1

Introduction

When the well's dry, we know the worth of water.

– BENJAMIN FRANKLIN (1706–1790), *Poor Richard's Almanac*, 1746

You can't always get what you want, but, if you try sometimes, you get what you need.

– ROLLING STONES, 1969

1.1 Objectives

1. Define separation processes and explain their importance to environmental applications.
2. Describe equilibrium- and rate-based analysis of separation processes.
3. List pollution sources for water, air, and soil.
4. Give examples of clean-up of existing pollution problems and pollution prevention.
5. Describe the hierarchy of pollution prevention.
6. Discuss the relationship between degree of dilution and cost of separations.
7. Be able to state the three primary functions of separation processes.

1.2 Why study environmental applications?

The National Research Council released a report [1] that states:

> The expanding world population is having a tremendous impact on our ecosystem, since the environment must ultimately accommodate all human-derived waste materials. The industries that provide us with food, energy and shelter also introduce pollutants into the air, water, and land. The potential for an increasing environmental impact will inevitably result in society's setting even lower allowable levels for pollutants.

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Table 1.1 *US Environmental Industry segments [2].*

Services	Resources	Equipment
Consulting and Engineering	Water Utilities	Water Equipment and Chemical
Waste Management	Energy Sources and Recovery	Instruments and Information Systems
• Solid waste	Resource Recovery	Air Pollution Control Equipment
• Hazardous waste		Waste Management Equipment
• Water		Process and Prevention Technology
Remediation		
Industrial Services		
Analytical Services		

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Table 1.2 *The Environmental Industry in the United States in 1992 [4].*

Sector	Approximate size	Approximate growth
Engineering and Consulting	\$ 12 billion	15% over 10 years
Water Supply and Treatment	\$ 30 billion	5%
Air Quality	\$ 6 billion	15%
Equipment/New Technology	\$ 11 billion	N/A

The report further concludes, “In the future, separation processes will be critical for environmental remediation and protection.”

Chemical separations are used to reduce the quantity of potentially toxic or hazardous materials discharged to the environment. In addition, separations that lead to recovery, recycle, or reuse of materials also prevent discharge.

The US Environmental Industry is made up of many segments. Table 1.1 lists the major segments and their chief components [2]. It is apparent that chemical separations play a large role in each of these areas. In addition, processes to separate and purify chemicals consume over 10^{15} BTU of energy (BTU = 1,055 joules) alone in the United States each year. They directly or indirectly generate considerable emissions, which pose challenges that will require new processing approaches [3].

The Environmental Industry in the US is large and projected to grow at a substantial rate. Table 1.2 provides some data related to environmental applications of separations. Even if the projections are “overly enthusiastic,” it is clear that this is an important technology area and will continue to grow.

1.3 Background

The topic of the material in this text is chemical separations with environmental applications. Separation processes are any set of operations that separate solutions of two or more components into two or more products that differ in composition. These may either remove a single component from a mixture or separate a solution into its almost pure components. This is achieved by exploiting chemical and physical property differences between the substances through the use of a separating agent (mass or energy).

Separation processes are used for three primary functions: purification, concentration, and fractionation. Purification is the removal of undesired components in a feed mixture from the desired species. For example, acid gases, such as sulfur dioxide and nitrogen oxides, must be removed from power plant combustion gas effluents before being discharged into the atmosphere. Concentration is performed to obtain a higher proportion of desired components that are initially dilute in a feed stream. An example is the concentration of metals present in an electroplating process by removal of water. This separation allows one to recycle the metals back to the electroplating process rather than discharge them to the environment. Lastly, in fractionation, a feed stream of two or more components is segregated into product streams of different components, typically relatively pure streams of each component. The separation of radioactive waste with short half-lives from that having much longer half-lives facilitates proper handling and storage.

Analysis of separation processes can be placed into two fundamental categories: equilibrium-based and rate-based processes. These separation categories are designated using thermodynamic equilibrium relationships between phases and the rate of transfer of a species from one phase into another, respectively. The choice of which analysis to apply is governed by which is the limiting step. If mass transfer is rapid, such that equilibrium is quickly approached, then the separation is equilibrium limited. On the other hand, if mass transfer is slow, such that equilibrium is not quickly approached, the separation is mass transfer limited. In some separations, the choice of analysis depends upon the type of process equipment used.

Equilibrium processes are those in which cascades of individual units, called stages, are operated with two streams typically flowing countercurrent to each other. The degree of separation in each stage is governed by a thermodynamic equilibrium relationship between the phases. One example is distillation, in which a different temperature at each stage alters the vapor-phase equilibrium between a typically binary mixture. The driving force for separation is the desire of a new equilibrium between the two phases at the temperature of each stage. The end result is the separation of two liquids with dissimilar boiling temperatures. Other equilibrium-based processes that will be covered in this text include extraction and solid extraction, or leaching. Extraction is the removal of a species from a liquid in which it is dissolved by means of another liquid for which it has a higher affinity, and leaching is the removal of a species from a solid phase by means of a liquid for which it has stronger affinity.

Rate-based processes are limited by the rate of mass transfer of individual components from one phase into another under the influence of physical stimuli. Concentration gradients are the most common stimuli, but temperature, pressure, or external force fields can also cause mass transfer. One mass transfer based process is gas absorption, a process by which a vapor is removed from its mixture with an inert gas by means of a liquid in which the vapor is soluble. Desorption, or stripping, on the other hand, is the removal of a volatile gas from a liquid by means of a gas in which the volatile gas is soluble. Adsorption consists of the removal of a species from a fluid stream by means of a solid adsorbent with which the species has a higher affinity. Ion exchange is similar to adsorption, except that the species removed from solution is replaced with a species from the solid resin matrix so that electroneutrality is maintained. Lastly, membrane separations are based upon differences in permeability (transport through the membrane) between components of a feed stream due to size and chemical selectivity for the membrane material.

1.4 Pollution sources

Sources of pollution vary from small-scale businesses, such as dry cleaners and gas stations, to very large-scale operations, such as power plants and petrochemical facilities. The effluent streams of industry are particularly noticeable because of their large volumes [1]. Sources include both point-source and non-point-source pollution. Point-source pollution can be traced directly to single outlet points, such as a pipe releasing into a waterway. Non-point-source pollutants, on the other hand, such as agricultural run-off, cannot be traced to a single definite source. The emissions from both span a wide range of gas, liquid, and solid compounds.

A large majority of air-polluting emissions come from mobile sources. The automobile is an obvious example, but other vehicles, such as trucks, trains, and aircraft also contribute. Emissions from mobile sources include CO_2, volatile organic compounds (VOCs), NO_x, and particulates. The last may also have heavy metals, such as lead or mercury, or hazardous organics attached. Stationary sources typically burn or produce fossil fuels – coal, gasolines, and natural gas. This produces gaseous sulfur compounds (H_2S, SO_2, etc.), nitrogen oxides (NO_x), CO_2 and particulates. Fuel producers and distributors also typically produce VOCs. Most of these pose human health concerns and many contribute to the acid-rain problem and global warming effect.

Water pollution also comes from a variety of sources. Agricultural chemicals (fertilizers, pesticides, herbicides) find their way into groundwater and surface water due to water run-off from farming areas. For example, agricultural drainage water with high concentrations of selenium threatens the Kesterson National Wildlife Refuge in California. Chemical discharge from sources ranging from household releases (lawn fertilizers, detergents, motor oil) to industrial releases into surface or groundwater supplies is an obvious problem. Industrial discharges can occur due to leaking storage facilities as well as process effluent. Municipal water treatment effluent is another prevalent source. MTBE, a gasoline additive used until recently to reduce air pollution, has been identified as a source of water pollution, demonstrating that the solution to one environmental concern can create a problem elsewhere. Isolation and recovery of these and other water pollutants pose a challenge to develop innovative separation techniques.

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Pollution of soils also occurs through a variety of sources. Municipal and industrial waste has been buried in landfills, which sometimes leak, even if lined with durable impermeable materials. Periodic news accounts of hazardous chemicals migrating through soil to threaten water supplies and homes are reminders of this issue. Chemical discharge directly onto surface soil from periodic equipment cleaning, accidental discharges (spills), abandoned process facilities or disposal sites is another environmental challenge. Subsurface contamination can also occur as a result of leaking underground storage tanks.

In addition to air, water, and soil pollution, large quantities of solid and liquid wastes generated by both industry and domestic use must be remediated, recycled, or contained. Industrial wastes include overburden and tailings from mining, milling, and refining, as well as residues from coal-fired steam plants and the wastes from many manufacturing processes. The nuclear and medical industries generate radioactive solid wastes that must be carefully handled and isolated. Effective ways of fractionating long-lived radioactive isotopes from short-lived ones are needed because the long-lived ones require more expensive handling and storage. The environmental problems of residential wastes are increasing as the population grows. It is important to segregate and recycle useful materials from these wastes. In many places, there are no effective options for dealing with toxic liquid wastes. Landfill and surface impoundment are being phased out. There is a strong incentive toward source reduction and recycling, which creates a need for separations technology [1].

All of the above separation needs are oriented primarily toward removal and isolation of hazardous material from effluent or waste streams. Pollutants are frequently present in only trace quantities, such that highly resolving separation systems will be required for detection and removal. The problem of removing pollutants from extremely dilute solutions is becoming more important as allowable release levels for pollutants are lowered. For example, proposed standards for the release of arsenic prescribe levels at or below the current limit of detection. Another example is pollution of water with trace quantities of dioxin. In research being carried out at Dow Chemical USA, concentrations of adsorbed dioxin at the part-per-quadrillion (10^{15}) level have been successfully removed from aqueous effluents. That technology has now been scaled up, such that dioxin removals to less than ten parts per quadrillion are being achieved on a continuous basis on the 20 million gallon per day wastewater effluent stream from Dow's Midland, Michigan, manufacturing facility.

1.5 Environmental separations

Based upon sources of pollution and the nature of polluted sites (air, land, or water), environmental separations can be categorized as follows.

1 Clean up of existing pollution problems

Examples:

- surface water contamination (organics, metals, etc.)
- groundwater contamination (organics, metals, etc.)
- airborne pollutants (SO_x, NO_x, CO, etc.)

- soil clean-up (solvent contamination, heavy metals, etc.)
- continuing discharges to the environment
  automobiles
  industries (chemical, nuclear, electronics, engineering, etc.).

2 Pollution prevention

Examples:

- chemically benign processing
  hybrid processing
  use of water instead of hydrocarbon/fluorocarbon solvents
  alternative chemical synthesis routes
- use of separation step(s)
  reduction in downstream processing steps
  eliminate solvent use (membranes instead of extraction, for example)
  eliminate purge streams (internally remove contaminants so purge stream is not needed)
  recovery and recycle instead of discharge (organics, water).

Figure 1.1 portrays a hierarchy for pollution prevention [5]. It is apparent that the difficulty of implementation decreases from top to bottom. Note that, the first four approaches on the hierarchy involve chemical separations (mass transfer operations).

The Chemical Manufacturers Association has published a strategy [6] for addressing pollution minimization or elimination in chemical processing facilities very similar to Figure 1.1. They suggest, in priority order:

1 Source reduction. Process changes to eliminate the problem.

These process changes can include:

- Reducing by-product formation through changes in processing and/or catalyst usage. This step can include changes in raw materials used.
- Better process control to minimize processing variations which lead to additional discharges.
- New processing flowsheets to minimize unwanted product generation and/or release.

2 Recycle. If source reduction is not feasible, then recycle

- within the process
- within the plant
- off-site.

3 Treatment. Post-process waste treatment prior to discharge to minimize the environmental impact.

A recent article [7] describes more than 50 pollution prevention strategies that do not require large investment costs.

The use of chemical separations is already very important in many industries. These include biotechnology, metals recovery and purification, fuels, chemical processing plants and feedstocks, municipal sewage treatment, and microelectronics. For these and other industries, the efficiency of the separation steps is often the critical factor in the final cost of the product.

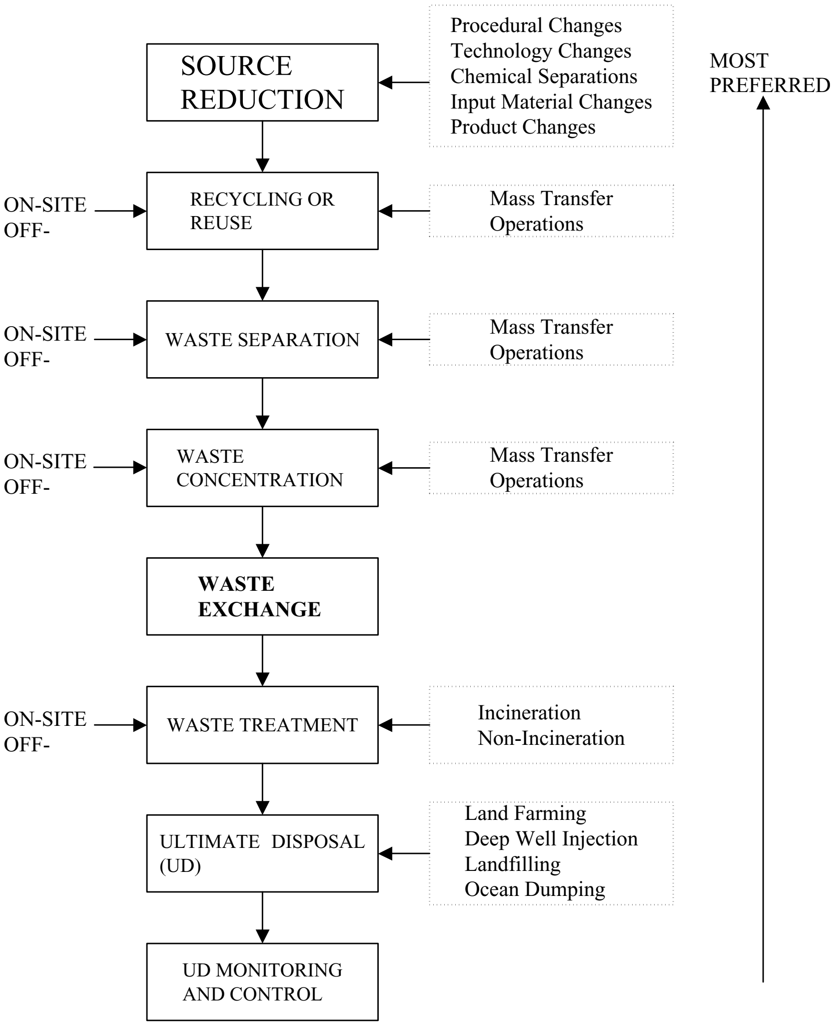

Figure 1.1 Pollution Prevention Hierarchy [5]. (Copyright © 1993, John Wiley & Sons, Inc.) This material is used by permission of John Wiley & Sons, Inc.

The separation cost is often related directly to the degree of dilution for the component of interest in the initial mixture. This cost includes the fact that most separations use 50 times the minimum energy requirement based on the ideal thermodynamic requirements. To put the energy consumption in perspective, the chemical and petroleum refining industries in the US consume approximately 2.9 million barrels per day of crude oil in feedstock conversion [1]. One method to visualize this cost factor is with the Sherwood plot shown in Figure 1.2.

This log–log plot shows that there is a reasonable correlation between the initial concentration of a solute in a mixture and its final price. For environmental applications, this correlation would translate to the cost of removal and/or recovery of a pollutant based on its initial concentration.

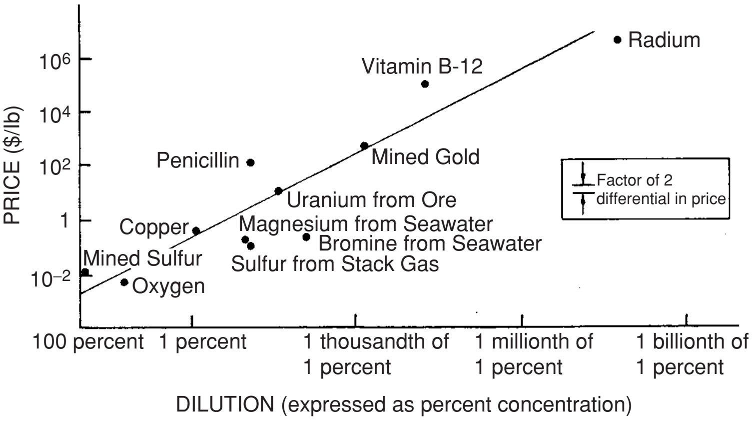

Figure 1.2 Sherwood plot [1]. Reproduced with permission of National Academy Press.

1.6 Historic perspective of environmental pollution

Rainwater is acidic due to atmospheric CO_2, SO_2 and nitrogen oxides; its pH is typically 5.6. Measurements of 4.6 are found in some regions of the US and values of 4.0 (and even 3.0) have been documented. Since pH is a log scale, these low pH values represent much stronger acids than occur naturally. The effects of these stronger acids on plants, animals, and materials have been well documented. Acid deposition can initially be dry. Gases and/or salts can be deposited. They can cause damage "as is," such as uptake by plants, or when hydrated [8]. In addition to contributing to acid rain, CO_2 also acts as a "greenhouse gas" and contributes to global warming.

The issue of chemical emissions and their effect on the environment is not limited to recent history. As shown below, acid rain was first documented in the 1600s. The chronology below lists some important events in the identification, monitoring, and steps to reduce emissions for acid rain and global warming [9].

1661–2	English investigators John Evelyn and John Graunt publish separate studies speculating on the adverse influence of industrial emissions on the health of plants and people. They mention the problem of transboundary exchange of pollutants between England and France. They also recommend remedial measures such as locating industry outside of town and using taller chimneys to spread "smoke" into "distant parts."
1734	Swedish scientist C. V. Linné describes a 500-year-old smelter at Falun, Sweden: ". . . we felt a strong smell of sulfur . . . rising to the west of the city . . . a poisonous, pungent sulphur smoke, poisoning the air wide around . . . corroding the earth so that no herbs can grow around it."
1872	English scientist Robert Angus Smith coins the term "acid-rain" in a book called *Air and Rain: The Beginnings of a Chemical Climatology*. Smith is the first to

	note acid-rain damage to plants and materials. He proposes detailed procedures for the collection and chemical analysis of precipitation.
1911	English scientists C. Crowther and H. G. Ruston demonstrate that acidity of precipitation decreases the further one moves from the center of Leeds, England. They associate these levels of acidity with coal combustion at factories in Leeds.
1923	American scientists W.H. MacIntyre and I.B. Young conduct the first detailed study of precipitation chemistry in the United States. The focus of their work is the importance of airborne nutrients to crop growth.
1948	Swedish scientist Hans Egner, working in the same vein of agricultural science as MacIntyre and Young, set up the first large-scale precipitation chemistry network in Europe. Acidity of precipitation is one of the parameters tested.
1954	Swedish scientists Carl Gustav Rossby and Erik Eriksson help to expand Egner's regional network into the continent-wide *European Air Chemistry Network*. Their pioneering work in atmospheric chemistry generates new insights into the long-distance dispersal of air pollutants.
1972	Two Canadian scientists, R.J. Beamish and H.H. Harvey, report declines in fish populations due to acidification of Canadian lake waters.
1975	Scientists gather at Ohio State University for the *First International Symposium on Acid Precipitation and the Forest Ecosystem*.
1977	The UN Economic Commission for Europe (ECE) sets up a *Cooperative Programme for Monitoring and Evaluating the Long-Range Transmission of Air Pollutants in Europe*.
1979	The UN's World Health Organization (WHO) establishes acceptable ambient levels for SO_2 and NO_x. Thirty-one industrialized nations sign the *Convention on Long-Range Transboundary Air Pollution* under the aegis of the ECE.
1980	The US Congress passes an *Acid Deposition Act* providing for a 10-year acid-rain research program under the direction of the *National Acid Precipitation Assessment Program*.
1980	The United States and Canada sign a Memorandum of Intent to develop a bilateral agreement on transboundary air pollution, including "the already serious problem of acid rain."
1985	The ECE sets 1993 as the target date to reduce SO_2 emissions or their transboundary fluxes by at least 30% from 1980 levels.
1986	On January 8, the Canadian and US Special Envoys on Acid Rain present a joint report to their respective governments calling for a $5 billion control technology demonstration program.
1986	In March, US President Ronald Reagan and Prime Minister Brian Mulroney of Canada endorse the *Report of the Special Envoys* and agree to continue to work together to solve the acid-rain problem.
1995	An Intergovernmental Panel on Climate Change, representing over 2,000 scientists from over 50 countries, concludes that "the balance of evidence suggests there is a discernable human influence on global climate." They also list some

striking projections by 2100 if the present trends continue:

- greenhouse gases could exceed 700 ppm levels not seen for 50 million years
- average atmospheric temperature will rise by 2 to 6.5 °F (1 to 3.5 °C), exceeding the rate of change for the last 10,000 years
- sea levels could rise between 6 to 37 inches (0.15 to 1 m).

1997 *Kyoto Protocol* agreement reached. This agreement is the first global approach to controlling greenhouse gas emissions.

Separations technology is already making an important contribution to ameliorating the acid-rain problem. Wet-scrubbing processes are the most widely used systems for removal of sulfur and nitrogen compounds from effluent stack gases. The limits of cost for wet-scrubbing techniques are such that they are not used to remove more than 75 percent of the sulfur-oxide compounds present and are currently of only limited effectiveness for removal of nitrogen oxides. Such systems also produce large quantities of sludge that present a solids disposal problem. New reagent systems that can be used in a more effective recycling mode are needed, and would be particularly useful if they could simultaneously remove both sulfur and nitrogen compounds in forms from which they could be converted into useful products. In any case, effective approaches must be brought into use to remove the nitrogen compounds.

1.7 The sulfur problem: where separations can help

Our principal sources of energy – fossil fuels – are all contaminated to some extent with sulfur compounds. When these fuels are burned, the sulfur compounds are burned to sulfur oxides, which are emitted to the atmosphere in the flue gas. In the atmosphere, these oxides are converted into the sulfur acids that are a principal cause of acid rain.

Separations technology plays a critical role in limiting sulfur-oxide pollution from sulfur-bearing fossil fuels. This technology is sufficiently advanced that there are no inherent technological limits to removing more than 95 percent of the sulfur present in natural gas, crude oil, and coal – many processes exist for accomplishing this before, during, or after combustion. The principal barriers to nearly complete sulfur removal are cost and practicality.

Natural Gas. The principal sulfur contaminant of natural gas is another gas – hydrogen sulfide. Because it is extremely toxic, civil authorities have long forbidden significant levels of this compound in natural-gas pipelines. Hydrogen sulfide is removed from natural gas by a variety of commercial processes including reaction with aqueous solutions of oxidants, absorption into aqueous solutions of bases, distillation, and selective permeation through membranes. The end product of these processes is elemental sulfur, which can be sold and, in some cases, is worth more than the co-produced natural gas. In 1984, about 24,000 tons (24 million kilograms) of sulfur was produced from natural-gas wells in the United States.