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Separation Science and Technology – An ORNL Perspective

D. J. Pruett

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Chemical Technology Division

SEPARATION SCIENCE AND TECHNOLOGY — AN ORNL PERSPECTIVE

D. J. Pruett

NOTICE This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

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When confronted with a task as formidable as a review of all of separation science and technology, the first response of a rational individual is to ignore the request, since it is obviously impossible. When the "powers that be" make it clear that ignoring the request is not an option, one seeks solace in the old cliché that the only difference between the difficult and the impossible is that the impossible takes longer. In this case, an 8-month period was allotted for accomplishing the impossible.

Fortunately, I was not forced to attempt the impossible alone. Dr. Alex Zucker and Dr. Fred R. Mynatt provided the funds and official administrative support for this study. Dr. M. L. Poutsma, Dr. W. D. Shults, and Dr. R. G. Wymer provided technical guidance and organized a steering committee to oversee the project. Dr. Wymer chaired the committee, which was made up of Dr. D. L. Donohue, Dr. B. A. Moyer, Dr. J. P. Nichols, Dr. R. S. Ramsey, Dr. C. D. Scott, and Dr. A. D. Solomon. Dr. C. J. King and Dr. J. C. Giddings served as consultants to the committee and to me. The importance of the contributions of these individuals to the completion of this report cannot be overstated.

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EXECUTIVE SUMMARY

INTRODUCTION

The purpose of this report was fourfold. First, schemes to define and categorize the field of separation science and technology were examined. Second, several of the major categories of separation techniques were reviewed to determine the latest developments and future research needs. Third, selected problems and programs that require advances in separation science and technology as a part of their solution were considered. Finally, suggestions for new directions in separation research at ORNL were proposed.

DEFINITION AND CATEGORIZATION

One of the most promising developments in separation science and technology is the realization that a relatively small number of underlying principles unite the field. Considerable progress has been made in understanding the mechanisms that control entire classes of separation processes. Continued development of theories of separation based on these underlying principles and mechanisms will expedite the application of advances in fundamental fields such as phase-equilibrium thermodynamics, coordination chemistry, transport processes, interfacial phenomena, and chemical kinetics to the improvement of existing separation processes and the development of new ones. Nonetheless, while the idea of an all-embracing theory of separation science holds great promise and marks a true frontier, it will be many years before the concept is fully realized.

A SURVEY OF SOME IMPORTANT SEPARATION TECHNIQUES

Solvent extraction. The most important fundamental research areas now under investigation by solvent extraction chemists and chemical engineers include the study of interfacial phenomena, the development of new reagents with higher capacity and greater selectivity, the development of pharmaceutical and biological extraction processes, mathematical modeling of extraction processes, and improved designs for solvent extraction equipment.

Ion exchange. To the degree that an ion-exchange resin may be considered a solvent extraction reagent immobilized on a solid phase, the two techniques share many common research needs and interests. The details of the structure and reactivity of the solid-liquid interface are poorly understood, and new techniques are needed to study them. The development of inorganic ion-exchange material that can withstand greater extremes of temperature, pressure, and corrosivity shows great promise.

Membrane separations. The development of improved membrane separation is an active area of research. Most applications have involved the processing of aqueous streams. Applications to nonaqueous solutions, gaseous systems, and gas-liquid systems are promising but relatively undeveloped. A number of common chemical principles are involved in many solvent extraction, ion-exchange, chromatographic, and membrane processes, and cooperation between workers in these fields will speed the development of each. Important research areas include interfacial and transport phenomena, new carrier reagents, better mathematical models, an expanded data base, and the development of inorganic and biological membranes materials.

Chromatography. One of the greatest challenges in chromatography is the scale-up of techniques that are commonly used in the laboratory to the size of an industrial process. This will require advances in the accuracy of models of large-scale chromatographic equipment, as well as new support materials and equipment design. The development of laboratory-scale chromatography continues across all fronts at an impressive rate. One of the most promising research areas, the wedding of chromatography and biotechnology, involves the development of affinity chromatography and affinity partitioning.

Distillation. Distillation continues to be the most commonly used separation technique. In systems where distillation cannot be economically replaced, the development of high-efficiency packing materials and better heat integration through improved process design are needed. There is a general lack of suitable theoretical and empirical models to describe mass transfer, heat transfer, flow, and interfacial phenomena in distillation

columns. New packing materials must be more wettable, more durable, more corrosion resistant, and easier to manufacture. Where possible, new, less energy-intensive processes must be developed to replace distillation.

Supercritical fluid extraction. The use of supercritical fluid extraction processes is attracting greater attention for some applications because of potential advantages such as lower energy costs, ease of solvent recovery, faster kinetics, improved process control, and high separation factors. Disadvantages include the need to operate some processes at high temperature and pressure, which leads to increased capital costs, safety hazards, and increased energy consumption. Current applications of supercritical fluid extractions are few, and further development has been hampered by the paucity of theoretical models and thermodynamic and kinetic data in these systems.

Photon-enhanced separations. The category of "photon-enhanced separations" includes any separation process in which light is used as an important part of the separation process. Examples include laser isotope separations (LIS) and the use of photochemical redox reactions to control oxidation states, and thus separation factors, in solvent extraction systems. LIS techniques have been developed primarily for the enrichment of uranium, but their application to the purification of stable and medical isotopes should be explored more extensively.

Electromagnetic separations (mass spectrometry). In this report, the term "electromagnetic separation" refers to mass spectrometry (MS) and its variations. It is recognized that methods such as electrophoresis, electro dialysis, electrostatic precipitation, and the electromagnetic separation of metals from refuse could be included under this heading. Conversely, resonance ion mass spectrometry (RIMS), which is one of the most interesting MS techniques currently under extensive investigation, can also be classified as a photon-enhanced separation technique. Electromagnetic separation is applied almost exclusively on the analytical scale, where it has become an increasingly complex and useful tool for chemical investigation at the molecular level. Mass spectrometry, especially when

combined with other separation methods to form the so-called "hyphenated" techniques (GC/MS, LC/MS, MS/MS, etc.), has become the premier technique for separation, identification, and structure determination of the small (microgram) scale. The useful range of MS has been extended to molecular weights approaching 10,000, leading to increased application in the biological sciences.

GENERIC RESEARCH NEEDS

While it is impractical to attempt to survey all of the important separation techniques and their variations in one volume, it is possible to identify a relatively limited number of generic research areas that are common to large groups of separation methods and applications. These include interfacial phenomena, selectivity of separation agents, critical data base development and mathematical modeling, the chemistry of dilute solutions, and system design (e.g., the effects of applying external fields to a separation system). The results of study in these generic areas will be useful in the continuing attempts to integrate the field of separation science on a theoretical and process level.

APPLICATIONS

Nuclear fuel reprocessing. Research to address specific problems in existing Purex plants is needed, especially in the area of waste handling and disposal. Long-term research should be focused on the development of radically different separations processes, such as pyrochemical and volatilization methods.

TRU processing. If the need for significantly increased quantities of ^{252}Cf , greatly reduced operating costs, or a second high-flux isotope reactor (HFIR) is realized, a substantially improved process for separating and purifying the transuranium (TRU) elements from HFIR targets will be needed. New methods based on improved aqueous or pyrochemical flowsheets show promise for this application.

Strategic materials. Materials for which the United States is heavily dependent on foreign, perhaps unreliable, sources may be termed "critical" and are a matter of some concern. Separation science can help reduce this dependence by developing improved methods for recovering and recycling these materials and by developing new processes for extracting them from dilute domestic sources.

Analytical separations. Many advances in separation technology come about as a direct result of methods discovered in analytical laboratories, and the development of generalized models and techniques for the systematic transfer of separation technology from analytical applications to industrial applications could result in the use of dramatically improved methods in many instances. Increasing pressure to determine lower and lower concentrations of chemical species in the environment, food, pharmaceuticals, forensic samples, and special materials for the electronics, nuclear, and other industries has led to the development of greatly improved analytical techniques. These new techniques often require the separation and preconcentration of the species of interest from a complex matrix. The development of high-resolution techniques to separate and analyze the components of complex biological fluids is a challenging, high-priority area with great promise for the improved detection, diagnosis, and treatment of disease.

Ultrapurification. The demand of modern science, technology, and society for materials, foodstuffs, environments, and pharmaceuticals of unprecedented purity will continue and accelerate. The production and analysis of such materials will, in turn, continue to be a major driving force for the development of improved separation techniques of all kinds.

Hazardous waste. The problems presented by the hazardous materials that have been, or are being, discharged to the environment are formidable, and the solutions to such problems will challenge the limits of separation science and technology on all fronts. While significant progress has been made by the application of improved separation techniques to environmental protection, the limits of the success of these processes also mark the starting point for research and development for improved methods.

The systematic improvement and application of all separation technologies are required to reduce the volume of hazardous and radioactive wastes to be treated, to clean up existing waste dumps, and to meet the increasingly stringent regulations for handling and disposing of hazardous and radioactive materials. The successful development and application of these technologies will require an unprecedented degree of cooperation between separation scientists and engineers from all of the disciplines that make up the field, as well as among analytical chemists, toxicologists, environmental chemists, and regulatory agencies.

Biotechnology. Continued progress in biotechnology depends heavily on progress in separation science, while developments in biotechnology have led to important developments in separation science. The isolation of homogeneous, functionally specific populations of cells is one of the chief obstacles to progress in biotechnology. The separation and purification of the desired components from fermentation broths in an efficient, economic way are major challenges to separation science. On the other hand, the development of improved separations agents based on biological enzyme-substrate models, the development of improved membranes based on the structure of biological membranes, and the use of genetically engineered microbes to degrade hazardous material in the environment are outstanding examples of the application of biotechnology to separation science.

Acid precipitation. The development of improved methods for separating toxic and hazardous materials from the solid, gaseous, and liquid wastes generated by the burning of fossil fuels will require an integrated, systems approach to treatment across the entire fuel utilization cycle. Processes for the treatment of natural gas appear to be adequate, but improved methods for treating oil will probably be needed as regulations become more stringent. Current techniques for removing sulfur and nitrogen oxides produced by the burning of coal are inadequate and often generate sludges that are themselves a disposal problem.

CONCLUSIONS

The greatest challenge in separation science and technology is to unify the theory and application of the many techniques that comprise the field. This unification must take place (1) on the theoretical level, where attempts to derive models describing large classes of separation processes on the basis of the fundamental principles that underlie them must continue; (2) on an experimental level, where generic research areas common to many separation techniques, such as interfacial phenomena, chemical selectivity, critical thermodynamic and kinetic data base development, mathematical modeling, and the chemistry of dilute solutions, must be given priority; and (3) on the process level, where the overall design of separation systems and their integration into the processes with which they must work must be optimized.

Separations research at the Oak Ridge National Laboratory (ORNL) is largely divided along the lines of the traditional separation techniques, and the work being done in these individual areas is sound. ORNL can better respond to the need to develop a more unified approach to separation science and technology by creating a Center for Separation Research. An appropriate focus for this Center would be a problem that is of national importance, relevant to the mission of the Laboratory, broad enough to require a multidisciplinary and multidivisional approach, and suitable for the expenditure of federal funds. The role of separation science and technology in solving problems related to waste and environmental management is a suitable subject for this purpose. Such a program will form a needed complement to existing waste management programs and will address most of the applications and generic research areas of separation science and technology identified in this report. The Center will be able to use the Laboratory's separations facilities, equipment, and human resources most efficiently in addressing separation problems and solutions in waste management.

A novel program within the Center will be the development of an expert computer system in separation science and technology. This system will aid in integrating the theoretical treatment, empirical models,

engineering models, data bases, and analytical methods that are important in separation science. The principles of knowledge engineering and artificial intelligence will be used to preserve and make available the expertise of specialists in many of the common separation techniques.

ABSTRACT

This report was prepared as a summary of a fourfold effort: (1) to examine schemes for defining and categorizing the field of separation science and technology, (2) to review several of the major categories of separation techniques in order to determine the most recent developments and future research needs, (3) to consider selected problems and programs that require advances in separation science and technology as a part of their solution, and (4) to propose suggestions for new directions in separation research at Oak Ridge National Laboratory (ORNL).

The greatest challenge, and long-range goal, in separation science and technology is to unify the theory and applications of the many techniques that comprise the field. This unification must take place on the theoretical, experimental, and process levels. While it was impractical to survey all of the important separation techniques and their variations in this study, it was possible to identify a relatively limited number of generic research areas that are common to large groups of such methods and their applications. These include interfacial phenomena, selectivity of separation agents, critical data base development and mathematical modeling, the chemistry of dilute solutions, and system design. The findings will be useful in all continuing attempts to integrate separation science on both theoretical and process levels.

Separations research at ORNL is largely divided along the lines of traditional techniques, and the work being done is sound. However, ORNL could better respond to the need to develop a more unified approach by creating a Center for Separation Research, which would be able to use the Laboratory's facilities, equipment, and human resources. An appropriate focus for the Center would be problems of national significance, such as those related to waste and environmental management. A specific thrust would be to develop an expert computer system which would aid in integrating the theoretical treatment, empirical models, engineering models, data bases, and analytical methods that are important in separation science. In this way, the expertise of specialists in many of the common separation techniques could be preserved and made available to all interested groups.

SEPARATION SCIENCE AND TECHNOLOGY --
AN ORNL PERSPECTIVE

D. J. Pruett

1. INTRODUCTION

Many of the major scientific and technological problems of concern to scientists, industry, and to the nation as a whole are, at least in part, separation problems. This is especially true in areas such as energy production, conservation and use, biotechnology, resource recovery, and the removal of natural and man-made contaminants from the environment. For example, the burning of fossil fuels generates a variety of gaseous and solid wastes that must be removed and isolated from the environment. The production and recycling of nuclear fuels require the separation of the useful fissile materials from the highly radioactive fission products, as well as methods to ensure that the hazardous wastes remain separated from the biosphere. Efficient insulation of homes has resulted in increased concentrations of potentially hazardous gases that previously escaped through cracks and crevices. In biotechnology, which promises to make major contributions in fields as diverse as energy production, environmental cleanup, and human health, one of the chief obstacles to progress is the difficulty in separating and purifying a homogeneous, functionally specific population of living cells. The removal or recovery of toxic or valuable materials from dilute waste streams or sources will require the development of new and innovative separations techniques, as well as improved understanding of the coordination and redox chemistry of material at trace concentrations.

Separations science and technology will play a key role in the solution of these and many other problems of national concern. We cannot afford to abandon any important method of energy production and conservation or our progress in biotechnology simply because the separation method needed to make the technology economically or environmentally acceptable

does not yet exist. Nor can we afford to ignore the possible impact of the products of this technology on human health and the environment. Therefore, we must continue to develop the separation methods needed to solve these problems and to remove and isolate any potentially hazardous materials that are generated or concentrated by these technologies.

Only recently have attempts been made to organize and describe all of the various processes, techniques, and methods that are used to effect chemical and physical separations under the collective umbrella of "separation science and technology." It is not immediately obvious that a small set of fundamental scientific principles underlie processes as diverse as zone refining, solvent extraction, and distillation, but considerable progress has been made in identifying such a set. In fact, several methods for categorizing the field on the basis of these principles have appeared in the literature. Further, the scientific community is now beginning to use an understanding of these underlying principles to devise rational strategies for pursuing fundamental research that will lead to improved separations techniques and processes.

The Oak Ridge National Laboratory (ORNL), recognized as a leader in the field of separation science and technology for many years, has established a range of facilities and expertise in the field that is unique in the world. Historically, most separations research at ORNL has been done in support of the development of nuclear energy. In fact, ORNL was founded with the mission of purifying uranium and plutonium and separating uranium isotopes for use in the first fission weapons. In fulfilling this mission, ORNL staff members have developed (and have maintained) unsurpassed expertise in the fields of solvent extraction, ion-exchange, and electromagnetic separations. This early success was quickly followed by the development of techniques for the separation of hydrogen and lithium isotopes for use in the fusion weapons program. Although the Laboratory has long since lost its military orientation, the knowledge and experience gained in the early years are now being applied to the separation of fissile elements for use in power reactors, radioisotopes for medical, analytical, and other applications, and stable isotopes for a variety of purposes.

While ORNL is probably best known for its separations expertise in fields that grew naturally from its original charter, it has also made significant contributions to other areas of separation science and technology. In the late 1960s, the birth of biotechnology at ORNL led to the development of truly innovative methods for separating and analyzing DNA, RNA, and the components of body fluids. This program has continued to develop and to apply new separations techniques in chromatography, distillation, membranes, and special biomaterials in support of fundamental and applied research efforts.

In recent years, ORNL expertise in separation science and technology has been focused on problems in waste management and pollution control. Methods that were developed to control the hazardous materials used and produced in the nuclear fuel cycle are now being modified and applied to a broad range of special separations processes for removing hazardous components from liquid and gaseous discharge streams and for cleaning up materials that have already escaped into the environment at concentrations ranging from the picomolar to the molar scale. Well-established separation techniques for macrolevel contamination are usually not effective at submicrolevels of the same contaminant. Therefore, new and innovative processes must be developed to reduce these already low concentrations so as to comply with the increasingly stringent environmental regulations.

The purpose of this report is fourfold. First, it will review some of the schemes that have been proposed to define and categorize the field of separation science and technology. Second, the status of many of the major processes, techniques, and disciplines that are covered by this broad label will be examined in order to identify the latest developments and to determine what direction new research should take in improving the state of the art. While physical separations are not excluded, the emphasis will be on chemical separations. Third, selected problems and programs in the fields of energy, resource recovery, biotechnology, and environmental protection will be reviewed to illustrate how advances in separation science and technology can contribute to their solution. Finally, suggestions for future direction in separation research at ORNL will be proposed.

2. DEFINITION AND CATEGORIZATION OF SEPARATION SCIENCE AND TECHNOLOGY

The first challenge in reviewing a field as diverse as separation science and technology is to adequately define and categorize its boundaries and components. Only recently has separation science come to be viewed as a single field, rather than as a group of fields made up of a series of unrelated separations methods. Strain, Sato, and Engelke published a systematic classification of driving and resistive forces in separations in 1954,¹ and Rony developed a general concept of partition states and extent of separation that was applicable to all separations methods beginning in the late 1960s;²⁻¹¹ however, the idea of separation science as a field did not gain widespread recognition until the 1970s. The classic textbook of Karger, Snyder, and Horvath¹² dealt largely with analytical separation techniques, but it acknowledged the common principles that underlie all separations. The authors also recognized that a lack of communication between specialists in different separations techniques hindered the progress of each technique as well as the progress and impact of the field as a whole. At about the same time, the first volume in a continuing series of monographs on separation science appeared.¹³ This series reports advances in the individual techniques that comprise the field of separation science but also includes papers describing systematic approaches to the development of the field as a whole, as well as advances in the understanding of the forces and processes that underlie all separations techniques. Concurrently, Giddings¹⁴⁻¹⁷ began to develop the idea that mass transport equations combined with chemical potential profiles could be used to construct a logical framework on which to classify the field of separation. The journal *Separation Science* (now *Separation Science and Technology*) was launched in 1966 as a vehicle for increasing communication between scientists and technologists working in different areas of the field.

As a result of all this activity, the idea that separation science and technology can be viewed as a unified field has now gained widespread recognition among scientists, engineers, university researchers, and funding agencies. For example, the American Chemical Society (ACS) has

established a Subdivision of Separations Science and Technology within its Division of Industrial and Engineering Chemistry (I&EC). The University of Texas has established a Separations Research Program to carry out generic, fundamental research that is relevant to a wide range of separations processes. This program is funded by a number of industrial and governmental sponsors. The U.S. Department of Energy funds basic and applied research in separation science under several of its programs. The National Science Foundation has created a new program on separation processes. Each of these agencies, organizations, and institutions has explicitly endorsed the concept of separation science as a unified field and underscored the need for a systematic, interdisciplinary approach to the development of separation science and technology based on the fundamental phenomena that underlie all separation methods.

However, while the principle of separation science and technology as a unified field has been established, the details of how best to categorize and unite the field are far from complete. The definitions of separation, separation science, and separation technology are reasonably well standardized, but a variety of different schemes for categorizing the field as a whole have been proposed. In general, a "separation" is an operation by which a mixture is divided into at least two fractions having different compositions. "Separation science" is the study of the fundamental properties and processes that make a separation possible. "Separation technology" is the application of this fundamental information to practical problems of separation and purification. These definitions must be quite general if they are to include operations as different as the electromagnetic separation of isotopes, the purification of materials by solvent extraction, and the processing of ores by froth flotation. Further, the dividing line between "fundamental" and "applied" work is no clearer in separation research than in any other area of scientific investigation.

While the definition of separation science and technology is straightforward, the development of a rational scheme to categorize all of the techniques, processes, and disciplines encompassed by this definition is not. Thus far, the broad scope of separation science and technology has

frustrated efforts to categorize all of the methods, techniques, and principles that are important to the field in a simple, yet comprehensive, way. Although many schemes have been proposed and considerable progress has been made, no single outline is completely satisfactory. Not surprisingly, workers who are concerned with the practical application of separation technology on a large scale choose a quite different basis for categorizing the field than do those more concerned with examining and understanding the underlying principle of the separation technique on a microscale. It is useful to consider representative outlines from both points of view when attempting to develop an understanding of the field.

Figure 1 shows a categorization of separation science and technology similar to those that are found in engineering texts¹⁸ or may be proposed by individual engineers.¹⁹ These schemes generally use the phase(s) of the mixture to be separated as the primary criterion for grouping the various separation processes, methods, and techniques. Figure 2 presents an outline based primarily on the size of the material to be separated and secondarily on the physical or biological properties of the matrix.²⁰ Historically, separation science and technology has been outlined using schemes such as these. They represent a pragmatic, applications-oriented approach to categorizing the field. They have great practical utility in aiding the scientist or engineer who needs to select a separation technique for a specific application; however, they generally do not address the more fundamental questions concerning how the techniques actually effect a separation.

More recent attempts to categorize separation science and technology are based on an understanding of the fundamental principles that govern the separations processes on a microscale. One reasonable scheme for categorization has been derived by considering that, for one (or more) components to be separated from an initial mixture, it (or they) must be translated through space relative to the rest of the original mixture. In all cases, some impelling force must be applied to one or more components of the system. This force may affect only some of the components in the mixture, as in the case of the electrophoretic separation of

SEPARATION SCIENCE AND TECHNOLOGY

I. Gases

- A. Absorption
- B. Adsorption
- C. Thermal Diffusion
- D. Centrifugation
- E. Electromagnetic
- F. Gaseous Diffusion

II. Liquids

- A. Distillation
- B. Solvent Extraction
- C. Electrophoresis
- D. Electroplating
- E. Ion Exchange
- F. Membranes
- G. Parametric Pumping

III. Liquid/Solid

- A. Precipitation
- B. Dissolution
- C. Filtration
- D. Centrifugation
- E. Cell Counting
- F. Drying
- G. Leaching
- H. Flotation

IV. Solids

- A. Electrical
- B. Gravitational
- C. Magnetic
- D. Riffling

V. Plasmas

- A. Electromagnetic
- B. Photoelectric

Fig. 1. Partial categorization of separation science and technology based on the phase(s) of the mixture to be separated.

SEPARATION SCIENCE AND TECHNOLOGY

- I. Isotopes
 - A. Electromagnetic
 - B. AVLIS
 - C. COLEX
 - D. ELEX
 - E. Gaseous Diffusion
 - F. Gaseous Centrifuge

- II. Elements
 - A. Gases
 - 1. Distillation
 - 2. Adsorption/Desorption
 - B. Liquids
 - 1. Electrolysis
 - 2. Solvent Extraction
 - 3. Ion Exchange
 - 4. Membrane
 - C. Solids
 - 1. Smelting
 - 2. Recrystallization
 - 3. Zone Refining
 - 4. Magnetic

- III. Molecules
 - A. Physical Properties
 - 1. Size
 - a. Filtration
 - b. Gel Permeation/Size Exclusion
 - c. Centrifugation
 - 2. Mobility
 - a. Electrophoresis
 - b. Ion Chromatography
 - c. Membranes
 - 3. Melting Point
 - a. Crystallization
 - 4. Boiling Point
 - a. Distillation
 - 5. Magnetism
 - a. Magnetic
 - 6. Optical Absorption
 - a. Molecular AVLIS
 - b. Photodissociation
 - B. Chemical Properties
 - 1. Chromatography (all types)
 - 2. Precipitation/Filtration

- IV. Cells
 - A. Physical Properties
 - 1. Size
 - a. Centrifugation
 - b. Filtration
 - 2. Shape
 - a. Cell Counting
 - b. Microscopy
 - B. Biological Properties
 - 1. Culture Growing
 - 2. Metabolic/Genetic control

Fig. 2. Partial categorization of separation science and technology based on the size of the components to be separated.

charged species from uncharged species. Alternatively, it may affect all of the components of the mixture more or less equally while some retarding force acts selectively on one or more of the components, as demonstrated when the species flowing through an ion-exchange column are retarded by interactions with the resin. Scott²¹ has proposed a simple categorization of separation science and technology based primarily on the impelling forces used to effect the separation (Fig. 3). A rigorously complete categorization of all types of separations would require at least a three-dimensional matrix that accounted for all of the impelling forces, retarding forces, and phase inhomogeneities in the system. Such a complete description, however, would be far too cumbersome for most practical applications. Thus, the outline shown in Fig. 3 is not complete, but it illustrates a convenient framework upon which the field of separation science and technology can be organized.

Perhaps the most complete categorization of chemical separations based on a consideration of fundamental forces has been developed by Giddings.¹⁴⁻¹⁷ Like Scott, Giddings recognizes that a separation requires the different components of a mixture to be transported through space at different rates, and the movement may be caused by a variety of different forces. Forces that produce bulk displacement of the mixture (flow or direct mechanical relocation) are nonselective and do not effect a separation, although they are often present in a separation system. Forces that produce relative displacement [i.e., forces driving (or retarding) the components of a mixture through their surrounding medium at different rates] result in a separation. The forces that effect the relative displacement may be further characterized as continuous (e.g., an electric field) or discontinuous (e.g., the change in chemical potential at the interface of two phases). Occasionally, both continuous and discontinuous forces occur simultaneously in a single separation method; electrodialysis is an example of one such system.

While relative displacement is required for separation to occur, bulk displacement is not. For convenience, Giddings classifies a flow system as one in which bulk displacement occurs and a "static" system as

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- I. Methods Based on Activity Gradients
 - A. Single stage (Equilibrium)
 - 1. Crystallization
 - 2. Flash Evaporation
 - 3. Precipitation
 - B. Multistage (Forced Convection)
 - 1. Percolation Processes
 - 2. Solvent Extraction
 - 3. Distillation
- II. Methods Based on Pressure Gradients
 - A. Filtration
 - B. Sedimentation
- III. Methods Based on Body Forces
 - A. Centrifugation
 - B. Sedimentation
- IV. Methods Based on Electric Field Gradients
 - A. Electrophoresis
 - B. Electrochemistry
- V. Methods Based on Magnetic Field Gradients
 - A. Electromagnetic Separation
 - 1. Mass Spectroscopy
 - 2. Calutrons
 - B. Particulate Separation
- VI. Methods Based on Thermal Gradients
 - A. Thermal Diffusion
 - B. Zone Refining

Fig. 3. Partial categorization of separation science and technology based on impelling forces.

one in which bulk displacement does not occur. Flow systems are further classified according to whether the forces causing relative displacement are parallel (e.g., in filtration) or perpendicular (e.g., chromatography) to the flow.

Using these three criteria (continuous or discontinuous forces, static or flowing, flow and force parallel or perpendicular), Giddings has found that most separation methods fall into the six simple categories listed in Table 1. The distribution of separation methods among these six categories is shown in Table 2. Note that the few unusual methods that employ continuous and discontinuous forces simultaneously to drive the relative displacement are not included here. Also, note that while methods that are commonly related to one another are grouped together, this classification scheme also produces some unexpected pairings such as ultrafiltration and zone melting. Even though these two processes may seem unrelated upon first inspection, a more fundamental examination reveals that both involve a flow that is perpendicular to a discontinuous force effecting the separation. In each case, a selective interface moves relative to the fluid mixture and extreme polarization occurs. More importantly, it has been shown¹⁴ that this qualitative similarity can be formalized by the development of a mathematical description encompassing entire classes of systems related under this categorization. This common mathematical framework can be used to predict the performance of a separation system based on a knowledge of fundamental parameters (e.g., diffusion coefficients, field strengths, molecular weights, and viscosities) that can be easily measured or can be calculated from first principles.

Overall, these recent attempts to categorize the field of separation science and technology based on a better understanding of the fundamental phenomena that control the separation will make a more significant contribution to advancing the field than will the historical, more pragmatically based schemes. Our greater understanding of the mechanisms that control entire classes of separations will increase our ability to modify and improve separation processes for a specific application without resorting

Table 1. Six categories for separation methods^a

Continuous forces ^b	Discontinuous forces ^b
Sc	Sd
F(=)c	F(=)d
F(-)c	F(-)d

^aInformation taken from ref. 14.

^bS = static; F = flow; c = continuous force; d = discontinuous force; F(=) = parallel flow; and F(-) = perpendicular flow (see text for definitions.)

Table 2. Distribution of separation methods among the six categories^a

Flow condition	Continuous forces	Discontinuous forces
Static	Electrophoresis, isoelectric focusing, dielectrophoresis, and electrostatic precipitation; sedimentation and isopycnic centrifugation	Single-stage extraction, adsorption, crystallization and sublimation; dialysis
Parallel	Countercurrent electrophoresis; elutriation	Filtration, ultrafiltration, reverse osmosis and pressure dialysis; zone melting
Perpendicular	Field-flow fractionation; thermogravimetric methods; electrophoresis-convection	Chromatography; distillation; countercurrent distribution, adsorption, and crystallization; foam fractionation; mineral flotation

^aInformation taken from ref. 14.

to expensive and time-consuming trial-and-error methods. This means that as our understanding of such fundamental fields as phase-equilibrium thermodynamics, coordination chemistry, mass transfer, heat transfer, interfacial phenomena, and chemical kinetics improves, so will our ability to improve existing separation processes and to develop new ones. Nonetheless, while the idea of an all-encompassing theory of separation science holds great promise and represents a realistic goal, it will be many years before the traditional, practical approaches to categorizing the field lose their utility and the need for trial-and-error methods is eliminated.

3. SEPARATION SCIENCE AND TECHNOLOGY: FRONTIERS, CHALLENGES, AND OPPORTUNITIES

Section 2 reviewed the various ways that have been attempted to organize the many fields, techniques, and disciplines important to the field of separation science and technology. Historically, each technique has been treated as an independent discipline, with little regard for the underlying principles that are common to many of them. Serious efforts are now being made to systematically examine the fundamental phenomena that control all separation processes. There is no doubt that this more fundamental, global view of the field will result in the greatest future advances. However, it is also clear that the historical divisions remain in widespread use, and that individuals, journals, and funding agencies are still geared toward these traditional disciplines. This is not inappropriate since there are important areas of research that are needed and are ongoing within each of the subcategories. The research frontiers of some of the most important separation technologies and applications will be reviewed in this section. The examples discussed will serve to illustrate the broader, generic needs that must be addressed to further the development of the field as a whole.

Several recent reviews are available that assess the status of one or more significant parts of separation science and technology. These include an assessment of membrane technology,²² a handbook on inorganic

ion exchange materials,²³ an assessment of fluid separation technologies,²⁴ and the most recent volumes of Recent Developments in Separation Science and Technology.¹³ Proceedings of recent key conferences, such as those for the International Solvent Extraction Conference (ISEC '83)²⁵ or the Symposium on Separation Science and Technology for Energy Applications²⁶ also offer excellent, up-to-date insight into some areas. Interested readers are urged to consult these references for a more comprehensive review of the areas covered.

3.1 A SURVEY OF SOME IMPORTANT SEPARATION TECHNIQUES

3.1.1 Solvent Extraction

The premier forum for reporting progress in solvent extraction science and technology is the International Solvent Extraction Conference (ISEC), which is held every three years. The proceedings of the most recent conference in this series, ISEC '83,²⁵ accurately reflect the research areas and applications that are of greatest concern to workers in this field. In addition, the proceedings of a recent symposium sponsored by the Industrial and Engineering Chemistry (I&EC) Division of the American Chemical Society (ACS) is a significant source of up-to-date information.²⁷ Bravo et al. have also presented an excellent review of extraction technology.²⁸

The most important fundamental research projects now under investigation by extraction chemists and chemical engineers include studies of interfacial phenomena (especially the kinetics and mechanisms of interfacial transport), the effects of external electromagnetic fields, the development of new solvent extraction reagents, pharmaceutical and biological extraction processes, mathematical modeling of extraction processes, and improved designs for solvent extraction equipment.

There is almost universal agreement that the major challenge in solvent extraction chemistry is the development of new, highly selective, solvent extraction reagents. Ideally, one reagent (or perhaps a pair of synergistic reagents) would be developed for each component of a mixture. Even though this goal may never be realized, it is the guiding principle

behind much current solvent extraction research. Advances in our understanding of the kinetics and thermodynamics of coordination chemistry are being applied to the design of new solvent extraction reagents. These reagents are being designed by inorganic chemists, who are building more complex molecules to satisfy the specific coordination demands of a given molecule or ion, and by biochemists, who are working to determine the structure of the active sites in complex biological macromolecules (e.g., enzymes) in order to build simpler molecules that will retain the functionality of the active sites without the excess molecular structure of large biological molecules. Advances in coordination chemistry, structural chemistry (solid and solution), biochemistry, and quantum mechanics, all of which are needed, will also contribute to realizing the goal of producing "designer molecules" for solvent extraction. In addition to greater selectivity, these reagents should have higher resistance to chemical, thermal, and radiolytic degradation, as well as improved solubility and emulsification characteristics.

The chemical and physical properties of interfaces have been largely neglected in the study of solvent extraction processes relative to the vast amount of information that has been reported on the equilibrium thermodynamics of the bulk systems. The kinetics and mechanisms of interfacial transport have been particularly difficult to study and interpret, but progress is now being made.²⁹ The results of excellent, detailed studies of drop-interface coalescence are becoming available.³⁰ These and similar studies are of considerable importance to the solution of some of the long-standing problems in the application of solvent extraction such as the origin, nature, and cleanup of interfacial emulsions (often referred to colloquially as interfacial "cruds"). As more information and improved theories of solvent extraction kinetics become available, separations based on kinetic effects rather than on equilibrium distributions are being designed. (A few separation methods based on kinetic effects are already in use, but the number is very small.)

There is a great need for the development of techniques to study liquid-liquid interfaces that are as powerful as those which have evolved for the study of solid surfaces. Trace amounts of surface-active materials

can drastically alter the performance of a solvent extraction system because their influence is concentrated at the critical interface through which transport must occur. Modern analytical tools, such as nuclear magnetic resonance (NMR), neutron scattering, and laser-light scattering, show some promise for studying the structure and reactions that occur at the interface and in the bulk solutions, but the thin size of the interface presents a considerable technical challenge to the application of most analytical methods. Nonetheless, such applications are at least theoretically possible, and the potential for progress in our knowledge of interfacial chemistry and for improvements in process and equipment design that would result from this knowledge is very high.

The effects of the application of external fields (electromagnetic, gravitational, etc.) on solvent extraction systems have begun to receive considerable attention.³¹ These studies are certain to lead to new separations processes and, at the same time, are being used to study the interfacial properties already discussed.

There is a need for improved mathematical modeling in almost all separations processes, and solvent extraction is no exception. Current models are generally (but not always) based on equilibrium data (since these are often the only data available) and may be based on theoretical considerations, empirical relations, or both. These models will be greatly improved when the information gained from the study of kinetic and interfacial effects is incorporated. Further, while it is true that a great deal of equilibrium data has been obtained for solvent extraction systems, the data base is scattered, contains large amounts of incompletely documented or otherwise unreliable data, and is not easily retrievable. Methods for improving the accessibility and quality of the solvent extraction data base have been the subject of recent debates in the solvent extraction community.

Modeling complex solvent extraction systems is difficult and will almost certainly require a sophisticated knowledge of applied mathematics beyond that of a typical chemist or chemical engineer. Collaboration

between these two disciplines is currently quite rare, but it shows great promise for advancing our ability to model separation systems and hence to optimize their design.

3.1.2 Ion Exchange

Much of what has been said about solvent extraction applies equally to ion exchange. Indeed, it is useful to think of ion exchange as a solvent extraction system in which the solvent extraction reagent has been immobilized on a solid support. Of course, this analogy may be misleading in some cases; however, the techniques share more commonalities than differences. As in solvent extraction, the application of ion exchange will be enhanced and broadened by the development of improved, more highly selective reagents. Details of the structure and reactivity of the solid-liquid interface are poorly understood, and new techniques are needed to study them. The kinetics of ion-exchange processes and the parameters that govern it are not well understood.

An important area in ion exchange technology that is less clearly analogous to solvent extraction chemistry is the development of inorganic ion exchangers. A review of the status of inorganic ion exchange has recently been published.²³ It is interesting to note that the early synthetic ion-exchange materials were primarily inorganic. They were quickly replaced by synthetic organic resins, however, because of the difficulty in manufacturing a reproducible inorganic material and because of the instability of these materials in acid solution. Organic resins were found to have limitations as well, especially in applications that required exposure to high temperatures or radiation fields. Thus, research on potential inorganic ion exchangers continued at a low level until a breakthrough came in the mid-1960s when studies showed that the group IV phosphates and arsenates could be prepared in crystalline form. These materials show great promise, not only as ion exchangers but also as membranes and as catalysts or catalyst supports.

3.1.3 Membrane Separations

An excellent assessment of membrane technology and applications has recently been published.²² This assessment, along with the proceedings of a symposium sponsored by the Subdivision of Separations Science and Technology of the I&EC Division of the ACS,³² summarizes the current status and frontiers in membrane technology. A thorough review of the history of membrane technology has been published by Lonsdale.³³ Bravo et al. have also reviewed the subject recently.³⁴ The following comments draw heavily on these sources.

Membrane separation technology is relatively new, but its use has expanded rapidly since the introduction of the first commercial electro-dialysis and microfiltration units in the 1960s. The first high-efficiency reverse osmosis membranes were also introduced in the 1960s, but reverse osmosis and ultrafiltration did not become commercially successful until the 1970s. Today, a number of membrane processes are routinely used on both laboratory and industrial scales. These include electrodialysis, reverse osmosis, microfiltration, ultrafiltration, dialysis, electro-osmosis, membrane extraction, pervaporation, and gas separation. Hwang and Kammermeyer³⁵ have prepared an excellent textbook describing these and other commonly used membrane separation unit operations. Such technologies, however, have been applied almost exclusively to the processing of aqueous streams. The application to nonaqueous solutions, gaseous systems, and gas-liquid systems is promising, but relatively unexplored.

It is important to note the close relationship between membrane separations, solvent extraction, and ion exchange. The most striking example is the case of liquid membranes (LMs) with facilitated transport, where a solvent extraction reagent (often called a "liquid ion exchanger" or a "carrier molecule" in this context, depending on the background of the investigator) is used to effect ion exchange or some other form of mass transport into or through the membrane phase. LMs may take the form of a discrete membrane layer, of an emulsion, or may be supported on a solid. They are among the most interesting classes of membranes currently

under investigation, and much of the research is being done by scientists who were previously labeled "solvent extraction chemists" and are, therefore, reporting their work at solvent extraction conferences.³⁶

At first glance, this blurring of the lines between solvent extraction chemistry, ion-exchange chemistry, membrane chemistry, and (as will be discussed below) chromatography may appear confusing. Once this close relationship is recognized, however, it becomes obvious that many common needs "cut across" these technologies and thus the advancements aimed at one technique will often result in improvements in the others. As with solvent extraction and ion exchange, membrane scientists recognize the need for better understanding of interfacial and transport phenomena, new carrier reagents (perhaps called "solvent extraction reagents," "ion exchangers," or "stationary phases" by practitioners of the other techniques), better mathematical models, and an expanded (or perhaps more readily available) data base. As in ion exchange, the development of inorganic membrane materials is an area that shows considerable promise. The most developed of these is the dynamic membrane, although inorganic membranes made of material such as palladium, quartz, and silver have also been developed for specific applications.

Biomembranes (membranes made from biological material or synthetic membranes designed to mimic the structure and function of biological membranes) show potential for a variety of applications, especially in the photochemical generation of electricity. Two excellent reviews that detail these applications have recently been published.³⁷⁻³⁹

The greatest limitations to the application of membrane separation technology are the narrow range of useful operating conditions, a lack of understanding of physicochemical phenomena in membrane systems, and high costs. Most membrane modules are limited to a relatively narrow temperature and pH range (45 to 60°C; pH 4 to 10) and are quickly attacked by organic solvents and corrosive gases. The development of new materials, most likely inorganic materials, is necessary if membrane separations are to achieve their full potential in areas such as food processing (where high

temperatures are required), nuclear and radiochemistry (where high radiation fields are present), and pharmaceutical chemistry (where organic solvents are common).

Membrane science and technology are currently very empirical, and new data are required at each stage of the development of a new membrane separation process. In the short term, this deficiency could be overcome by the systematic development of a broader data base of membrane properties that would allow the construction of empirical models which would be valid over a useful range of operating conditions. In the long run, a much better understanding of fundamental membrane-solute interactions, membrane-solvent interactions, fouling, polarization, boundary layer theory, and transport phenomena both to and through the membrane is needed. The manufacture of membrane materials is also an extremely empirical science because the chemistry of membrane formation is complex and poorly understood.

The high costs of membrane separation processes are not as much an independent deficiency in the technology as a reflection of the problems with material limitations and the high degree of empiricism in the manufacture and application of membranes. It has been suggested²² that the short operating life of many membranes is the most important factor contributing to system cost, followed closely by the low flux that can be achieved in membrane modules. Both of these problems can potentially be solved by the development of improved membrane materials.

The third factor contributing to the high cost of membrane separations processes is the need to develop each process, application, and membrane essentially from the ground up. When a sufficiently broad data base and theoretical framework become available, the manufacture of new membrane materials and their application to new processes will be greatly expedited and the costs correspondingly lowered.

3.1.4 Chromatography

For the purposes of this report, the general term "chromatography" is used to include the gas, liquid, paper, thin-layer, and affinity techniques. Ion-exchange chromatography is discussed separately in

Sect. 3.1.2. A thorough review of progress in the development of each of these techniques is published in even-numbered years in the journal *Analytical Chemistry*,⁴⁰ and good discussions of the general theory of chromatography may be found in several texts.⁴¹ That many significant reviews of chromatographic techniques appear in a journal devoted to analytical chemistry points to a great deficiency in the field, namely, the difficulty in scaling up most chromatographic techniques to an industrial size. The speed, resolution, and ability to handle very small samples have made chromatographic techniques among the most useful in analytical separations. The application of chromatographic techniques to large-scale problems, however, has been frustrated by many of the same deficiencies that exist for the separation techniques already discussed. These include the need for technological advances that would allow the practical, cost-effective scale-up of analytical chromatographic systems and the need for theoretical advances, especially in the areas of transport and interfacial phenomena, that would allow accurate modeling of the behavior of these large-scale systems. Many hundreds of references to the theory of chromatography have been reported in recent years, and the development of new packing materials, supports, column designs, column materials, mobile phases, stationary phases, detectors, and instruments continues at an impressive rate. Still, such developments are more evolutionary than revolutionary, and one of the most exciting prospects in chromatography is for a breakthrough that will permit all of these advances to be applied on an industrial scale.

One form of chromatography that already operates on a scale consistent with the industry to which it is most often applied is affinity chromatography. This is an interesting case in which the separation technique (affinity chromatography) is both an application of and is applied to the same science (biotechnology). Two recent papers review the development and status of this relatively new method.^{42,43} Affinity chromatography uses highly selective biological molecules immobilized on a solid support to effect the separation of a specific molecule, or class of molecules, from a mixture. This separation technique uses the extreme specificity of enzymes, antibodies, and other biological molecules to approach the

ideal of "one solute-one separation agent" first discussed in Sect. 3.1.1. It should be noted that immobilized inorganic ligands are used to effect the separation of biomolecules as well. The potential of this technique in the biological sciences is extremely high and represents an active area of research; the potential in inorganic systems is also significant (the affinity of certain inorganic ligands for biomolecules works both ways) but is less developed.

In summary, progress in the general field of chromatography depends on progress in many of the same areas that have been discussed for extraction, ion-exchange, and membrane technology. The theory of mass transport and the physical chemistry of interfaces in these systems must be developed. New materials for stationary phases, mobile phases, and supports are needed. The highly specific stationary-phase materials being developed by chromatographers should prove useful in other areas, just as new solvent extraction reagents, ion-exchange materials, and membrane materials should find use as stationary and mobile phases in chromatography.

3.1.5 Distillation

Bravo et al. have published an excellent summary of the state of the art and current research frontiers in distillation science and technology.⁴⁴ An excellent discussion of the theory and use of distillation may also be found in refs. 12 and 18.

Distillation has been the most widely used method for separating liquid mixtures for over two centuries, despite the fact that it is one of the most energy-intensive separation technologies. This was not an important consideration before the dramatic rise in energy costs that began in the early 1970s. Prior to that time, the low capital costs, reliability, ease of operation, and wide applicability more than offset the energy costs. Even today, this unique combination of features makes it difficult to find cost-effective alternatives to distillation, despite the high energy costs. Indeed, in plants where a surplus of low-pressure steam is available to provide heat for distillation, distillation will probably never be replaced.

Nonetheless, distillation consumes about 3% of the total energy used in the United States each year⁴⁵ and about 95% of the energy used in separations.⁴⁶ Thus, the potential for energy savings is very great. There are two basic approaches to reducing the energy costs of distillation: (1) to develop alternative, less energy-intensive technologies; and (2) to improve the efficiency of the process itself. If energy efficiency were the only relevant criterion, one could argue that all research in separation science and technology should be directed toward developing methods specifically to replace distillation operations currently in use. In systems where the heat required for distillation must be purchased independently rather than obtained as a by-product from another part of the process, the challenge is to develop these alternative technologies. Each of the separation technologies discussed in this report may (and undoubtedly will) replace distillation in some applications.

The fact remains, however, that there are many situations where distillation will never be economically replaced. Even in those systems where one or more alternative technologies might be developed, the change will not occur in the near future. Thus, significant short-term improvements will come about only through the development of high-efficiency column packings, and this is the route that is being most actively pursued by academic and industrial researchers. Unfortunately, distillation has long since lost any attraction as a "fundamental" science, and almost all improvements are effected on an empirical, trial-and-error basis. New materials and geometries are tested and if they improve the efficiency of the column, the results are rationalized ex post facto. No comprehensive model is available to guide the development of these packings; nor does a sufficient data base exist, at least in the open literature, to develop such a model. As in the other separation techniques already discussed, there is a general lack of suitable empirical or theoretical models to describe mass transfer, heat transfer, flow, and interfacial phenomena (wetting, turbulence, surface tension, etc.) in a distillation column. New packing materials that are highly wettable, durable, corrosion resistant, and easy to manufacture are needed. It is probably safe to

say that very few materials scientists are working on something as mundane as the packing material for a distillation column; yet a significant improvement in these materials would be worth millions of dollars per year.

3.1.6 Supercritical Fluid Extractions

The potential of using supercritical fluids in separations was recognized over 100 years ago when it was observed that pressure had a significant effect on the solubility of potassium iodide in ethanol.⁴⁷ Relatively few applications were developed over the years, but the unique characteristics of supercritical fluid extraction (SFE), especially the energy-saving potential, have attracted increased attention in recent years. Several recent reviews of the technology are available.⁴⁸⁻⁵⁰

Conceptually, SFE is very similar to other forms of extraction (liquid-liquid, liquid-solid, gas-liquid, etc.), but the fact that the solvent is used in a supercritical state offers several potential advantages. First, the solvent can be easily recovered as a gas simply by reducing the pressure (or increasing the temperature). This can be a significant advantage over a nonsupercritical solvent which may require an energy-intensive distillation step or a relatively complicated (and often ineffective) chemical washing step before the solvent can be reused. Second, diffusion is much faster in these so-called "dense gases," so that the mass transport and overall kinetics of a process may be enhanced in a supercritical solvent. Third, extremely tight process control is possible, since very small changes in temperature and pressure can cause wide variations in the solubility of a material in a supercritical fluid. Fourth, additives called "entrainers" may be added to enhance extractive properties. Finally, very high distribution ratios and separation factors can be achieved in SFE.

There are, of course, disadvantages to a SFE process. For example, it is often necessary to operate at extreme conditions of pressure and temperature, and solvent recovery, whether by pressure reduction or by temperature increase, requires additional energy and equipment.

Current applications of SFE are few. They include the decaffeination of coffee using supercritical carbon dioxide;⁵¹ the ROSE™ process, which uses supercritical pentane to recover hydrocarbon liquids from heavy oils;⁵² and the use of supercritical water to destroy organic compounds in wastewater.⁵³ Carbon dioxide is, by far, the most common supercritical solvent, and almost all separations done with SFE involve organic compounds (usually in the food or fuels industries).

One major barrier in the development of SFE is the extreme paucity of data and theoretical models for supercritical systems. A substantial amount of equilibrium thermodynamic data is available (although not necessarily readily accessible) for most separations processes, but there is a need for kinetic data. In the case of supercritical fluid systems, there is only a small set of thermodynamic data and simple models available for nonpolar systems, and essentially no data, or theoretical models, thermodynamic, kinetic, or otherwise, available for polar solvents and solutes. The mechanism by which entrainers enhance the solubilities of materials in supercritical fluids (which are perhaps roughly analogous to synergists in solvent extraction) is still uncertain. A great deal of fundamental research is needed before reliable judgments can be made concerning just how widely SFE may be applicable. This research must include the determination of substantial amounts of thermodynamic data (e.g., phase equilibria, solubilities, and equilibrium constants), kinetic data (e.g., diffusion coefficients, reaction rates, and heat transfer rates), and data on the effects of entrainers. Such information must be obtained systematically for both polar and nonpolar systems and in such a way that it may be used to derive useful empirical and theoretical models of these systems.

3.1.7 Photon-Enhanced Separations

The development of the laser as a source of pure, monochromatic electromagnetic energy has effected rapid changes in many fields of science and technology. In general, exposing a mixture to laser light will not cause a separation, but the laser photons may be thought of as

a tunable, highly selective "reagent" that can react with one component of a system and change (e.g., ionize, oxidize, or reduce) it to a species which can be easily removed from the mixture by some traditional separation technique.

Perhaps the best known examples of the application of laser technology to separations are the laser isotope separation (LIS) methods.⁵⁴⁻⁵⁶ Table 3 summarizes the history of their development. The most advanced LIS methods are Atomic Vapor Laser Isotope Separation (AVLIS) and Molecular Laser Isotope Separation (MLIS). While the isotopes of many elements have been separated by LIS techniques since the method was discovered in the early 1970s, most of the work has concentrated on the separation of the isotopes of uranium for use as fuel in nuclear reactors and in nuclear weapons.

Table 3. Progress in laser isotope separation^a

Year	Development
1960	Invention of the laser
1965	Discovery of the principles of LIS
1966	Tunable dye laser
1972	LIS becomes a viable process
1974	Various LIS methods adopted; economic analyses
1976	Production of approximately 0.1 g of 3% enriched uranium
1982	U.S. Department of Energy selects AVLIS over MLIS
1984	Intensive development work on uranium and plutonium LIS; evaluation of industrial photochemistry
1985	AVLIS selected by U.S. Department of Energy as replacement technology for gaseous diffusion; development of gaseous centrifuge halted
1987	Military LIS of plutonium
1992	Industrial LIS of uranium

^aAdapted from ref. 53, Table I, p. 128.

In AVLIS, an atomic vapor is produced and exposed to laser photons that have been tuned to selectively ionize a single isotope (typically ^{235}U , although the same technology can be applied to virtually any other isotope). The positively charged ions can then be removed from the vapor electromagnetically. In MLIS, a molecular vapor is generated (uranium hexafluoride, for example) and then excited by a laser that has been tuned to cause dissociation of the molecules containing the isotope of interest. The dissociated molecule subsequently reacts to form a different chemical species which, now enriched in a single isotope, is removed by an appropriate separation process. In the case of uranium enrichment, this separation can be particularly easy since any lower fluoride formed by the dissociation/reaction of the hexafluoride will have a lower volatility than the starting material and simply fall out of the gas phase as an enriched solid.

Over a period of about 10 years, the U.S. Department of Energy evaluated the potential utility of several MLIS and AVLIS processes for the enrichment of plutonium and uranium. By 1985, a specific AVLIS process currently being developed at Lawrence Livermore Laboratory (LLL) and ORGDP had been selected over all competing LIS methods, as well as gaseous centrifugation. AVLIS is the primary enrichment technology being pursued in the United States. Details of the key research needed to complete the development of AVLIS for this purpose are classified.

While a single LIS process has been chosen for uranium enrichment in the United States, other processes of this type are being developed and used for a variety of other applications.⁵⁵ In addition, a substantial amount of what has been facetiously called "laser alchemy" has been reported in the literature.⁵⁶ Unexpected behavior has been observed in a number of chemical systems when they are exposed to laser radiation, especially when the molecules involved are complex. Considerable research will be required before the details of these reactions can be explained. It is clear, however, that these laser-induced reactions have a large, if still somewhat ill-defined, potential as a key step in new separations processes.

In many cases, the monochromatic radiation of a laser may not be required to perturb a chemical system in such a way that a separation is feasible. Toth^{57,58} and his co-workers have used radiation from a mercury lamp to selectively adjust the oxidation states of various actinides in solution in order to improve the separation of these elements from each other using solvent extraction.

The use of photons, whether from lasers or from conventional light sources, as a "reagent" in a separation system has a number of advantages, including the ease with which they can be produced, high selectivity, minimal waste generation, and low cost. The potential of lasers as an integral part of new separation systems has begun to be explored only recently. It is reasonable to expect many new techniques and applications to be developed using these powerful tools.

It should be noted that a category of "electron-enhanced" separations could also be discussed. In these techniques, electrons (rather than photons) are fed into (or removed) from the system in order to control an oxidation state. These techniques are also relatively unexplored.

3.1.8 Electromagnetic Separation (Mass Spectrometry)

Traditionally, the term "electromagnetic separation" has referred to mass spectrometry (MS), which is the technique discussed in this section. However, it would be entirely valid to include techniques such as electrophoresis, electrodialysis, electrostatic precipitation, and even the use of electromagnets to separate magnetic materials from refuse under this heading. The AVLIS technology discussed in the preceding section is also a type of electromagnetic separation. To add to the confusion, one of the more exciting research areas in MS, Resonance Ion Mass Spectrometry (RIMS), can also be classified as a "photon-enhanced separation." Nonetheless, the traditional meaning for "electromagnetic separation" will be used here, with due recognition of the degree to which the restriction is arbitrary.

At present, electromagnetic separation is applied almost exclusively on an analytical scale. MS has become an increasingly complex and useful tool for chemical investigations at the molecular level,⁵⁹ but no

economical production-scale application other than the calutron facility (Appendix A), has been developed.⁶⁰ MS, especially when combined with other separation methods to form the so-called "hyphenated" techniques (GC/MS, LC/MS, MS/MS, etc.), has become the premier technique for separation, identification, and mass and structure determination on the small (microgram) scale. The development of soft ionization techniques (i.e., methods of ionizing large, fragile molecules to generate a substantial number of molecular ions without breaking the molecule into smaller pieces) and high-field magnets has extended the useful range of MS to molecular weights approaching 10,000. Thus, the technique is finding increased use in the biological sciences.

RIMS is a particularly interesting MS technique because of its close relationship to AVLIS and other LIS methods. In RIMS, a high-powered laser is used to ionize the atoms of a single element or isotope, and the ions are then separated by more or less conventional MS techniques. This technique has contributed substantially to spectral studies of the lanthanides and actinides,⁶¹⁻⁶⁴ and it may be possible to scale up the process for use in the production of stable isotopes at a substantial savings of time and cost.

3.1.9 Other Separation Methods

A complete list of important separation techniques would be very long, especially if any attempt was made to include all of the variations on the major methods. The preceding material has covered only a few of the separation technologies included in Figs. 1-3, and the figures are themselves incomplete. Certain areas of needed research, both fundamental and applied, were mentioned in the discussion of each field. Similar needs can be identified for each of the other separations technologies that are in use or being developed on any scale. These research needs present opportunities for individual scientists and engineers, or even sizable research groups, to make considerable contributions toward the advancement of each technique and to the solution of many significant problems that require advances in separation technology.

Far more important for the advancement of separation science and technology as a whole, however, is the realization that certain research areas are quite generic and that progress in these areas will result in broad, rapid progress across many fields at once. This, in turn, will lead to the development of new options for solving a variety of separations-related problems simultaneously. Thus, rather than attempt to inventory the specific status and needs of every separation method (a task far beyond the scope of this or any other report), this section will conclude with a discussion of some general research needs that are common to all (or, at least, most) separation technologies.

3.2 RESEARCH NEEDS

Almost all separation methods would benefit from considerable work in five research areas: interfacial phenomena, selectivity, critical data base development and mathematical modeling, the chemistry of dilute solutions, and improved system design. In many separation techniques (especially chemical separations), the lack of a detailed understanding of the interfacial phenomena that play a critical role in all separation methods can be cited as a barrier to further advancement. Similarly, there is a general need to elucidate the factors that influence selectivity in a separation system and to apply what is already known more effectively to the development of new, more highly selective separation systems. Progress in both of these areas requires that the existing data base for each technique be critically evaluated and supplemented, if necessary, so that improved empirical and theoretical models may be derived. The lack of an adequate theoretical and experimental data base describing the chemistry of dilute solutions is an especially acute problem for many applications. An improved theoretical and experimental understanding of interfacial phenomena and selectivity, along with an accessible, accurate data base, will greatly facilitate progress in the development of better separation methods and more integrated, better-designed, and more energy-efficient separation systems.

While these generic research areas are not mutually exclusive (e.g., the stability of interfacial complexes and the rate of interfacial mass transfer can be determining factors in the selectivity of a separation process), it is convenient to discuss more specific needs in each area individually. The overlap of these generic research areas with all separations and with each other is emphasized in a final section on the need to develop separation science and technology as a unified field.

3.2.1 Interfacial Phenomena

In many separations systems, an interface is formed at the point where a phase enriched in the component of interest meets a phase depleted in that component. This interface is often, though not always, important in the separation. Many separation methods, such as solvent extraction, froth flotation, and adsorption, depend entirely on the chemical and physical characteristics of an interfacially active material. In distillation, efficient condensation and wetting at the vapor-packing material interface are crucial to an effective process. In crystallization, the crystal may grow cleanly at the solution-solid interface, or it may occlude, entrain, or adsorb impurities. Interfacial mass transfer, which may be enhanced or impeded by the presence of surface-active agents, is a key parameter in many separation processes. In short, most separation processes involve at least one interface, and the phenomena occurring at that interface determine, totally or in part, the overall success of the process.

Despite the undisputed importance of interfacial phenomena in separation science and technology, the area is grossly understudied. A major reason for the lack of activity in the field is the difficulty in studying interfacial regions which, in many instances, are two-dimensional structures with no thickness (or at least no more than a few molecules of thickness). However, modern electrochemists have had considerable success in studying and modeling liquid-solid interfaces, and many new methods for the study of solid surfaces have been developed in recent years. Some of these same ideas and methods should be applied to the study of interfaces that are important in separations, and considerable

attention should be given to developing new techniques for examining the structure of interfaces. In addition, many "old" techniques, such as NMR, neutron scattering, and laser light scattering, have been developed to the point that they may be applied to what was previously considered too small a target.

Equally important to the understanding of the structure of interfaces is the understanding of mass transport across the interface. The effects of the structure of the interface and the presence of surface-active agents at the interface on mass transfers rates are well recognized; the effect of mass transfer on the structure of the interface via the Marangoni and other effects⁶⁵ is perhaps less well appreciated.

The formation of third phases ("slimes," "cruds," solids that foul membranes or coat columns, etc.) is frequently controlled by interfacial effects and the presence of surface or interfacially active agents. The composition and control of these materials are poorly understood despite their importance in many industrial processes. The appearance of a new phase usually degrades the performance of a separation system, as when an interfacial "crud" blocks mass transport in a liquid-liquid extraction system or when a precipitate fouls a membrane. Occasionally, however, a surface-active agent may be introduced deliberately to form an emulsion and increase the surface area available for mass transport (e.g., emulsion liquid membranes).

Many other aspects of the physics and chemistry of interfaces present significant research opportunities. A worthwhile goal of any study of interfacial phenomena is to relate the structure and dynamics of the interface to more easily observed bulk properties, such as overall mass transport and phase disengagement rates. The effect of external fields on interfacial structure and mass transport is an interesting area that is just beginning to attract attention. It should also be recognized that the mathematics needed to model chemistry, mass transport, and heat transport in a dynamic, two-phase system is not trivial. Useful models, which include the results of these proposed studies of interfacial phenomena, will be developed only with the help of the latest advances in applied mathematics and computer technology.

While the importance of developing a better understanding of interfacial phenomena cannot be overstated, this does not imply that bulk physical and chemical properties of a system are not important in separations processes. Of course, interfacial phenomena and bulk properties are related, and a description of interfacial effects based on readily measurable bulk properties would be most useful. Considerable work is needed in areas such as the thermodynamics of solutions of electrolytes and nonelectrolytes, chemical kinetics, mass transport, coordination chemistry, dispersion, and flow in the bulk phase. The influence of an applied field on the bulk properties of a system can affect a separation. Indeed, one of the newest separation methods was designed by considering the effect of an external field on the components of a flowing mixture.⁶⁶ Nonetheless, while the description of bulk properties and their influence on separations is far from complete, the deficiencies in the theory and knowledge of interfacial phenomena are much greater and offer a much wider field of study and greater potential for significant advances.

3.2.2 Selectivity

An ideal separation process would remove 100% of a desired component from a mixture regardless of how dilute the component or how complex the original matrix might be. Further, the process would remove only the desired component and reject all others. Finally, it would isolate the component in a form from which it would be readily recoverable in a pure state, and all reagents and equipment used in the process could be completely, quickly, and easily regenerated for reuse.

Although an ideal separation will never be developed, it is a useful standard against which progress in separation science and technology can be measured. No separation reagent or process operates on a single material, but highly selective separations can be, and are being, designed. Perhaps it is more accurate to say that the principles that could be used for designing such processes are beginning to be understood. This is an important area of research having great potential for aiding advancement in separation science and technology.

Consider, for example, the design of increasingly specific complexing agents for use as solvent extraction reagents, ion exchange materials, and so forth. It has long been recognized that oxygen-donating ligands are selective for one class of metal ions, nitrogen-donating ligands for a second class, and sulfur-donating ligands for a third class. These generalizations were part of the basis for the development of the concept of "hard" and "soft" acids and bases.⁶⁷ The principles of bonding theory and quantum mechanics have now been developed to the point where these observations can be explained and predicted on the basis of very fundamental principles and theories. The routine use of quantum mechanical principles for the prediction of molecular properties in separation systems will require considerable evolution of the theory and practice of such computational chemistry, but it represents an exciting frontier that will play a major role in the development of general theories of separation processes.

These principles and theories (sometimes supplemented with a bit of luck) have, in turn, been applied to the systematic design of increasingly selective complexing agents. The evolution of the so-called "crown" compounds,⁶⁸ which show selectivity due to the size of their two-dimensional cavity, to the cryptate ligands,⁶⁹ which show selectivity due to the size of their three-dimensional cavity, to the CYCAMS and LICAMS,⁷⁰ which were specifically designed to satisfy both the coordination number and geometry of the target metal ion, demonstrates how reagents of increasing selectivity can be designed based on fundamental bonding considerations.

Despite these impressive examples, very little systematic development, versus trial-and-error discovery, of specific separation reagents has been done. Metal ions represent the simplest case; yet many relatively minor problems, such as finding an extraction reagent that is specific for Mn(II) in the presence of Cu(II), have not been resolved. In addition, the possibilities of separating metals by selective reduction to low oxidation states (perhaps photochemically) in order to take advantage of the resulting changes in coordination chemistry have not been explored. Highly selective methods and principles for separating simple organic molecules by extraction

or adsorption are even less well developed. Many separation processes are based on either chemical selectivity (e.g., solvent extraction, ion exchange) or steric selectivity (size-exclusion chromatography, ultrafiltration), but relatively little has been done to design reagents or membranes that use both steric and chemical effects to enhance selectivity. Chiral stationary phases in chromatography, which can be used to separate optically active isomers based on both their chemical and structural properties, are a notable exception. So far, the use of these phases has been restricted to the separation of relatively small molecules (e.g., amino acids, small polypeptides), but the importance of optical activity in biological compounds should stimulate the development of this technique and others that are both chemically and structurally selective.

Even as modern inorganic and theoretical chemists have begun to design molecules for their potential selectivity in a separation process, biochemists have begun to apply the principles they have learned from studies of the very high selectivity of certain biological materials (e.g., enzymes, antibodies, etc.). Unlike separation systems designed in the laboratory, natural separation systems make good use of both chemical and steric factors to achieve this high selectivity. Affinity chromatography makes direct use of the high specificity of certain biological molecules for specific substrates. An appreciation of how metal ions are bound and transported in biological systems played a major role in the development of LICAMS and CYCAMS,⁷⁰ which are an interesting new class of compounds designed to sequester and remove actinide elements (especially plutonium) from biological systems. These are only two examples of the potential of using the material and principles derived from studies of biological selectivity in separation science and technology. They are notable, not only for their success but also for their novelty. Obviously, we have just begun to tap the potential of methods based on biological phenomena in separation processes.

Photon-enhanced separations make use of a purely physical phenomenon to achieve a selectivity which rivals that of biological systems in some applications. LIS (Sect. 3.1.7) is the most impressive example of this

selectivity, but the potential of using photons as a reagent to make new separations possible or more efficient is largely unexplored. In some cases (e.g., LIS), the highly monochromatic radiation of a laser is essential; in other cases, such as the separation of metal ions by selective photo oxidation or reduction, more conventional light sources are adequate. The use of photons (or electrons, which can function in much the same manner) to enhance the effectiveness of separations should be thoroughly explored.

3.2.3 Critically Evaluated Data Bases and Mathematical Models

In most cases, separation methods have been developed for specific applications. Data were collected solely to optimize a process to solve the problem at hand, with little thought for the systematic collection of experimental data that could serve as the basis for the formulation of comprehensive empirical or theoretical models for the separation method being used. As a result, new separation methods (or new applications of old ones) cannot be evaluated or implemented without an expensive and time-consuming collection of experimental data.

Perhaps the most extreme example is in solvent extraction chemistry. It has been estimated that more than 1.1 million distribution coefficients have been published in the literature.⁷¹ A critical examination of these data reveals that at least one-half of them are useless due to incomplete recording of the conditions under which the measurements were made. Of those adequately reported, many are single measurements for a specific system so that a critical comparison with other measurements is impossible. While many values have been measured under very similar conditions in some systems, new values continue to be measured because it is easier to perform additional experiments than to find and evaluate the published values. In still other cases, many measurements have been made and correlated over a broad range of conditions; however, the results are either classified, as in the case for data relevant to the nuclear industry, or proprietary, as in the case for data in the hydrometallurgical industry.

If solvent extraction suffers from an overabundance of data that is underevaluated, inaccessible, and haphazardly obtained, the development of many other separation techniques suffers from a lack of data. There is an acute shortage of reliable physicochemical data on membrane systems, the design and performance of high-efficiency distillation column packings, and supercritical fluid systems, to name only three. What data exist for membranes and high-efficiency packings, for example, are often held as proprietary information by the manufacturers and vendors of these materials. The data that do appear in the literature are limited and unsuitable for formal analysis and the derivation of generalized models and theories. Currently, the only program to collect data on separation systems is the SEPSYS data base program at ORNL.⁷² It was intended to be a general separations data base and incorporated many of the ideas regarding the classification of separation science and technology that were discussed in Sect. 2. The feasibility of the SEPSYS concept was successfully demonstrated using some 4000 publications limited largely to the field of solvent extraction. Further development has been halted because of a lack of funding.

The systematic acquisition, evaluation, and dissemination of reliable data are crucial to the entire field of separation science and technology. The continually decreasing cost and increasing speed of computerized data bases should be extremely useful in this regard, but the best way to apply this technology to the problem is still a matter of debate. The ACS will hold a symposium on this topic as part of the First International Conference on Separations Science and Technology⁷³ in 1986 in an effort to determine the most promising approach to accomplishing this goal. The availability of a reliable data base will lead to the development of more comprehensive mathematical models (both empirical and theoretical) for separation systems. In turn, these models will facilitate the design and evaluation of new separation schemes. Ironically, the development of improved theoretical models is often considered "forefront" science, but the compilation of the data bases needed to build and verify these models is considered a secondary activity at best.

3.2.4 Fundamental Chemistry of Dilute Solutions

Increasingly stringent environmental regulations and the need to recover rare, valuable, or toxic materials from dilute sources have led to a need for an improved understanding of the chemistry of dilute solutions. Products in biotechnological processes are also frequently generated in a very dilute form. The National Research Council has scheduled a workshop for the purpose of defining the needs in this area.⁷⁴ Interestingly, one of the goals of the workshop is simply to define a "dilute solution." For the purposes of this report, a dilute solution is considered one in which the component of interest is present in a concentration of no more than a few parts per million. Note that this definition does not exclude the possibility that other components may be present in macroscopic concentrations.

It is anticipated that the proceedings of the upcoming workshop will be a valuable source of recommendations for research in this area. Nonetheless, a few points should be included here. From a fundamental perspective, it is important to realize that the behavior of materials and processes on a macroscale cannot be automatically extrapolated to the microscale. For example, Pu(V) is extremely difficult to maintain in the laboratory at normal concentrations but is the dominant form of plutonium in seawater.⁷⁵ Similarly, resins that readily sorb uranium from relatively concentrated solutions are much less efficient than predicted at recovering uranium from seawater.⁷⁶ In some cases, these effects are simply due to the shifts in equilibria that occur as the concentrations of the various species decrease. In other cases, the changes are due to the effects of trace components in the system that are too dilute to measurably perturb the chemistry of those species which are present in macroscopic amounts. From a practical point of view, the recovery of valuable materials from dilute sources (whether natural ores or a biochemical "soup" generated in the laboratory) will require the development of substantially more efficient and economical methods than those currently available.

In addition to understanding the chemistry of dilute solutions or recovering materials from dilute sources, the related problem of determining extremely low concentrations of an analyte (Sect. 3.3.4) must be resolved. The analysis of high-purity materials for trace contaminants is of fundamental importance to the semiconductor industry, for example (Sect. 3.3.5). Enrichment techniques or sensing devices that would permit such determinations are urgently needed.

3.2.5 System Design

Improvements in the design of separation systems are needed on two levels: (1) the individual separation unit operation and (2) an integrated, multistep separation process. The speed and capacity of individual unit operations must be increased, while the complexity and energy requirements are minimized. The overall economic feasibility of a separation unit operation may be controlled by energy costs (as in some distillation processes) or by capital costs (as in some membrane processes), but there is a general need to reduce both types of costs in all separation systems. In those operations where energy costs are of paramount importance, methods of utilizing process heat more efficiently, or even replacing energy-intensive processes altogether, must be explored. It is true that, in some instances, the energy requirements of a distillation or evaporation process have been so well integrated into a plant that no net energy penalty is imposed,⁴⁴ but such instances are the exception rather than the rule and relatively little work has been done to develop general methods for determining equipment configurations that optimize heat utilization.

In systems where capital costs are of paramount importance, methods of decreasing the size and complexity of separation operations are needed. Obviously, the size of the separation equipment can be reduced if the speed and capacity of the process can be increased. Increasing the selectivity of separation processes (Sect. 3.2.2) will lead directly to enhanced capacity. Of course, increased speed will require improvements in the control of process hydrodynamics, interfacial areas, and mass

transfer rates. The parameters controlling these processes are poorly understood even in laboratory-sized equipment (Sect. 3.2.1); it is generally much easier to control flow patterns, interfacial conditions, etc., in the laboratory than on an engineering scale. The identification, description, and optimization of rate-controlling processes in separations are important areas for both fundamental and engineering research.

Few of the separation methods in use today have been optimized for speed, capacity, and energy consumption, even in applications where they have been used for decades. Thus, their application to many of today's complex technological problems, such as acid precipitation, waste dump cleanup, and nuclear fuel reprocessing, which cannot be solved by the application of a single separation process, is made even more difficult. The development of integrated separations systems, consisting of several separation processes working in parallel or in series, is needed in order to solve these problems.

The problem of the emission of hazardous materials during the burning of coal is an instructive example. Various attempts have been made to reduce these emissions by direct pretreatment of the coal, by the use of "getters" during the burning of coal, by the use of scrubbers and precipitators to treat the gaseous effluents of a coal-fired plant, and by treatment of the solid wastes generated when coal is burned, liquefied, or gasified. Each of these approaches utilizes a radically different technology, and none has proved completely successful. It is likely that an integrated system of separation processes operating at each stage of the coal utilization cycle will be needed to control the emission of hazardous materials and to recover any potentially valuable materials. The selection and optimization of separation processes, based not only on how successfully they accomplish a single job but also on how effectively they can be integrated into a complex series of operations, are formidable challenges that will require unprecedented cooperation between scientists and engineers working in all areas of separation science and technology.

3.2.6 Separation Science and Technology as a Unified Field

The concept of separation science and technology as a unified field that could be described on the basis of a relatively small set of fundamental principles was presented in Sect. 2. The soundness of this concept was further demonstrated in this section, where an examination of several representative separation techniques which historically have been viewed as separate disciplines showed a considerable number of research needs that cut across all, or most, separation technologies. These general areas are interrelated; for example, an improved understanding of interfacial phenomena will lead to more selective separation systems, and the availability of a substantial, critically evaluated data base will aid in the design of improved separation systems. The recognition of the unity of separation science and technology by federal agencies, universities, industrial laboratories, and professional societies has also been documented.

Nevertheless, separations research continues to be fragmented along traditional lines. Relatively few scientists have the broad background and perspective necessary to continue the development of unified theories of separation science. Most universities or industrial research laboratories have expertise in only a few of the major separation technologies, and interaction even among the limited number of disciplines at any one site is minimal. Many federal programs that sponsor separation research are either highly application oriented or support only very fundamental studies, in contrast to the unusually strong interaction between fundamental and applied research that is needed for progress in separation science and technology.

Thus, the further development of separation science and technology as a unified field will require progress in both the technological and the philosophical arenas. The results of research in the broad areas outlined above must be used to advance the efforts that are being made to develop a complete mathematical description of the fundamental concepts underlying separation science and technology. The philosophy of separation science and technology as a unified field must be adopted

by more researchers who currently limit themselves to one discipline or another. Communication between chemists, engineers, mathematicians, biologists, environmental scientists, and other groups whose expertise is needed to advance the field as a whole (and who will benefit from such advancement) must be increased. While the theoretical and philosophical challenges that this concept presents are formidable, the potential of this approach for progress toward the solution of important technological problems is very great.

3.3 APPLICATIONS

Separation science and technology is, by its very nature, an applied field. A mathematician may solve a complicated equation merely because it is an interesting exercise, or a physicist may study the interactions of subatomic particles with no thought of practical application. On the other hand, it is rare for a chemist or an engineer to develop a separation process simply as a laboratory exercise. The applications of separation science and technology are almost endless, touching on every area of human activity from pure research to energy production, to the food industry, and to the biological sciences. It would be impossible to list, let alone review, all of the major applications of separation technology. Thus, the following programs and applications should be viewed as examples selected from a very large number of possibilities. Most of these examples were chosen because of their current or potential importance as programs or research areas at ORNL. However, they should not be taken as an exhaustive list of applications which fit that criterion.

3.3.1 Nuclear Fuel Reprocessing

The Purex process remains the only technology that is in widespread use for recycling spent nuclear fuel. Despite more than 40 years of experience, many problems with the process have not been solved. From an operational point of view, methods have been developed to minimize the effects of the most severe problems; however, the fundamental causes and

control of solvent degradation, the formation of interfacial precipitates, and marginal decontamination factors for troublesome fission products such as zirconium, technetium, ruthenium, and neptunium are still under investigation. While research in these areas is important, it will result in incremental, rather than revolutionary, improvements in the process. There are, however, a number of unresolved questions regarding the best method for handling the wastes and useful by-products that are generated in this process. Further, the decision to defer indefinitely the construction of any civilian reprocessing facilities in the United States creates an opportunity to explore radically new process chemistries for possible use in the twenty-first century.

When construction of the AGNS Reprocessing Plant at Barnwell, South Carolina, was halted and the Clinch River Breeder Reactor Program was cancelled, it became certain that no commercial fuel reprocessing plant would be constructed in the United States for several decades. This means that fuel reprocessing on a significant scale will continue only at the existing plants at Hanford and Savannah River (and on a small scale at Idaho Falls), at least through the end of this century. It is difficult to conceive of a rational scenario in which a new reprocessing plant, civilian or military, will be built in the United States in less than 30 years. Under these conditions, it is clear that we will not be able to maintain a leadership role in Purex processing since developments in other countries that have vigorous R&D and construction programs in place are bound to be more rapid.

Thus, the status of nuclear fuel reprocessing technology in the United States is largely defined by efforts presently under way at existing facilities and projects that might be done in collaboration with other countries. A number of important separations problems have been identified at these facilities, and short-term research to improve separations technology in the reprocessing industry should be aimed at their resolution. Long-term research should be focused on developing an improved understanding of the base technology of the Purex process and closely related modifications, such as the use of alternative extraction reagents [e.g., tri(2-ethylhexyl) phosphate, sulfoxides, carbamoylmethylphosphonates,

etc.]. Moreover, the long interim period between the present and the time when a new reprocessing facility will be constructed affords an excellent opportunity for developing alternative, radically different, reprocessing schemes to the point where critical evaluations can be made concerning the most desirable technology for deployment in the twenty-first century. Examples of such alternative technologies include several nonaqueous methods, such as pyroprocessing^{76,77} and fluoride volatilization using dioxygen difluoride or krypton difluoride,⁷⁸⁻⁸¹ as well as new aqueous methods employing membrane technology or the alternative extractants already mentioned. These novel separation methods were too undeveloped to be considered for use in a facility to be built before the end of the century; however, there is now time for further development and evaluation of these technologies before a new reprocessing plant is likely to be built in the United States. While the lack of a vigorous reprocessing program based on Purex technology is regrettable, the opportunity for a head start in the development of twenty-first century reprocessing technology is an exciting one.

One of the most pressing separations problems of immediate concern at existing U.S. reprocessing facilities is a need for a continuous process for recovering cesium from the acid waste generated in the Purex process. The waste is currently made alkaline before storage, and existing methods for recovering ¹³⁷Cs (which is in high demand as a gamma source) are adequate to meet market requirements. When the glass encapsulation methods for waste isolation come on-line, however, the waste will not be made alkaline, and the only processes currently available for recovering cesium from acid waste are inefficient, inconvenient batch-type methods. A continuous method (preferably based on solvent extraction technology to ease integration with existing processes) is sorely needed. Ideally, a complete process for recovering and partitioning both cesium and strontium from the waste could be developed.

Nuclear fuel reprocessing generates large volumes of organic wastes that must be disposed of or destroyed. These wastes include both spent solvents (TBP, carbon tetrachloride, hydrocarbon diluents) and aqueous

solutions of organic complexing agents. For example, about 4 million gal of aqueous wastes containing significant concentrations of tetraphenyl boron are currently stored at the Hanford reservation. These solutions, which have boron and organic contents that are too high for disposal by conventional methods (e.g., grout), must remain in tanks until a method of removing or destroying the organic species is found. The removal or destruction of organic compounds from aqueous solutions is a generic problem in waste management, and methods developed in the nuclear industry should find wide applicability.

There is a general need in the nuclear industry for a process to separate the lanthanide elements from the trivalent actinides in a nitrate-based rather than a chloride-based system. The use of chloride complicates flowsheets by requiring nitrate-to-chloride and chloride-to-nitrate conversions and by accelerating equipment corrosion. (See Sect. 3.3.2 for a discussion of this problem in the Transuranium Processing Plant.)

The dissolution of plutonium oxide (and other refractory metal oxides not necessarily related to the nuclear industry) in scrap, waste, or spent fuel is an old problem with no solution. Why is some material so difficult to dissolve even when fluoride or other catalysts are added? Practical solutions, as well as fundamental explanations, are needed in this area.

A major research program on the main part of the Purex flowsheet is not warranted. The Europeans and Japanese have active programs in this area, but the research is designed to fill the gaps in the data base and to address some of the remaining trouble spots, such as Np, Tc, Ru, or Pd chemistry, and valence adjustment. These efforts are worthwhile and should be a part of a continuing base-technology program in the United States, but they do not form the basis for a large research program. However, the prototypic, high-burnup, mixed-oxide fuel that has recently become available from the Fast Flux Test Reactor should be thoroughly studied and used to test proposed reprocessing schemes of all types, including those that are highly speculative (e.g., fluoride volatility processes based on dioxygen difluoride).

Although research in the application of LIS technology (Sect. 3.1.7) to separations problems in the nuclear industry has been directed almost entirely at the separation of uranium isotopes, other applications are possible. For example, ^{137}Cs , a short-lived isotope that can be disposed of simply by storing until it decays away, has already been cited as an important gamma source. Unfortunately, ^{137}Cs is almost always contaminated with ^{135}Cs , a long-lived isotope that requires elaborate, long-term, retrievable storage. An effective method of separating the useful, more easily handled isotope from the less valuable, more difficult-to-handle isotope would be very useful. LIS might be an economical solution to this problem.

3.3.2 TRU Processing

The Transuranium Processing Plant (TRU) has been operating for almost 20 years. During that period, it has gained prominence as the primary center for the production of transcurium elements. The flowsheet used to recover these elements from targets irradiated in the High Flux Isotope Reactor (HFIR) has been modified several times during the life of the plant,^{82,83} mostly on an ad hoc basis, to solve specific problems such as corrosion or new process requirements. While the desirability of replacing certain steps in the process, such as those requiring the use of chloride solutions, is well recognized, the risks involved in replacing a proven, well-known process with a new flowsheet have always offset the potential advantages of a process that may prove to be less effective when implemented.

There are, however, at least three factors that may make it more attractive, and perhaps necessary, to install a new TRU process flowsheet. One is the potential demand for substantially larger quantities of ^{252}Cf for use in radiography, which could not be met with the capacity of the current process. The current flowsheet also requires that the facility be essentially fully staffed continually because the caustic scrubbers used to remove the HCl generated in the process must be monitored at all times. A substantial savings in operating costs would result if a

process could be developed that would be rapid and safe enough (i.e., would not generate HCl) to allow the elimination of one or more shifts. Finally, the construction of the Center for Neutron Research and the new HFIR will also place new demands on the facility, especially if both HFIRs are operated simultaneously.

Fortunately, advances in actinide separation chemistry have produced methods that may satisfy the need for a new process that is faster, has a higher volumetric throughput, and eliminates the generation of chloride vapors. Aqueous methods using the carbamoylmethylphosphine oxides (CMPOs)^{84,85} would require relatively little R&D to develop and may satisfy all of these criteria. The application of pyrochemical methods to processing HFIR targets for the recovery of the transcurium elements would require a substantial amount of long-term R&D but might result in a tremendous decrease in the scale of the process equipment (i.e., would greatly increase the volumetric throughput). Efforts to develop new TRU process flowsheets based on either of these technologies can be justified, not only on the basis of their potential application in the TRU facility but also on the insight that would be gained into the fundamental chemistry of the actinide and lanthanide elements.

3.3.3 Strategic Materials

The United States is almost completely dependent on foreign sources for a few materials that are critical in some military and civilian applications. Among the most important of these are metals such as chromium, cobalt, manganese, niobium, the platinum group metals, and tantalum. Almost 100% of domestic requirements for these metals is met by importation. This vulnerability is a result of several factors, including small (or nonexistent) reserves of high-grade domestic sources, and lack of separation technologies for the recovery of these metals from low-grade domestic ores that could compete, on an economic basis, with the abundant, inexpensive supplies available from foreign sources. Current policy for dealing with the threat of a cutoff of the supply of these materials calls for the maintenance of strategic stockpiles for use in the event of a national emergency. The complete, long-term resolution

of this problem will require a combination of partial solutions, including the development of alternative foreign sources, substitution of vulnerable materials with more available ones, an expanded recycle program, and an expanded R&D program for the recovery of material from dilute domestic sources.⁸⁶ Separation science can make a contribution in these last two areas (which overlap somewhat).

The general need for an improved understanding of the chemistry of dilute solutions has already been discussed (Sect. 3.2.4). The recovery of strategic materials is a specific area of application for that research. In this case, "dilute solutions" refer to low-grade ores, effluent streams from processing plants where strategic materials are in use, or waste dumps where equipment containing strategic metals have been disposed. Improvements in adsorption and hydrometallurgical techniques brought about by progress in the generic research areas discussed in Sects. 3.2.1 to 3.2.6 are likely to play a large part in this area, and the probability of new membrane methods and biotechnology making contributions in this area is significant.

The status of efforts to develop an economic process for the recovery of uranium from seawater is an instructive example of how research in the recovery of strategic material is dictated not only by scientific progress, but also by accidents of geology and politics. Domestic supplies of uranium are ample in the United States, especially since the development of methods to recover it as a by-product from phosphoric acid production. Therefore, uranium is not classed as a strategic material in the United States, and little work has been done to develop a process for its recovery from seawater. The Japanese, however, have virtually no domestic sources of uranium and consider its recovery from seawater to be of great strategic importance in their efforts to gain energy independence through aggressive use of the nuclear energy. Their work has led to the development of new, more effective adsorbents, such as the polyacrylamidoxime chelating resins,⁸⁶ and novel separation techniques, such as the magnetic adsorbent process.⁸⁷ The work done in this country, although limited, has led to the design of shipborne, high-performance systems for the recovery of uranium from seawater,^{88,89} important observations about the behavior of

adsorption processes operating in the ocean environment,⁷⁵ and indications that the corecovery of other elements along with the uranium in seawater may prove to be important even for countries that have adequate supplies of uranium from conventional sources.⁹⁰⁻⁹² The overall question of the need to recover uranium from seawater can be answered only in the context of a given geopolitical situation; however, from a purely technical point of view, it is clear that the research being done in this area will lead to significant advances in our understanding of the chemistry and technology needed to separate valuable and strategic materials from dilute sources.

3.3.4 Analytical Separations

Virtually all separation techniques that are used on an industrial scale are also used on an analytical scale. Indeed, many advances in separation technology have come about as a direct result of separation science research that was done in an analytical development laboratory. For example, the reagents that are used for the hydrometallurgical recovery of copper were first used as analytical reagents for copper. Unfortunately, all analytical separation methods cannot be scaled up so easily. For example, the application of many chromatographic techniques on a large scale is hindered by the difficulties in producing packing and support materials that can be packed efficiently in large columns and by the general lack of adequate theoretical or empirical models to describe the behavior of large columns (Sect. 3.1.4). In general, new separation methods that are developed in the analytical laboratory are not efficiently transferred to large-scale applications. There are, of course, exceptions, but even when scale-up is relatively straightforward, as in the case of a new extraction reagent, for example, technology transfer can be slow. Expediting the transfer of separation methods from the analytical laboratory to industrial applications and the development of generalized models that will allow those methods to be efficiently optimized on a large scale could result in the use of dramatically improved techniques for many applications.

The status of many analytical separation techniques is reviewed in detail each year by noted authorities writing in *Analytical Chemistry*.⁴⁰ Fundamental advances are reviewed in even-numbered years, and applications are reviewed in odd-numbered years. Giddings¹⁶ has written an excellent article on future pathways for analytical separations. No attempt will be made here to reproduce the tremendous amount of information already collated in these readily available works. In summary, it can be said that the increasing pressure to determine lower and lower concentrations of all types of chemical species in the environment, food, pharmaceuticals, forensic samples, special materials for the electronics, nuclear, and other industries, and a myriad of other applications has led the analytical community to develop techniques that would have been considered impossible only a few years ago. In many cases, this progress has come about not as a result of improvements in the analytical technique itself, but in the development of separation methods that preconcentrate the sample to levels high enough for routine analysis.

It should not be inferred that an analytical separation technique must be applied on an industrial scale before it becomes important. Modern medicine relies heavily on the analysis of small samples of body fluids for assessing the health of an individual, diagnosing diseases, and monitoring drug levels. Such analyses are often dependent on high-resolution chromatographic techniques to separate the hundreds of constituents that are present in biological fluids at very low concentrations. While considerable progress has been made in this area, much remains to be done. The fluids to be analyzed contain species ranging in size from simple atomic anions and cations to macromolecules, to cell substructures and whole cells, and the concentrations of these species range from picomolar to one-tenth molar. The development of high-resolution techniques for separating and identifying the components of these fluids is a tremendous challenge but carries with it an even greater promise of improved detection, diagnosis, and treatment of disease.

3.3.5 Industrial Purification

The demand of modern science, technology, and society for materials, foods, and pharmaceuticals of unprecedented purity has never been greater; moreover, it continues to increase and even accelerate. As the size of the circuits etched in solid-state components shrinks to the submicron range, each atom of radioactive elements such as thorium and uranium, which are ubiquitous in the silicon, germanium, and gallium arsenide semiconductors used in the electronics industry, acts as a small time bomb in the circuits. When these bombs "explode" (i.e., decay), they can destroy the tiny components of a semiconductor device. The results may be relatively harmless, as when a hobbyist gets an unexpected "parity check" error on his home computer, or it may be quite serious, as when a critical chip in a missile guidance system is damaged. The development of ultraminiaturized semiconductor devices, which was once thought to be limited by the physics of the system, is now being impeded by the need for ultrapure materials.

The manufacture of electronic components using ultrapure materials also demands an ultraclean working environment.⁹³ Submicron circuits can be shorted by submicron particles falling from the air; therefore, rooms that were once considered clean (containing perhaps 400 particles greater than 0.2 μm per cubic meter) are now considered quite dirty since requirements for both the number and size of the particles are reduced by an order of magnitude. It is clear that advances in semiconductor technology will continue to challenge the separation scientist to provide materials and environments of ever greater chemical and physical purity.

The nuclear industry (weapons, power, and medicine) would benefit from the development of an inexpensive and efficient method for decontaminating low-level wastes to subtracer levels so that the volume of radioactive waste generated would be greatly reduced. Waste containing the TRU elements requires special handling, and a highly efficient process for removing these elements from radioactive wastes would result in the simplified handling and disposal of the "purified," non-TRU portion of the waste.

The biotechnology and pharmaceutical industries also require exceedingly pure starting materials and products. Bioreactors are extremely sensitive to trace amounts of enzymes or other biomolecules that can act as highly efficient inhibitors to the desired reaction or catalysts for undesirable side reactions. Because the specific activities of many biological molecules are very high, a trace impurity can dominate the chemistry of the system and turn the expensive starting material in a reactor into completely useless product. Similarly, pharmaceuticals manufactured by the newer biotechnological methods or by classical synthetic routes must often be purified to ensure the absence of potentially toxic materials, which may have a greater specific biological activity than the desired drug.

In the food industry, even such prosaic items as peanut butter must be screened to ensure a very high degree of purity with respect to aflatoxins, a class of naturally occurring compounds that are among the most carcinogenic known. The coffee industry has been under pressure to reduce the trace amounts of chlorinated solvent residues left in decaffeinated products. While this concern may be unjustified, it has created a very real demand for improved purification procedures and, in many cases, has spurred the development of alternative decaffeination methods using water or supercritical carbon dioxide. In general, standards for the purification of food products with respect to both chemical and physical contaminants will continue to become more stringent.

3.3.6 Waste Management

The problems presented by the hazardous materials that have been (or are being) discharged to the environment are overwhelming, and their solutions often challenge the limits of separation science and technology. Pollutants that must be separated from the environment may be solids, liquids, or gases; they may be simple anions or cations, organic or inorganic, natural or man-made, dilute or concentrated, radioactive or stable. They come from the smokestack industries, energy production, automobile exhausts, the health-care industry, and residential waste treatment units. Some of the problems are ongoing, while others are left

over from an era when little thought was given to how waste materials were discharged to the biosphere. The news media are diligent in pointing out where hazardous and radioactive wastes are, were, or might one day be stored or discharged. Standards for what constitutes an environmentally acceptable level of discharge to the environment are becoming increasingly stringent, and there is every indication that this trend will continue.

Such a litany of gloom may make the problem seem intractable, but that is far from the case. Significant breakthroughs have been made, and the techniques and research needs discussed in Sects. 3.1 and 3.2 point the way for even greater progress. The application of highly selective, more efficient solvent extraction, ion exchange, adsorption, and membrane separation (primarily, reverse osmosis and ultrafiltration) techniques has successfully reduced the concentrations of many of the pollutants that were once common in aqueous industrial effluent streams. Emissions of the oxides of sulfur from coal-fired electrical plants have been reduced substantially by pretreating the coal to remove inorganic sulfur and by scrubbing the flue gas after the coal is burned. Biotechnologists have developed microbes with the ability to decompose hazardous halogenated compounds,⁹⁴ nitrates,⁹⁵ and cellulosic materials⁹⁶ in the soil, solid wastes, aqueous waste streams, and waste ponds. Supercritical water has been used to destroy organic material in waste streams.⁵²

The limits of the success of these processes also mark the point at which the need for R&D of improved techniques begins. Allowable limits for the discharge of many species, such as arsenic and dioxins, are already at or below the limit of detection. New methods of analysis, analytical separations, and process-scale separations are needed. The development of these methods will require advances in each of the five generic research areas discussed in Sect. 3.2: interfacial phenomena, selectivity, critical data-base evaluation and mathematical modeling, the chemistry of dilute solutions, and system design. It is easy to foresee that many difficulties would be encountered in devising a separation process that can efficiently remove very small amounts of dissolved or

suspended material from very large volumes of aqueous effluents, especially since the chemical and physical behavior of species in very dilute solution is so poorly understood and reliable data are very scarce.

The successful application of biotechnology to waste problems has been very encouraging thus far, but existing techniques barely scratch the surface of the possibilities for this technology. The working examples of biotechnological solutions to waste problems are impressive, but few. The microbial degradation of halogenated compounds, for example, is still experimental. In addition to the technical questions concerning how well this method would work on a large scale, there are broader philosophical, social, and regulatory questions that must be answered about the introduction of genetically altered microbes into the biosphere. Nevertheless, the potential of developments in biotechnology for solving many environmental waste problems is very great.

The relationship between separations developed to reduce waste and the problem of strategic and valuable materials (Sect. 3.3.3) should also be noted. To the degree that process effluents currently being discharged to the environment contain precious or strategic materials, improved methods of separating, concentrating, and recovering these species before they are discharged will reduce the demand for additional supplies. In favorable cases, the value of the recovered materials may offset all, or most of, the cost of the waste treatment process.

The reduction in the emissions of the oxides of sulfur from the burning of coal has already been cited as an example of an area needing more work (Sect. 3.2.5), but it is mentioned in this section as an example of progress in waste separation technology. There is no contradiction; both statements are quite true. Although sulfur dioxide emissions have been cut dramatically, they are still much too high, and the efforts to reduce the emissions of the oxides of nitrogen and other pollutants have been much less successful. It has already been pointed out that an integrated, systems approach will be needed to achieve a completely satisfactory solution to the problem of emissions that occur during the burning of fossil fuels. This observation can be generalized to include many processes that produce hazardous and radioactive waste.

Little research has been done to determine when, or if, two less effective separation processes, perhaps installed at different points in a larger process, might be combined to produce better overall results than one, highly effective process being pushed to the limits of technology. Nor, in general, have processes been designed with full consideration of how the waste streams generated will be treated. As the costs of waste management continue to increase, it will become increasingly important to consider the separation methods used to ensure that process effluents meet regulatory requirements as an integral part of the overall process, rather than as an add-on to be retrofitted as needed.

The need for close cooperation between analytical chemists, toxicologists, environmentalists, separation scientists, and regulatory agencies should also be stressed. It is certain that analytical chemists will continue to develop methods for determining species that are present in lower and lower concentrations, and separation scientists will continue to develop ways to reduce emissions into the biosphere. Considerable work is needed, however, to determine how low the limits for the emission of a potentially hazardous chemical must really be in order to adequately protect the environment and the health and safety of the public. Regulations governing these limits should be based on sound toxicological and environmental data rather than on such arbitrary guidelines as "the limit of detection" or "as low as reasonably achievable." Limits based on criteria such as the latter could be ruinously expensive to achieve as analytical and separation capabilities continue to improve.

3.3.7 Biotechnology

The relationship between biotechnology and separation science and technology is particularly interesting since future developments in biotechnology depend heavily on progress in separation science and progress in separation science is catalyzed by developments in biotechnology. Examples of this symbiosis have already been discussed several times in this report. Depending on the observer's point of view, affinity chromatography (Sect. 3.1.4) may be considered an advance in separation science, chromatography, biochemistry, or biotechnology.

The progress that is possible through the combination of all (or at least several) parts of separation science can be seen in the recent success that has been achieved in cell separation by affinity partitioning.⁹⁷ The isolation of homogeneous, functionally specific populations of living cells has been cited as one of the chief obstacles to progress in cell biology.⁹⁷ Progress is being made in the separation of these carefully partitioned cell populations by the use of affinity partitioning, which is based on the principles of affinity chromatography but uses what is effectively a solvent extraction system to apply them. In this technique, the ligands that would ordinarily be bonded to a chromatographic support are, instead, dissolved in one phase of a two-phase aqueous polymer system. Thus, the specificity of affinity chromatography (which came from the application of the principles of biochemistry to chromatography) is combined with the high capacity and easy scale-up of solvent extraction (which was developed most vigorously and is still largely applied to separating inorganic species) to help solve one of the most difficult problems in biotechnology.

The list of applications of biotechnology to separation science (and vice versa) is long and still growing. The development of biomimetic membranes, one of the most exciting areas in membrane research (Sect. 3.1.3), both fuels and is fueled by advances in biomembrane science. Increasingly selective extraction reagents (Sect. 3.1.1) are being designed based on what is being learned about the factors that govern enzyme-substrate specificity in biological systems. The methods being developed for the analysis of body fluids could have been as easily discussed in this section as in the one on analytical separations (Sect. 3.3.4). The use of genetically engineered microbes to degrade halogenated compounds and nitrates in the environment (Sect. 3.3.6) is a graphic example of the potential of biotechnology in separations. To reiterate the key point: future progress in biotechnology depends heavily on advances in separation science, and advances in biotechnology will contribute heavily to advances in separation science.

3.3.8 Acid Precipitation

The causes, extent, and consequences of acid precipitation are still subjects of scientific and political debate; however, it is clear that the large amounts of sulfur and nitrogen oxides released during the processing of iron pyrites and the burning of fossil fuels make a significant contribution to the total amount of atmospheric acids. Natural gas, oil, and coal frequently contain substantial amounts of sulfur compounds, and the average sulfur contents of these fuels are rising as the low-sulfur sources are depleted. Methods for the desulfurization of natural gas and oil are quite well developed. Natural gas is contaminated with hydrogen disulfide, but the technology for removing this highly toxic gas and converting it to elemental sulfur for sale is both efficient and economic. Hydrodesulfurization reduces the sulfur content of oil to levels that are acceptable under current regulations, but future regulations might require improved methods. High-sulfur coal is the most polluting of all of the fossil fuels with respect to sulfur and nitrogen oxide emissions, and, unfortunately, the technology for controlling emissions from this source is the least effective. Currently, up to 50% of the inorganic sulfur (mostly iron disulfide) is removed from coal before combustion by grinding, washing, and magnetic separation. No economically viable method has been developed for removing the organic sulfur before or during the combustion process; thus, further desulfurization is done by means of flue-gas scrubbers. Ten to thirty percent of the gaseous sulfur effluents (and virtually all of the oxides of nitrogen) escape from these scrubbing systems, which also produce a sludge that is itself a disposal problem. The need for an integrated, systems approach to improved methods for handling the toxic and hazardous materials produced by burning fossil fuels has already been discussed (Sects. 3.2.5 and 3.3.6).

4. SEPARATION SCIENCE AND TECHNOLOGY AT ORNL: CONCLUSIONS AND RECOMMENDATIONS

Separations research at ORNL is largely divided along the lines of the traditional separation techniques, and the work being done in these individual areas is sound. The current challenge in separation science, however, is to find ways to integrate the theory and application of all of the areas that make up the field. This integration must occur on the fundamental, theoretical, and applied levels. A possible ORNL response would be to create a Center for Separation Research to address this challenge across a broad front. The Center would coordinate separation research at ORNL, take a lead role in the development of separation science and technology as a unified field, and act as a resource to aid in making the Laboratory's separations technology and human resources more available to industry, academia, and the general public. Fundamental research efforts would focus on the broad areas described in this report. In addition, the application of the latest developments in computer science, including parallel processing and artificial intelligence, as a tool for developing a unified approach to separation science and technology would be a novel and important part of the Center's activities.

Clearly, however, it is not possible to acquire all of the resources necessary to fully fund, staff, and equip a center with such a broad charter in a single step. A more practical approach is to focus the operation of the Center on the application of separation science and technology to a single, well-chosen and well-defined problem area. This problem area must be of national importance, relevant to the mission of the Laboratory, broad enough to require a multidisciplinary and multidivisional approach, and readily recognizable to the DOE and other funding agencies as appropriate for the expenditure of federal funds. It must also have the potential to grow naturally so as to encompass many of the other applications and generic research areas identified in this report, including the development of the application of expert computer systems to separation science and technology.

Of all of the fields in which advances in separation science and technology are needed, the area of hazardous and radioactive waste management best fits these criteria. The problem of handling, regulating, and disposing of waste materials is national, even international, in scope. ORNL is already committed to dealing with its own waste problems and to developing procedures and methods that will serve as models for solving similar problems at other locations. While an extensive Nuclear and Chemical Waste Program is already in place at the Laboratory, there is no formal provision for carrying out the basic research that is needed to develop new separations methods in support of this program. The Center for Separation Research would be charged with identifying waste management problems that require advances in separation science and technology as a part of their solution. It would also carry out the R&D needed to bring about those advances.

The close relationship between separation science and technology and waste management can be seen by considering the steps that are normally taken when dealing with a waste problem. In many cases, the most desirable first step is to reduce the volume of the waste to be handled. This immediately implies a separation of the hazardous or radioactive material from some inert matrix. Further separations may then be required to isolate the radioactive material from the hazardous material. Radioactive waste may be further subdivided into TRU and non-TRU components, and hazardous wastes may also be separated into various fractions for incineration, recycle, encapsulation, or other purposes. Once the waste has been packaged for final disposal, it is necessary to ensure that it does not re-separate and become dispersed in the environment. The exact number and sequence of these steps will vary from problem to problem, but the general point is clear: the treatment of hazardous and chemical wastes requires frequent use of separation science and technology.

Table 4 lists some examples of waste problems at the four Martin Marietta Energy Systems, Inc., sites that require advanced separation technologies for their solution. The listing is not complete; nor does it imply that the problems listed should be given special priority. It

Table 4. Examples of Energy Systems waste problems requiring advanced separation technology

	ORNL	Y-12	Enrichment
Analytical methods	Separation and identification of 55 organics	Determination of 0.05 ppb Hg	EPA certification as environmental support lab.
On-line monitoring	Radionuclides in water	Hg in water; radionuclides in stack gases	Radionuclides in stack gases
Treatment technology development and demonstration	Removal of radionuclides from process and ground waters	Hg in water; radionuclides in stack gases	Radionuclides, organics leaching from grout LLW Facility
	Removal of organics from process water		Decontamination of scrap metal
Volume reduction	Substitute for hydrofracture	Solvent cleanup for recycle	
	Separation of hazardous from radioactive waste	Metal recovery	
	Ca, Mg removal with minimum sludge		
Remedial action	Treatment of runoff from burial grounds; oil spills	Treatment of groundwater in flood plains from ponds, burial grounds	

does, however, reflect the scope of the problem and include some of the extremely difficult separation problems that exist. Moreover, these problems are, in general, ubiquitous. While the Energy Systems sites have a greater concern with radioactive materials than would be true for most commercial sites, the problems of detecting, separating, and isolating toxic metals and organic compounds are generic. For example, the EPA has identified 850 hazardous waste sites that are eligible for remedial cleanup funds under the Comprehensive Environmental Response Compensation and Liability Act of 1980 ("Superfund").⁹⁸ In many cases, the technology for cleaning up these sites does not exist, and substantial research is needed. Similarly, a 16-volume report has been compiled which characterizes the hazardous waste from all of the Defense Program sites in the United States.⁹⁹ Some of these wastes can be dealt with via existing technology, but many will require substantially improved separation methods in order to be treated satisfactorily.

The primary driving force behind the need to develop improved waste management technology is the increasingly stringent regulations governing the amounts of contaminants that can be discharged to the environment. For example, Table 5 lists six common components of aqueous process waste streams for which the regulations already require discharge levels that are at, or below, current levels of detection. Methods to concentrate, separate, and quantitatively measure polychlorinated biphenyls, chlorinated pesticides, and 55 specific organic compounds are also needed.¹⁰⁰ Monitoring and treating aqueous waste streams to achieve this level of purity will require significant advances in separation science on every scale from the analytical laboratory to the process water treatment plants used in large cities.

No single separation technology will serve to solve all of the problems in waste management. Thus, the fundamental research at the Center must focus on the generic research areas (Sect. 3.2) that will do the most to advance separation science as a whole, rather than to improve a single separation method or class of methods. A better understanding of the chemistry of dilute solutions and the development of new separation agents and processes with significantly greater selectivity

Table 5. Detection limits and emission standards
for selected pollutants^a

Pollutant	Tennessee detection limit (ppb)	Stream standards (ppb)
Cadmium	2	0.025
Chloride (residual)	100	10
Lead	10	3.8
Mercury	1	0.05
Phenols	1	1
Silver	6	2

^aData taken from ref. 100.

and capacity are especially important in this context. Better design and integration of complete separation systems, perhaps involving a series of separation methods operating together, will be needed. As the requirements for waste treatment technologies become more stringent, it will become increasingly advantageous to integrate these processes into the overall operation of a facility, rather than treat them as add-ons at the end of a process.

Advances in separation science have traditionally been driven by the need to solve specific problems. Typically, these problems could be solved by improvements in a single technique or small group of techniques. However, the importance and scope of the waste management problem are of such magnitude that advances are needed in virtually every separation method and an integrated approach is required for their application. Thus, there is a powerful driving force for the development of a more unified approach to separation science and technology and for promoting interactions among separation scientists and engineers working in different areas, as well as between these groups and analytical chemists, toxicologists, environmental chemists, and regulatory agencies.

A major problem in developing a comprehensive, unified approach to the theory and application of separation science and technology is the large volume of information that must be considered. The regulations defining the advances that are needed in the waste management field occupy many volumes and are constantly expanding. The relevant chemical and engineering data, when they exist, are scattered throughout a number of data bases. The theoretical and empirical models for the chemistry and engineering of separation systems are complex, as are those that are used to custom-design molecules for use as separation agents. It is not difficult to find an expert in the theory and application of a single separation method (e.g., ion exchange or distillation), but very few people can evaluate the potential of more than one or two separations techniques for their application to a problem, and no individual could be expected to master all of them. Even if the theory of all separation methods could be reduced to a few simple equations, the regulatory, chemical, analytical, and engineering theory and data required to put the theory into practice are extensive.

In principle, however, it is possible to design a system that can integrate all of the theory, models, and information that are useful in separation science and technology into an electronic, knowledge-based expert system. Figure 4 is a conceptual diagram showing the major components that would be included in such a system. This system could analyze a waste sample, determine which components need to be separated in order to meet the relevant regulations, report what methods had been used successfully in the past (along with the proper scaling factors and cost estimates), and suggest new methods based on separation agents designed by ab initio calculations of optimal molecular properties. A complete system of this complexity may not be practical, but most of the individual components exist (at least in some form), and the knowledge that would be gained in improving and integrating even a relatively small number of the existing modules and in attempting to develop the new ones would be significant. For example, the construction of expert systems in some of the more important separation methods would be useful in conserving

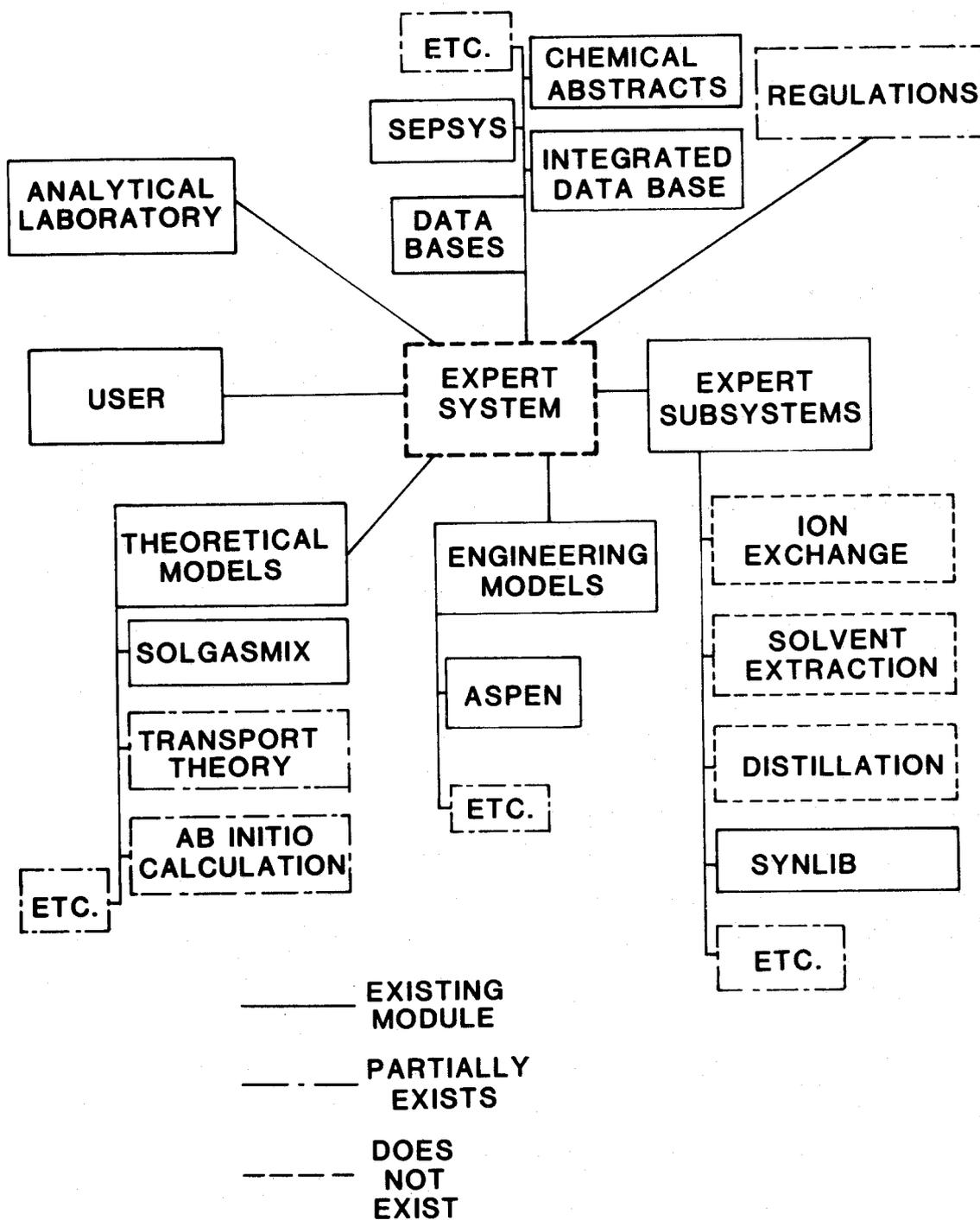


Fig. 4. Conceptual diagram of a separation science and technology "Expert System."

and making more readily available what is already known by human experts in the field, even if the systems could only be used as stand-alone modules.

In summary, ORNL can best respond to the challenge of integrating the field of separation science and technology by directing its fundamental separations research toward the research areas that will be most useful in advancing the field as a whole. This research will be driven by the need to develop the substantially improved separation technology required to solve the complex problems in waste management. It is obvious, however, that the fundamental and applied research carried out in order to solve waste management problems will find applications in many other areas as well. Finally, a program should be initiated to explore the potential of the latest developments in artificial intelligence and computerized information retrieval as a tool for integrating and making available the tremendous amount of theory, data, and information that are needed to design separation systems.

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Appendix

MAJOR SEPARATIONS FACILITIES
AT OAK RIDGE NATIONAL LABORATORY

Several unique separations facilities at ORNL have helped to contribute to the establishment of a substantial expertise in separations science and technology at the Laboratory. These facilities are described briefly in the following paragraphs. In most instances, a reference is given to a report that describes the facility in more detail.

Stable Isotopes Separations Facility

This facility, located in the Y-12 area, has 39 operable electromagnetic separators of three basic types. The primary production unit is the conventional 61-cm-radius 180° beta Calutron (mass spectrograph), which has been modified with more versatile ion sources and receivers since its original use with uranium. The second type of separator is a 255° double-focusing spectrometer with an inhomogeneous magnetic field. Six of these units and three groups of eight beta-type separators are arranged in four magnetically isolated chambers. Therefore, isotopes of four or more elements can be separated concurrently. Eight additional beta-type separators, located within a radioactively contained facility in an area adjacent to a "hot" controlled laboratory, are available for radioisotopic separations, including the heavy elements. The third type of separator is a 180° sector device which differs from the other two in that the source and object are external to the magnetic field. This type is a 180° focusing, inhomogeneous device with a 61-cm orbit radius. The primary use of this device is to obtain extremely high enrichment in a single pass (especially low-natural-abundance isotopes) and in the fabrication of surface-deposited enriched targets and ion implantation studies. (ORNL-5172)

Solvent Extraction Test Facility

This facility, located in Building 7920 at the ORNL site, is a versatile experimental device for testing solvent extraction flowsheets in Purex nuclear fuel reprocessing schemes. The facility is operated in one of the hot cells in Building 7920 in order that highly radioactive feed streams can be tested. It is built around three banks of mixer-settler contactors. Each mixer-settler bank contains 16 extraction stages. The system can handle aqueous and organic stream flow rates of approximately 1 L/h. Typical aqueous streams consist of U, Pu, fission product elements, and corrosion product elements dissolved in nitric acid. Typical organic streams consist of 30% tributyl phosphate (TBP) in dodecane.

Off-Gas Decontamination Facility

This facility, designed for the distillation/absorption removal of krypton from liquid carbon dioxide, consists of two packed columns for gas-liquid contacting and associated support items, including gas compressors, pumps, condensers, heaters, process controls, and complete sampling and monitoring capabilities. Process cooling is achieved by means of two conventional evaporative-type refrigeration units. The facility is designed to operate at nominally 20-atm pressure and temperatures between -40 and 150°C. With few exceptions, 304L stainless steel was used as the material of construction throughout the process for both vessels and piping. All-welded construction was used, except in cases where screwed connections are required for instrumentation. Typical flow rates for the various streams will range from 5 to 10 scfm for gases and 1 to 2 gpm for liquids. This is a versatile facility for investigating distillation/absorption/stripping operations over a wide range of process parameters. (ORNL/TM-4596)

Continuous Chromatograph Test Facility

This facility, located in Building 4501 on the ORNL site, consists of a prototype stainless steel annular chromatograph, feed and product tanks, various recirculation and metering pumps, and instrumentation and controls. The annular chromatograph consists of two concentric stainless steel cylinders, the annulus between which is filled with a sorbent bed material. This unit rotates slowly and performs multicomponent separations on a continuous basis using liquid chromatography. There are two 500-gal fiberglass feed tanks and two similar product collection tanks. There are ten metering pumps with 0.05- to 0.5-gpm capacity and two recirculation pumps of 2-gpm capacity. Interconnecting piping is constructed of PVC and Carpenter 20 stainless steel. Rotameters, strip-chart recorders, and pressure gauges are panel-mounted for convenient process control. This is a versatile development facility in which continuous chromatography and other similarly sized separations devices can be tested on many systems and over a wide range of process parameters. (ATS No. 80-8-19)

Superconducting Magnetic Separation Facility

This facility allows development of open-gradient magnetic separation using a superconducting solenoid test magnet. This type of magnet can generate extremely large forces in an open volume in order to utilize the weakly paramagnetic properties of many minerals to effect separation. The magnet can be operated in either of two modes by changing the direction of current flow in the windings. The windings can be connected so that the magnet becomes a single large solenoid, which makes it suitable for high gradient magnetic separations (HGMS) testing, or it can be connected so that it forms a cusp-mode solenoid, which is the configuration used for open gradient magnetic separations (OGMS) testing. The solenoid measures 30 cm in the vertical direction and is suspended in the cryostat around a 90-mm warm bore through which the material to be separated is fed. The magnet generates a separating force of approximately 0.7 Ts/cm at a distance of 3 cm from the windings with a current density of 27,200 A/cm². This facility is located in Building 9201-3 at the Y-12 site. (ORNL-5764)

Modular Portable Water Treatment Process Development Unit

A modular transportable process development unit (PDU) for R&D studies on water treatment polishing processes was designed and constructed. This PDU contains modules for feed pretreatment and storage, carbon adsorption, reverse osmosis, and ozonation. The nominal aqueous throughput is 1 gpm, and the unit processes can be operated singly or in any series combination. The PDU is housed in two 40-ft-long semivan trailers, which can be transported to and operated at any site. (TA 466/X)

Integrated Equipment Test Solvent Extraction Facility

This facility was constructed to provide testing of equipment and processes prototypical of those for a nuclear breeder reactor fuel reprocessing plant. It consists of a nonradioactive reprocessing system through one cycle of solvent extraction using depleted uranium to simulate the nuclear fuel materials. The separations equipment for solvent extraction includes two eight-staged arrays of mixer-settlers and one 4-in.-diam by 21-ft-long pulsed column containing rosette plates. These three contactors may be arranged in various configurations that allow independent tests of extraction, scrubbing, and stripping in each unit. All necessary peripheral equipment (tankage, pumps, chemical makeup systems, heat exchangers, decanters, airlifts, and flow meters) and a solvent washing system are included. Control instrumentation includes an in-line photometer for uranium. All controls are interfaced to a control room, which includes state-of-the-art display and control consoles and a distributed data acquisition and control (computer) system.

High-Temperature Fluidized-Bed Test Facilities

Two high-temperature fluidized-bed pilot facilities exist at ORNL which allow the development of processes for separation of components of high-temperature gas streams. The first facility, located in Building 9201-3 at the Y-12 site, is an atmospheric fluidized-bed test unit with a diameter of 25 cm. It is designed to operate over a range of fluidizing velocity between 1.2 and 3.0 m/s at a temperature of 760 to 870°C. Solids

can be fed to the unit either by metered pneumatic transport or by metered gravity flow. The fluidized-bed vessel is constructed from 25-cm-diam, sched 40 304 stainless steel pipe and contains horizontal cross-tube heat exchangers immersed in the bed for temperature control. The facility is thoroughly instrumented for temperature, pressure drop, and off-gas composition. (ORNL/TM-8383)

The second facility, located in Building 2528 at the ORNL site, is a 20-atm fluidized-bed test unit with a diameter of 10 cm and a fluidized-bed depth of 254 cm. This facility is designed to operate at temperatures up to 650°C and pressures up to 2170 kPa. Solids can be fed to the unit from a pressurized feed hopper using metered pneumatic transport, and solids overflow from the bed to a pressurized solids receiver. Vessel off-gas passes through a water scrubber, a cold trap, and is filtered before being vented. The system is thoroughly equipped with temperature, pressure, and gas flow controls. An on-site PDP-11/40 is available for data acquisition and manipulation. Off-gas composition is continuously monitored with a Bendix process gas chromatograph. (ORNL/TM-6693)



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