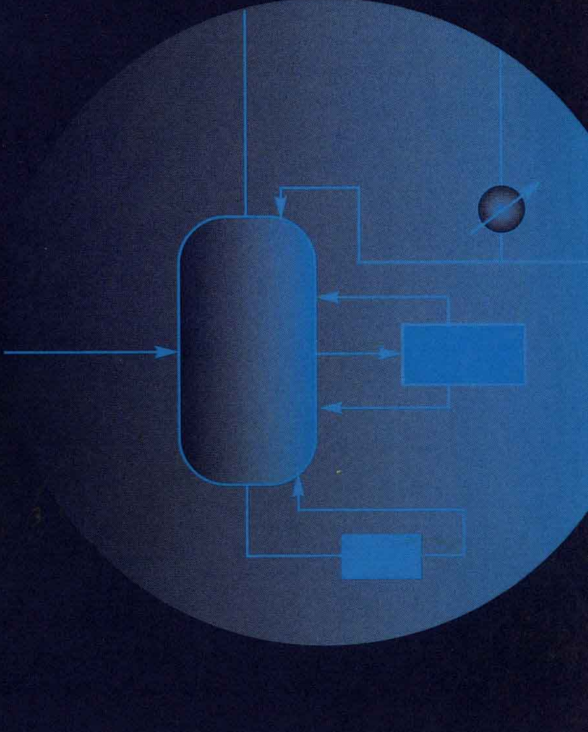
Principles of Chemical Separations with Environmental Applications



Richard D. Noble and Patricia A. Terry

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Richard D. Noble
University of Colorado, Boulder

and

Patricia A. Terry
University of Wisconsin, Green Bay

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Principles of Chemical Separations with Environmental Applications

Chemical separations are of central importance in many areas of environmental science, whether it is the clean-up of polluted water or soil, the treatment of discharge streams from chemical processes, or modification of a specific process to decrease its environmental impact. This book is an introduction to chemical separations, focusing on their use in environmental applications.

The authors first discuss the general aspects of separations technology as a unit operation. They also describe how property differences are used to generate separations, the use of separating agents, and the selection criteria for particular separation techniques. The general approach for each technology is to present the chemical and/or physical basis for the process, and explain how to evaluate it for design and analysis.

The book contains many worked examples and homework problems. It is an ideal textbook for undergraduate and graduate students taking courses on environmental separations or environmental engineering.

RICHARD NOBLE received his Ph.D. from the University of California, Davis. He is a professor of Chemical Engineering and Co-Director of the Membrane Applied Science and Technology Center at the University of Colorado, Boulder.

PATRICIA TERRY received her Ph.D. from the University of Colorado, Boulder, and is an associate professor in the Department of Natural and Applied Sciences at the University of Wisconsin, Green Bay. She has also held positions at Dow Chemicals and Shell Research and Development.

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Preface

Separation – the process of separating one or more constituents out from a mixture – is a critical component of almost every facet of chemicals in our environment, whether it is remediation of existing polluted water or soil, treatment of effluents from existing chemical processes to minimize discharges to the environment, or modifications to chemical processes to reduce or eliminate the environmental impact (chemically benign processing). Having said this, there is no text today for this subject which describes conventional processing approaches (extraction, ion exchange, etc.) as well as newer techniques (membranes) to attack the serious environmental problems that cannot be adequately treated with conventional approaches. Existing texts for this subject primarily focus on wastewater treatment using technology that will not be suitable in the larger context of environmental separations. Interestingly, most chemical engineering texts on separations technology are primarily based on whether the separation is equilibrium or rate based. Thus, it is difficult to find one source for separations technology in general.

This text is meant as an introduction to chemical separations in general and various specific separations technologies. In Chapter 1 we give a generalized definition of separation processes and their environmental applications. Following this, the approach to the organization of this text is to first discuss, in Chapter 2, the generic aspects of separations technology as unit operations. This chapter will include a discussion of the use of property differences to generate the separation, the use of a separating agent to facilitate the separation, as well as some discussion on the criteria for selection of a particular separation process. This last point is usually discussed at the end of a text on separations, but we felt that it was better to give students this "food for thought" prior to any description of specific technologies.

Mass transfer fundamentals, including equilibrium- and rate-based mechanisms, are introduced in Chapter 3, before any description of specific technologies. Many readers will be chemists, civil engineers and others with little or no previous experience in the design or analysis of these processes. It is important that everyone be "brought up to speed" prior to any discussion of a specific process. If this is not done, each technolog appears to have its own set of rules and design algorithms. This "unique" set for eac process diminishes the ability of the reader to use generic principles to compare alternative and evaluate new approaches as they become available. Once this major division of th approaches has been covered, later chapters describe the specific technologies.

The section in Chapter 3 on equilibrium stage separations will include both graphica and analytical techniques. The graphical techniques are useful to visualize the process fc the student and the analytical methods reinforce the principles. Rate-based separations wi focus on diffusional processes and convective/dispersive effects which can be describe by mass transfer coefficients (k). Initial discussion will focus on which approach to us based on what information is available and what one wants to determine. For analyse using mass transfer coefficients, both the use of correlations to estimate a value for k an the determination of an overall mass transfer coefficient (K) will be covered.

In discussing individual separations technologies in Chapters 4 through 9 we conside separations using physical property differences as well as chemical interactions. Distilla tion, extraction, absorption, adsorption, ion exchange, and membranes are covered. Ou approach to each technology is not to provide an exhaustive description. Rather, we wa to explain the physical and/or chemical basis for the process and how to evaluate it fc design or analysis. Books that describe a given technology in detail will be given as refe ences. Membrane separations represent a new and emerging technology which has bee used commercially for filtration and gas separation. It is a topic that is rarely discussed i any text on separations, so we plan to insure that it receives adequate coverage.

Special thanks go to the students that assisted us including Kendra Axness, Katie Benk Liz Galli, Jill Gruber, Blue Parish, Laura Weber, and Tony Worsham. We also want t thank others in the chemical separations community that helped to encourage us alon the way including Ed Cussler, Phil Wankat, Jud King, Ed Lightfoot, Norman Li and Bi Koros. I (RDN) would like to thank Ben McCoy who taught my first separations class an started me, perhaps inadvertently, on this career path.

We are deeply indebted to Ellen Romig. Without her help in the typing and editing, is highly doubtful that this book would have seen the light of day.

Contents

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.

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.

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.)