied by a number of investigators for application to contaminated soils. Reviews are provided by Groves et al. [107] and Modell [108]. Supercritical extraction has several potential advantages, especially for solids decontamination. First, a relatively innocuous solvent (e.g., CO_2), may be used. Second, a volatile solvent such as CO_2 is easily removed from the solids.

Dooley et al. [109] and Andrews et al. [110] present typical results. A cosolvent is required to obtain good soil decontamination factors; 5% methanol additions to CO_2 are a good choice. Also, the treatment effectiveness de-

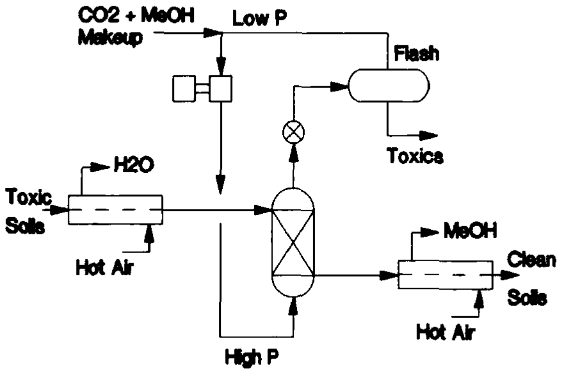

Figure 5: Conceptual flowsheet for soil decontamination using supercritical CO_2 extraction.

pends upon the water and organics concentrations in the soils and sediments. Thus, a conceptual flowsheet (e.g., Figure 5) should include an initial solids drying step and solvent drying after decontamination to remove residual methanol concentrations.

Adsorption

Carbon adsorption is a well-established technology for polishing wastewaters [72, 111, 112]. Its efficiency is limited by the phase equilibrium properties of various solutes and the ease with which the sorbent can be regenerated. Media with higher distribution coefficients during loading enable greater initial concentration factors, but this advantage is frequently offset by the greater difficulties associated with sorbent regeneration. Nirmalakhandan and Speece developed predictive models for estimating activated carbon parameters [113]. Ying et al. provide adsorptive capacities based on experimental data for many organics in wastewaters [114].

Adsorption may also be enhance by the addition of reagents to well-known solid matrices to enhance performance. Cadena and Garcia present an example in which benzene adsorption is enhanced by treating bentonite clay with quaternary amines [115].

Chen et al. [116] investigated an adsorption-based recovery using a composite adsorbent consisting of magnetite particles coated with a $Fe(OH)_3$ precipitate (ferrihydrite). They studied the removal of soluble Cr(VI) and Zn from 0.01 M $NaNO_3$ solutions. In their chromium studies they found that the coated magnetite had about twice the adsorption capacity of uncoated magnetite. Chromium was best adsorbed at pH 11 and desorbed at pH 3. Zinc was adsorbed at pH 8 and desorbed at pH 4. Initial loadings were about 0.4 mg Cr/g of adsorbent. Loadings decreased with repeated adsorption and desorption cycles. The decline in performance was attributed to a gradual accumulation of adsorbate on the solid, rather than the loss of adsorbent.

Inorganic fluorine species are increasingly present in industrial effluents. Nomura et al. describe the use of hydrous cerium oxide adsorbent for reducing F^- concentrations to about 1 mg/L [117]. Their system has higher selectivity and capacity than many current alternatives.

Electrosorption is one alternative that may enhance the usefulness of adsorption processes in removing dilute organics from wastewaters. Eisinger and Keller [118] present results in which a carbon bed is loaded and regenerated using electric potential. Although a solid bed is used, chemicals are not required to adsorb and desorb ethyldiamine. The process cycle is driven by a voltage swing across the bed. (In the present classification, it is ESA-driven.) The current requirements are modest, but the bed does have capacity and requires some time to cycle. The exact mechanisms of electrosorption are unclear, but the technology may prove useful for removing Pearson "soft" bases from aqueous streams [119]. Eisinger and Keller operated their tests at a pH near 10 without adjustment.

Membranes

Membranes exploit the selective passage of a solute or solvent through a thin membrane which may be fabricated of any number of materials. The type of membrane process is largely determined by the size of the species that permeate it. Hyperfiltration is used with both ions and organics. It allows passage of species with molecular weights from about 100 to 500. Ultrafiltration is used to retain organic solutes with molecular weights from 500 to one million. The permeate for both consists of water and lower molecular weight solutes. These methods are particularly useful for concentrating suspended oil, grease, and fine solids in water [120].

Reverse osmosis is the most widely used membrane technique. It is selectively permeable to water, but excludes ionic species. High pressure is used to force permeate through the membrane and produce a concentrated brine waste. Membrane fouling is a major problem when treating hazardous wastes, although their use is being studied and they are being employed on broader classes of liquid streams [121–123].

Electrodialysis membranes are composites of those permeable to cations and those permeable to anions. The driving force for separation is a direct current between two electrodes. Alternate layers between the membranes contain brine and purified water. This device can be used to concentrate plating wastes, but is also subject to fouling.

Affinity dialysis is another promising method for removing metal ions from wastewater. Hu et al. present experimental results and a theoretical model for describing such processes [124].

MacNeil [125] reviews membrane applications in detail. Numerous flowsheet applications have been suggested, including the few mentioned here. Their use is well established as a polishing step for wastewaters, but less so for nonaqueous applications. Fouling is always a major concern, especially when one contemplates wastewater treatment, because compositions and trace impurities (e.g., colloidal suspensions) are often poorly defined, but can have substantial effects on membrane performance.

Lipski and Côté [126] and Wijmans [127] discuss pervaporation applications for the removal of organic contaminants from water [126]. This flowsheet is essentially pressure driven and rate limited. In principle, flowsheets can be devised that include all of the features normally associated with fractionation (e.g., reflux, enrichment and stripping sections). Figure 6 illustrates one concept.

Biological Separation Agents

Biological processes are usually designed to degrade certain species and thus reduce the overall biological oxygen demand (BOD) in an aqueous stream. In most cases, separations also occur either because of the biological activity or because of operations to maintain the biomass [e.g., aeration which also liberates volatile organic carbon (VOC)]. Higher molecular weight species which degrade slowly may accumulate in the biomass. Lindane is one example [128], but there are others [129–131]. Boyer and Chapra provide a review [132]. In the case of some priority pollutant pesticides, bioaccumulation may be the

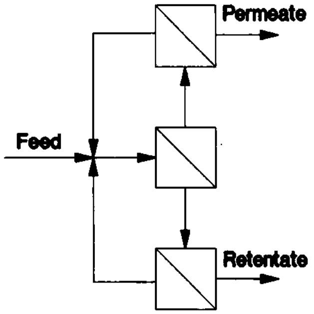

Figure 6: Conceptual pervaporation flowsheet illustrating countercurrent stripping and rectification.

only practical method for achieving extremely high levels of decontamination (e.g., parts per quadrillion or less) from large aqueous streams.

Biosorption is a potentially important separation method for metals. Robinson et al. review the use of algae [133]. The concentration (or decontamination) factors one can achieve depend heavily on the microbe and its preparation, if immobilized. Watson et al. [134] present recent results for strontium removal. They present a separation method which is often overlooked—the synergistic combination of microorganisms and polymeric adsorbents. The same bioaccumulation factors that compel regulatory agencies to issue very low release limits can be used to advantage. The authors explain how relatively inexpensive biological materials can be incorporated into particulate forms, such as gel beads, and used to effectively remove dissolved metal ions from wastewaters. Table 6, adapted from their work, illustrates the range of results one may expect.

Biosorbents may also be manufactured using the nonviable biomass derived from microbes. This approach has some advantages because heavy metal ions are toxic and cell viability is difficult to maintain at the higher, more efficient loadings. In this case, the biomass is incorporated into a suitable supporting matrix that, in effect, yields a separation operation similar to conventional ion exchange.

Darnall [135] describes one such system that uses algal-derived materials immobilized into a polymeric matrix to promote flow through the bed. It

Table 6: Range of distribution coefficients for Sr removal. [Adapted with permission from J. S. Watson et al., Evaluation of a cell-biopolymer sorbent for uptake of strontium from dilute solutions, In *Emerging Technologies in Hazardous Waste Management*, Volume 422 of *ACS Symposium Series*, American Chemical Society, Washington (1990)].

Organism	Distribution Coefficient[a]
Rhizopus	26,240
Micrococcus	9,980
Bacillus	5,240
Escherichia	1,230
Pseudomonas	870
Caulobacter	450

[a] μg Sr bound to cells/g dry cells divided by the μg Sr in solution/g solution.

is effective for Ag, As, Cd, Cu, Hg, Ni, Pb, U, and Zn. These species can be selectively separated from the most plentiful hard water species (i.e., Ca, K, Mg and Na) which have little or no effect on heavy metal loadings. High selectivity is a key advantage, compared to conventional ion exchange materials, because the most plentiful metals usually determine the frequency of bed regeneration.

Darnall's system is designed for wastewater treatment in the electroplating, metal finishing, and printed circuit board manufacturing industries where rinse waters contain 100 ppm or less of heavy metal ions. It is effective for groundwaters and leachates and can preferentially concentrate these species from concentrations as low as a few parts-per-billion. This system is also claimed effective for removing heavy metals down to drinking level standards and in the recovery of precious metals [136, 137].

Chitin has been used as biotrap [138]. It consists of unbranched water-insoluble polymer of β-1,4-linked N-acetylglucosamine subunits. By deacylating chitin in an autoclave with NaOH, chitosan is produced. It has free amino-groups that can more readily bind heavy metals and a capacity over an order-of-magnitude greater than chitin. Chitosan has higher solubilities at lower pH (≤ 5), but can be cross-linked to reduce this problem [139].

Crusberg [140] has studied chitosan-based biotraps for removing heavy metals. He notes that the effectiveness of derivatives from a particular microbial system largely depend upon the ability of the living system to tolerate and adsorb a particular metal ion. The fungus *Penicillium ochro-chloron*, for example, tolerates relatively high copper concentrations (up to 5 g/L of copper sulfate at pH 2). Crusberg [141] found that copper binding follows an adsorption isotherm with the form

$$\frac{1}{\nu} = \frac{1}{\nu_{max}} + \frac{K_d}{\nu_{max}[\mathrm{Cu}^{2+}]_{free}} \tag{4}$$

using air-dried mycelia prepared from acetone and alcohol extraction [142]. He found that Cu, Cd, and Ni were effectively bound using mycelia of *P. ochro-chloron*. His conceptual flowsheet shows adsorption at a pH of 4 and bed stripping at 1% to 1 M HCl. Crusberg suggests that such systems can be used without encapsulation to immobilize the biomass.

Galun [143] studied *Penicillium digitatum* and found it preferentially adsorbs heavy metals in the order

$$\mathrm{Fe}^{3} > \mathrm{Ni}^{2+} > \mathrm{Zn}^{2+} > \mathrm{Cu}^{2+} > \mathrm{Cd}^{2+} > \mathrm{Pb}^{2+} > \mathrm{UO}_2^{2+} \tag{5}$$

This approach appears to have wide applications, especially for systems where Ca, Mg, Na, and K are only weakly adsorbed.

In the case of organics removal, the BSA consists of the biomass which ingests the pollutants and degrades them to lower molecular weight species, H_2, and CO_2. Although Superfund leachates have been treated biologically without dilution, pretreatment is usually required and care must be taken to acclimate the biomass and provide nutrients (typically nitrogen and phosphorous) to maintain viability. Howard describes pilot tests, for example, processing pretreated aqueous hazardous waste leachates obtained from two different Superfund sites [144]. These leachates initially contained high concentrations of metals and organics. Pretreatment consisted of lime precipitation, clarification, and sand filtration. Howard concluded that this technique is feasible, but its effectiveness is leachate dependent.

Utgikar and Govind discuss the use of a biofilter to control volatile organic chemicals (VOCs) [145]. They present a mathematical model and summary calculations for 90% VOC removal. Their approach utilizes a countercurrent packed column (or trickle bed filter) to transfer VOCs from the air to a liquid phase. A microbial culture is attached to the packed column (e.g., activated carbon) and nutrients are provided through recirculation of the liquid phase which is introduced into the top of the packed column. Experimental data are presented for the removal of toluene and methylene chloride. They used biomass (a mixed culture) from an activated sludge plant that had been acclimated to toluene and methylene chloride.

Bioprecipitation and Liberation

Many metal sulfates are more soluble than their sulfides. This property can be exploited to liberate metals by oxidizing sulfides to sulfates or to precipitate or immobilize them by reduction. The former option has been studied as a coal pretreatment technique using *Thiobacillus ferrooxidans* to reduce sulfur concentrations in coal [146]. The main problem is the estimated leach dump times which appear to be on the order of years. The latter has been studied as an immobilization strategy for Hg and Cd using naturally occurring soil bacteria [147]. Gypsum additions to mercury contaminated soil plots reduced the mercury concentrations in lysimeter effluents. Reductive conditions have also been observed to reduce leach rates in soil remediation [148] and landfills [149, 150].

Microbial reduction has also been studied as a technique to immobilize uranium [151, 152]. The Fe(III)-reducing bacteria, GS-15, and *Shewanella putrefaciens* are capable of this action. In the case of iron, the enzymatic reaction under anaerobic conditions yields:

$$CH_3COO^- + 8\,Fe(III) + 4\,H_2O \rightarrow 8\,Fe(II) + 2\,HCO_3^- + 9\,H^+ \quad (6)$$

In the case of uranium reduction, these microbes promote:

$$CH_3COO^- + 4\,U(VI) + 4\,H_2O \rightarrow 4\,U(IV) + 2\,HCO_3^- + 9\,H^+ \quad (7)$$

This mechanism is faster than many abiotic reduction routes and is offered as a possible explanation for uranium deposition in aquatic sediments and aquifers. It also suggests a possible method for biological remediation of environments contaminated with uranium. More generally, this approach may have applications for immobilizing (i.e., via precipitation) many dissolved metal ions which undergo redox reactions without the addition of precipitating agents.

Hybrid Processing

Two or more technologies are used to complete the task in hybrid separation processes. Flathman et al. [153], for example, describe a hybrid process for removing dichloromethane from groundwater. In their case,

Table 7: Technologies for removing volatile species from wastewater. [Adapted with permission from P. E. Flathman et al., Remediation of dichlormethane-contaminated groundwater, In *Biological Processes*, pages 25–37., Technomic Publishing Co., Lancaster, PA (1991)].

Operation	Efficiency	Reference
Spray aeration	Low	[154]
Diffused aeration	$< 90\%$	
Granular, activated carbon adsorption	High	
Packed-column air stripping	High	[155]

dichloromethane was contaminating groundwater due to the rupture of an underground pipeline which contaminated about 11,000 m^3 of soil. Their first technology, packed column air stripping was used to remove about 97% of the solvent from groundwaters recovered from the contaminated field. Solvent concentrations were observed to decrease exponentially in groundwaters recovered from the monitoring wells. A packed column air stripper provided an efficient means of separating the solvent from the groundwater by evaporation so that the groundwater could be sent to conventional treatment.

After about three months, this treatment was discontinued. The residual dichloromethane concentrations in the soil were sufficiently immobile to render the treatment inefficient. A second stage of biological treatment was then begun to liberate and mineralize the solvent residuals by adding nutrients and exploiting the indigenous microbial population. Based upon feasibility studies, ammonia and phosphate were added to achieve a 100:10:1 ratio in the soil [156]. Theoretical chloride release was estimated by:

$$CH_2Cl_2 + O_2 \rightarrow CO_2 + 2HCl \tag{8}$$

The injection and recovery wells that were first used for air stripping were then used for biological treatment. Instead of air stripping above ground, a modified activated sludge process was used to improve efficiency and introduce adapted bacteria into the soil through groundwater recycle. As the measured CH_2Cl_2 concentrations in the recovered groundwater decreased,

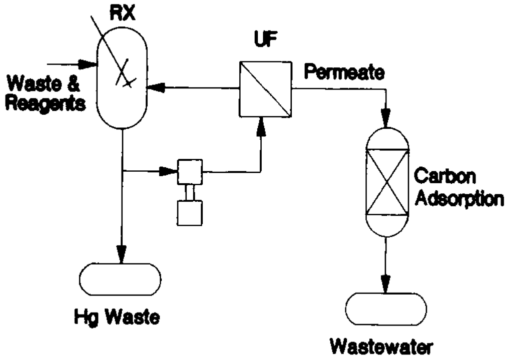

Figure 7: Hybrid process for Hg removal using chemical reaction, ultrafiltration, and activated carbon adsorption. [Adapted with permission from from R. J. Magliette et al., An at-source treatment for organomercury-containing hazardous liquid waste, *Environ Prog*, 10(3):192–197 (1991)].

chloride concentrations increased. Thus, they were able to decrease CH_2Cl_2 concentrations from about 9000 to 300 ppm by groundwater removal and air stripping, and to below 1 ppm in the groundwater by biological treatment.

Magliette et al. describe a hybrid process consisting of a reactor to reduce the mercury in thimerosal from Hg^{2+} to Hg^0 using sodium borohydride [157]. The reactor effluent contains colloidal Hg that can be removed by ultrafiltration and activated carbon. Figure 7 illustrates the concept.

Fleming provides another hybrid example in which adsorption is combined with chemical reaction in a single unit operation that both purifies wastewater and destroys the pollutants [158]. He studied the application of radiation induced oxidation on adsorption beds. Filtered wastewaters are treated by pumping them upflow through a bed of activated carbon. Air sparging at the bottom provides oxygen; a gamma source in the bed provides radiation. The net effect is ozone production and a series of oxidation reactions that degrade pollutants which adsorb onto the activated carbon. The process thus achieves steady-state. Although the use of a gamma source is impractical, the basic idea could be implemented using other radiation sources (e.g., UV) to generate ozone.

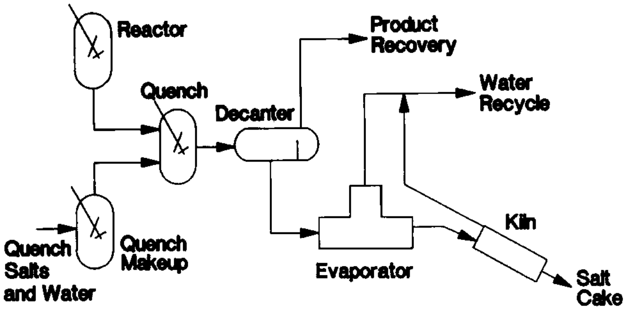

Figure 8: Conceptual flowsheet for brine waste management in specialty chemicals. Brine wastes are treated by evaporation and calcination to produce a solid waste form.

Process Synthesis and Design

Invariably, separation technologies will comprise part of a larger processing system that may include production and waste management operations. The optimal waste management strategy necessarily reflects the whole operation, rather than the most favorable conditions for any one unit, and the most attractive waste management schemes may involve hybrid separation systems. Stream recycle clearly must play an important role. The following examples briefly illustrate how separations, process synthesis, and waste management can be used to create better systems.

Brine Recycle

The first example is illustrated in Figures 8 and 9. The process manufactures an organometallic which, as a final step, undergoes hydrolysis to generate an organic-soluble product and an aqueous brine waste. This step is completed by mixing an alkaline salt with an intermediate organometallic and then decanting the two-phase system. As illustrated in Figure 8, the organic product is recovered in a solvent phase while the aqueous brine waste reports to an evaporator and rotary kiln dryer where a salt cake is produced for landfill disposal. Used water is recovered and recycled to the quench tank and other in-plant applications.

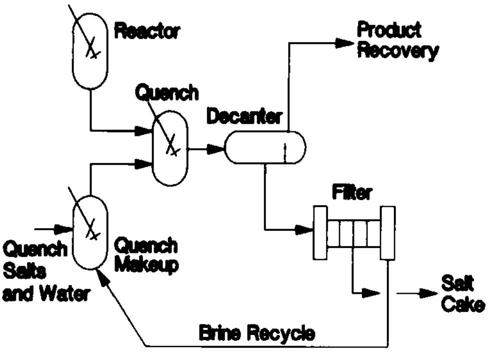

Figure 9: Conceptual flowsheet for brine waste management in specialty chemicals. Brine wastes are treated by waste recycle and filtration to recover a salt cake.

A more effective waste management strategy uses brine recycle as illustrated in Figure 9. In this case, both the expensive evaporator and kiln are eliminated from the flowsheet. They are replaced with a much less expensive carbon-steel plate-and-frame filter press. During plant operation, aqueous brine wastes are continuously recycled to the quench makeup tank where fresh quench salts are added to adjust the pH to the correct alkalinity. This brine mixture is then reused by recycle through the quench tank, decanter and filter press.

No salt cake is recovered until the brine waste concentrations reach their saturation levels, but the flowsheet in Figure 9 is preferable to that in Figure 8 for several reasons. In addition to reducing capital costs by eliminating an expensive evaporator and kiln, brine recycle reduces energy costs. More importantly, the additional salting from brine recycle increases product recovery and reduces solvent losses to the aqueous phase. Because this brine recycle strategy makes it possible to process the waste streams at ambient temperatures, severe corrosion problems are greatly reduced and the waste systems can be fabricated out of carbon steel rather than hastalloy or titanium. Thus, there are multiple benefits from this simple, but effective, waste recycle scheme.

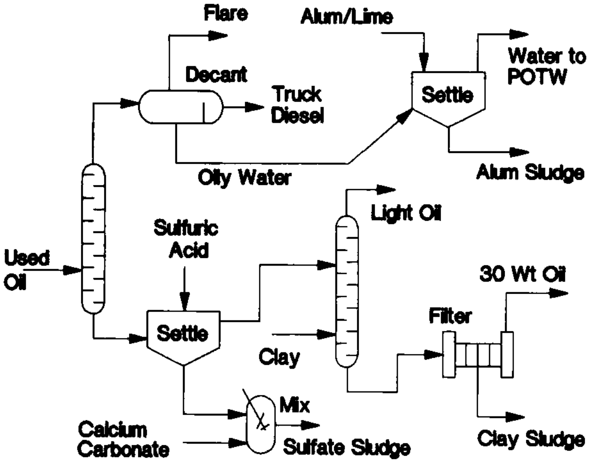

Figure 10: Acid-clay process for used motor oil reuse and recycle. [Adapted with permission from S. F. Miler, Making the most of bottoms and residuals. In *Solvent Waste Reduction*, pages 97–104. Noyes Data Corporation, Park Ridge, NJ (1990)].

Used Oil Reuse

Miller presents another, more striking, example of how waste recycle can yield large benefits [159]. His base flowsheet is shown in Figure 10. In the original process, used motor oils are distilled and recycled using a sulfuric acid wash and treatment with activated clay. The first distillation column in Figure 10 liberates water and a light fuel fraction. The bottoms product is treated with strong H_2SO_4 (e.g., 98%) to sulfate and precipitate all sludge components except stable lube oils. The acid sludge is then neutralized with $CaCO_3$ to yield an oily, $CaSO_4$ sludge that is landfilled.

The first column distillate in Figure 10 is decanted to yield an oily wastewater, truck diesel, and noncondensibles that are flared. The oily wastewater is treated using alum and lime precipitation to produce a second sludge waste that is landfilled. The aqueous wastewater overflow is sent to a public wastewater treatment facility.

The flowsheet in Figure 10 produces a third waste sludge as the acid-washed bottoms product is treated by a second distillation using activated

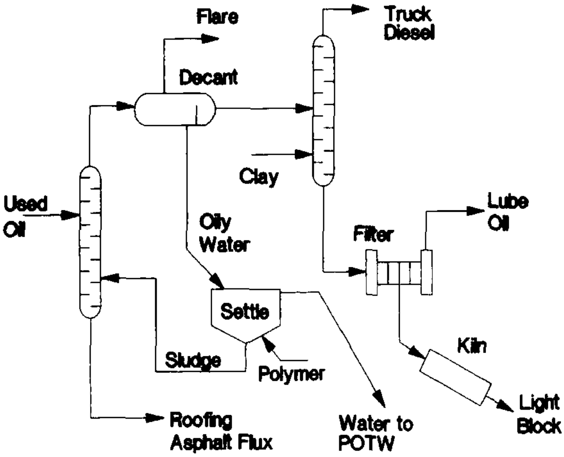

Figure 11: Miller process for used motor oil reuse and recycle. Note that all solid wastes are eliminated or used beneficially. [Adapted with permission from S. F. Miler, Making the most of bottoms and residuals. In *Solvent Waste Reduction*, pages 97–104. Noyes Data Corporation, Park Ridge, NJ (1990)].

clay to remove color bodies. The distillate from the second column is a light oil product. The bottoms product is treated by filtration to produce an oily spent-clay waste while the filtrate yields a 30 weight motor oil.

The original acid-clay recycle scheme in Figure 10 produces three sludge wastes, all of which are hazardous. Miller's recycle scheme in Figure 11 eliminates all of these wastes while still producing useful oil products for reuse. The key features are sludge recycle between the oily-water settler and the first distillation column, and the use of a polymeric coagulant instead of alum and lime to produce a wastewater suitable for treatment by a public utility.

Figure 11 illustrates several other features that give this process superior systems properties. First, the $CaSO_4$ sludge is eliminated because sulfuric acid (and subsequent $CaCO_3$ neutralization) are no longer required. Second, the metals present in the used motor oil are incorporated into a new product, a roofing asphalt flux, instead of the sulfate sludge. Thus, the polymeric coagulant serves two purposes. It enhances the oil water separation by producing a sludge that settles faster, and it enables the metals in the sludge to become incorporated into the asphalt flux while in the distillation column.

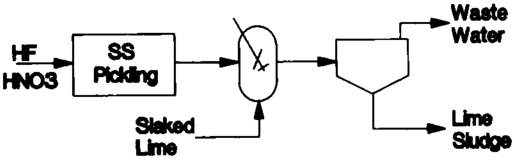

Figure 12: Conventional pickling acid waste management.

The second tower and filter are virtually identical to those in Figure 10. The kiln in Figure 11 is new, but it could also be applied to the spent clay sludge in Figure 10. The concept is simple, but effective. Instead of landfilling the spent clay, it is used to manufacture lightweight aggregate for concrete block (e.g., cinder block). This strategy converts the third sludge waste to a usable by-product.

The remaining products generated from used motor oil in Figure 11 are similar to those generated in Figure 10. In addition, the flowsheet in Figure 11 eliminates two essential unit operations in Figure 10 (a settler and a mix tank to neutralize the sulfuric acid). In addition to eliminating much of the wastes, Miller's concept is also attractive because it otherwise utilizes the same separation operations as in Figure 10. Thus, retrofit problems are minimal.

Acid Recycle

The most attractive technologies for recycle also offer reagent regeneration. In this way, the additional waste management costs can be partially offset by reduced reagent requirements. Thornburg et al. provide one example for recovering nitric and hydrofluoric acids from spent pickling liquors [160]. In a conventional pickling operation, acids are neutralized using slaked lime to produce a sludge waste and wastewaters as shown in Figure 12.

Acid recovery is implemented by using KOH rather than $Ca(OH)_2$ to neutralize the acids. Metal sludges are still precipitated as hydroxide wastes which are recovered as solids using filtration. Brine filtrate is then recycled using electrodialysis to split water and regenerate usable acids:

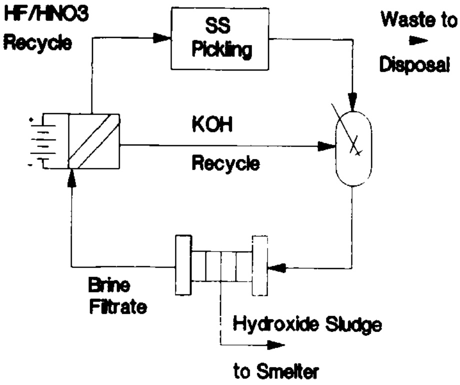

Figure 13: Pickling acid waste management and recycle using electrodialysis. [Adapted with permission from G. Thornberg et al., Recovery and recycle of valuable constituents in spent pickling acid, *Environ Progress*, 9(4):N10–N11 (1990)].

$$KF + H_2O \rightleftharpoons KOH + HF \qquad (9)$$

$$KNO_3 + H_2O \rightleftharpoons KOH + HNO_3 \qquad (10)$$

Figure 13 illustrates the entire recycle concept.

Dual-pH Precipitation

Batchelor et al. [161] discuss an advanced lime precipitation concept that uses two pHs to achieve a higher degree of cooling water recycle. A conventional process operates as indicated in Figure 14. A single pH, typically 9.5–10.5, is used to maintain water quality. A cooling water bleed is used to control the buildup of dissolved salts.

The dual-pH (or ultra-high lime) concept is illustrated in Figure 15. Water is still treated at a pH of 9.5–10.5 prior to use, but the bleed stream is recycled by additional (ultra-high) liming to a pH of 11–12. This strategy precipitates silicates and magnesium salts. Lime use is controlled by recycling the ultra-high lime effluent to the high-lime mix tank. This concept illustrates an advanced precipitation concept that is significantly enhanced by

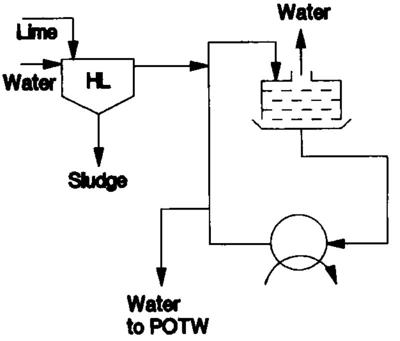

Figure 14: Conventional cooling water treatment with high lime treatment at a single pH.

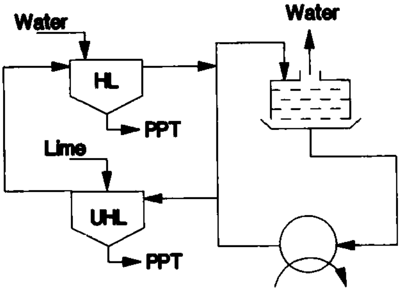

Figure 15: Cooling water recycle using ultra-high lime treatment (dual pH) concept. [Adapted with permission from B. Batchelor et al., Technical and economic feasibility of ultra-high lime treatment of recycled cooling water, *Res J Water Pollut Control Fed*, 63(7):982–990 (1991)].

process integration. By eliminating (or at least reducing) the cooling water bleed stream, the potential exists for reducing chemical usage somewhat. The dual-pH scheme also reduces the production of secondary wastewaters.

The above examples illustrate the creative possibilities that exist and the growing importance of systems analysis to separations design and waste management. Benforado et al. present an intriguing specialty-chemicals example that achieves similar benefits for a batch process [162]. They substitute a reactive distillation step for a pressure reactor to achieve higher product yields. This modification together with improved cleanup and reagent recycle separations yields an almost 90% reduction in waste production.

Berglund and Lawson distinguish between *intrinsic* and *extrinsic* wastes in their systems analysis [163]. The former are inherent in the fundamental process configuration (e.g., raw materials). They are eliminated by adopting new manufacturing technology. Extrinsic wastes are associated with auxiliary operations (e.g., fugitive emissions and secondary wastes). Berglund and Lawson cite ethylene oxide manufacture via the chlorohydrin route versus the direct-oxidation process to make their point. Jacobs also emphasizes the importance of waste-elimination (or intrinsic) considerations in the initial process design [164].

Summary

Hazardous wastes are a growing problem in today's world. They are increasing in both quantity and toxicity. At the same time, government regulations to restrict their disposal and release are becoming more stringent. Since wastewater concerns are most prevalent, they will continue to dominate our immediate needs and focus.

Separation technologies can be helpful in decontaminating waste streams. On the other hand, decontamination and discharge may not be the best long-term strategy. Stream recycle and pollution prevention may be more attractive, especially as release limits continue to drop and design criteria change. Separations can play key roles in the synthesis of new processes that efficiently achieve these latter goals.

Many of the traditional separation processes are inefficient for the removal of trace contaminants. Consequently, there are still many research opportunities that may utilize unit operations which are more energy efficient or novel. Membrane-based technologies which enable the regeneration and recycle of reagent acids and bases are of particular interest.

Biologically-induced separations exhibit considerable potential because of their low cost and relatively benign characteristics. Microorganisms will continue to play important roles in water purification through immobilization on beds, and the exploitation of their naturally occurring bioaccumulative properties. Their abilities to oxidize and reduce various species should not be overlooked, as these abilities can be exploited to either liberate or precipitate metals.

Waste recycle will become increasingly important, particularly in its interaction with process separations. Specialized separations can provide new and improved alternatives for process synthesis, but the overall system performance determines its effectiveness as a waste management strategy. Process synthesis and integration are particularly important, and it is essential to have an overall strategy and a clear vision.

Separation technologies, both old and new, can play important roles in the discovery of new processing configurations that greatly reduce or eliminate waste production. Generally speaking, the best strategies will convert wastes into assets, reduce production costs, and provide more robust networks. Improvements in waste management can also improve product recovery, and this factor should always be considered in planning an overall strategy.

Notation

BOD	biological oxygen demand
BSA	biological separation agent
ESA	energy separation agent
K_d	dissociation constant of Cu-mycelia complex
P_i^{sat}	pure component vapor pressure for species i
LNAPL	light non-aqueous liquid hydrocarbons
MCL	maximum concentration limit
MCLG	maximum concentration limit goal
MSA	mass separation agent
TLV	threshold limit value
VOC	volatile organic chemical
α_{ij}^{∞}	infinite dilution relative volatility for solute i in solvent j
γ_i^{∞}	infinite dilution activity coefficient for species i
ν	μg Cu^{2+} bound per mg mycelia adsorbent
ν_{max}	maximum Cu loading onto mycelia

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