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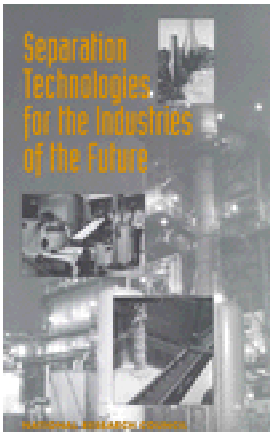

Separation Technologies for the Industries of the Future

Panel on Separation Technology for Industrial Reuse and Recycling, Committee on Industrial Technology Assessments, Commission on Engineering and Technical Systems, National Research Council

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THE NATIONAL ACADEMIES
Advisers to the Nation on Science, Engineering, and Medicine

Separation Technologies for the Industries of the Future

Panel on Separation Technology for Industrial Reuse and Recycling
Committee on Industrial Technology Assessments
National Materials Advisory Board
Commission on Engineering and Technical Systems
National Research Council

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This report has been reviewed by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the NRC' s Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the authors and the NRC in making the published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The content of the review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their participation in the review of this report: Mari Chesser, Weyerhauser; Edward Dowling, Cleveland Cliffs, Inc.; Merton Flemings, Massachusetts Institute of Technology; C. Judson King, University of California;

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PREFACE

The seven industries discussed in this report have widely divergent interests, concerns, and priorities. During the course of this project, the panel discovered how broadly and narrowly "separation" can be defined and had to grapple with the task of focusing the definition in a way that would be useful to our sponsors. In the process, we all learned a great deal about the various industries and changed our definitions of separation technology.

I wish to thank the members of the panel for their hard work and enthusiasm in searching out potential cross-cutting areas of research in separation technology. I hope that readers will find this report to be enlightening and worthwhile. Comments and suggestions can be sent via electronic mail to nmab@nas.edu or via facsimile to the National Materials Advisory Board at (202) 334–3718.

GEORGE E. KELLER II, CHAIR
PANEL ON SEPARATIONS TECHNOLOGY FOR
INDUSTRIAL RECYCLING AND REUSE

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EXECUTIVE SUMMARY

Separation processes, or processes that use physical, chemical, or electrical forces to isolate or concentrate selected constituents of a mixture, are essential to the chemical, petroleum refining, and materials processing industries. In addition to the important process roles separation technologies play in each of these industries, separation technologies present opportunities for reducing waste and using energy and raw materials more efficiently. New developments in separation technologies are, therefore, critical for the productivity and global competitiveness of U.S. industries.

Since 1993, the U.S. Department of Energy's Office of Industrial Technology (OIT) has managed its research program according to a "market pull" strategy, in other words, basing its project selection on industry-identified technology needs and priorities. The purpose of this strategy is to increase and document the commercial impact of OIT's programs. To determine industry's needs and priorities, OIT has developed partnerships with a number of energy-intensive and waste-intensive industries, called the "Industries of the Future" (IOF).

Several IOF industries identified separation technologies as an important area for research. The National Research Council Panel on Separation Technology for Industrial Recycling and Reuse was established to identify the most important needs for separation processes in the IOF; to identify separation technologies that can meet these needs, especially technologies that are applicable to two or more IOF industries; and to suggest criteria for identifying and coordinating research and development in separation technologies.

KEY NEEDS FOR SEPARATION PROCESSES

The panel included in its analysis the seven IOF industries that were involved in the program at the beginning of this study: chemicals (Chapter 2), petroleum refining

(Chapter 3), aluminum (Chapter 5), steel (Chapter 6), metal casting (Chapter 7), glass (Chapter 8), and forest products (Chapter 9). The separation needs of each of these industries are identified in the appropriate chapters and summarized in Chapters 4 and 10. Although a number of separation issues that affect more than one IOF industry were identified, the panel concluded that the needs of these industries are highly diverse and warrant individual treatment. In fact, the panel found that many important separation problems were unique to one industry.

CROSS-CUTTING RESEARCH OPPORTUNITIES

Although separation technologies are essential to all seven IOF industries, only a few represent opportunities for cross-cutting research, i.e., research likely to benefit the majority of them. Because of the diversity of raw materials, product forms, and processing conditions in these industries, most research opportunities are industry-specific. The panel, therefore, does not believe that OIT's program would be significantly more efficient if a single cross-cutting research program in separation technology were established.

Nevertheless, relatively well developed separation technologies in one industry might be transferable to another industry. In addition, a few technology areas are relevant to more than one, in some cases all, of the IOF industries. The panel, therefore, recommends that the technical program managers at OIT coordinate separation research among the IOF industries, and monitor and disseminate the results. The panel identified five opportunities for coordinated programs: separation processes for the chemical and petroleum refining industries; bulk sorting technologies for the materials processing industries (especially aluminum, steel, metal casting, glass, and the polymer-recycling sector of the chemical industry); separation technologies for dilute gaseous and aqueous waste streams; drying and dewatering technologies; and lower cost oxygen production processes.

Separation Processes for the Chemical and Petroleum Refining Industries

A number of issues are common to the chemical and petroleum refining industries. In addition to general improvements in process efficiency, the panel identified two separation technology areas with the potential to meet a number of needs in these industries:

- **separation methods using multiple driving forces,** including processes in which a naturally occurring driving force for a specific operation is enhanced by an intervention that changes the system thermodynamics or in which two or more separation techniques are combined (e.g., membrane

- separation and distillation; affinity-based adsorbent separation; and electrically aided separation)
- **separation associated with chemical reaction,** in other words, methods that combine reaction and separation in one process step (e.g., reactive metal complex sorbents and chemically facilitated transport membranes; combined chemical synthesis and separation processes; membrane reactors; and electrochemical methods of separation)

Bulk Sorting Technologies for the Materials Processing Industries

A number of the materials processing industries (aluminum, steel, metal casting, glass, and the polymer-recycling sector of the chemical industry) identified separation needs that can be classified as materials handling and sorting, specifically, the high-speed separation of scrap. Research and development in this area should focus on bring down the cost of these processes. Improved high-speed sorting technologies, such as air jet and conveyer belt technology systems, would facilitate this. Research and development should include:

- **on-line sensors for high-speed analysis** of the composition of streams and the makeup of individual objects in these streams
- **physical separation techniques,** including gravity separation (e.g., air jet and flowing film separation), froth flotation, magnetic separation, and electrical separation (e.g., electrostatic separation and tribo-electrification)
- **high-speed sorting technologies,** including the fundamental mechanics of high-speed conveying, techniques to position individual scrap pieces in sequential arrays before analysis, and methods for physically diverting analyzed pieces by material type

Dilute Gaseous and Aqueous Streams

All of the IOF industries identified the separation of components from dilute gaseous streams, dilute aqueous streams, or both as important needs for their industries. Potential areas for cross-cutting research include:

- **methods of separating components from dilute gaseous streams,** such as adsorption, high-selectivity membranes, inorganic membranes, and advanced-particle-capture technologies for the removal of micron-sized particles
- **methods of separating components from dilute aqueous streams,** such as reactive metal complex sorbents, reducing agents, air oxidation combined with absorption, membranes, steam and air stripping, electrically facilitated

separation, destructive-oxidation techniques, electrodialysis, ion exchange, and crystallization

Drying and Dewatering Technologies

Several industries identified needs that could be met by improvements in drying and dewatering technologies. Examples include: the removal of solvents from polymers (devolatilization) in the chemical industry; the removal of entrained water from crude oil and the drying of natural gas in the petroleum refining industry; the drying of ceramic casting materials and reclamation sand in the metal casting industry; the drying of paper in the forest products industry; and the drying of sludges from waste gas scrubbing and wastewater treatment.

Lower Cost Oxygen Production

The chemical, petroleum refining, aluminum, steel, and glass industries have stated that lower cost oxygen would be beneficial to them in combustion and other processes. The advantages of oxygen over air as a fuel or reactant are greater thermal efficiency; lower production rate of nitrogen oxides; lower volume, which can make the recovery of products or contaminants easier; and, in some cases, higher chemical efficiencies. Oxy-fuel is more energy efficient because there is no need to heat the nitrogen component of air. Currently, the relatively high cost of oxygen is a significant barrier to its widespread use in several emerging technologies.

RESEARCH OPPORTUNITIES FOR ENABLING TECHNOLOGIES

The panel identified five enabling technologies that, although they are not separation processes, would promote improvements in industrial separation. Research areas include new membrane materials, sorbent materials for specific applications, on-line diagnostics and sensors, an improved understanding of thermodynamics, and particle characterization. The panel recommends that OIT focus its long-term, fundamental research in these areas.

RECOMMENDED CRITERIA

Based on the research opportunities identified by the panel for each industry and the maturity of separation technologies, the panel identified four general criteria for selecting research and development projects:

- **Time Scale.** Research in this area should focus on high-impact technologies that have been demonstrated in the laboratory and will be ready for commercial application in five to seven years.
- **Cross-cutting Criteria.** OIT should only support cross-cutting research in separation technologies that are either (1) embryonic technologies that could lead to major advances in several industries or (2) improvements in mature, high-use technologies where incremental improvements could have a substantial effect.
- **Impact on Existing Processes and Equipment.** Proposed projects should be evaluated for the potential economic impact of a new separation method and for the potential effect of that new method on existing processes and equipment. OIT should consider funding the development of fundamental data when knowledge of such data can produce substantial improvements in existing separation processes.
- **New Technologies.** Projects for the development of new separation technologies should be multidisciplinary and should be potentially scaleable to production volume, both in technical and economic terms.

1

Introduction

INDUSTRIAL SEPARATION PROCESSES

Separation processes are essential to the chemical, petroleum refining, and materials processing industries. The word "separation," however, refers to different processes and functions for different industries. Separation processes comprise a large portion of the activity in the chemical and petrochemical industries. In the forest products industry, separation ranges from separating wood chips of different sizes to converting black liquor for reuse. In the aluminum and steel industries, as well as the metal casting and glass industries, the most important area of separation technology is separation of different types of scrap, sand, and cullet. Finding common ground among these definitions of separation processes or technologies is a difficult task. For the purposes of this report, however, separation processes are defined as processes using physical, chemical, or electrical forces to isolate selected constituents from a mixture.

Separation processes can be thought of in general terms as performing similar functions in all industries. Figure 1-1 is a schematic illustration of these functions and their relationships. The materials streams may be composed of homogeneous solids, liquids, gases, or supercritical fluids, or they may be composed of heterogeneous mixtures containing any combination of these phases. The functions of separation processes include the removal of impurities from raw materials, products, and by-products; the separation of recycle streams; and the removal of contaminants from air and water waste streams.

For the chemical, petroleum refining, and materials processing industries as a group, separation technologies are critical for reducing waste, improving energy efficiency, and increasing the efficiency of raw material use. For example, separation technologies have the potential to reduce waste and increase productivity by separating valuable materials that can be used or sold as by-products from waste streams. As environmental regulations become increasingly stringent, the costs associated with waste management are expected to rise. By reducing these costs, separation technologies can contribute to the competitiveness of U.S. industries. Similar examples can be given for energy efficiency and raw materials efficiency. Research that increases the fundamental knowledge necessary to improve existing separation processes and develop new ones can, therefore, have a large impact on these industries. Separation technologies are critical for the productivity and global competitiveness of U.S. industries.

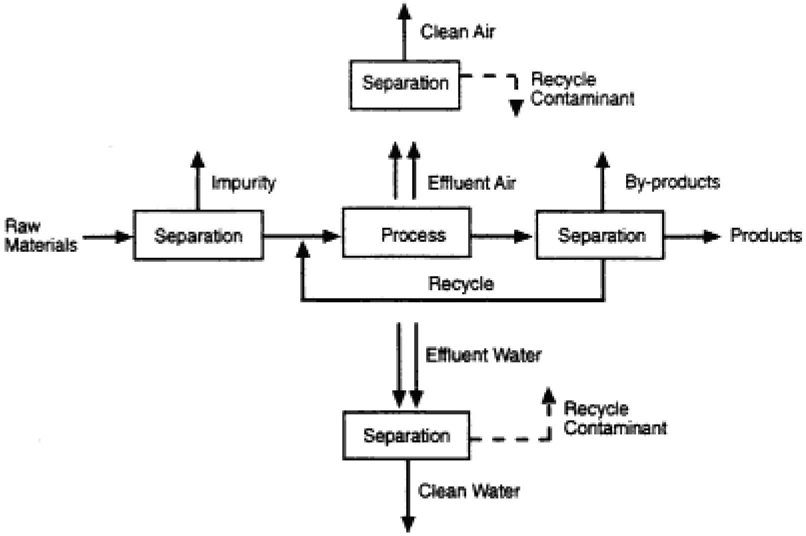

Figure 1-1
Separation in manufacturing processes. Adapted from Humphrey and Keller, 1997.

OFFICE OF INDUSTRIAL TECHNOLOGY RESEARCH PROGRAM

The Office of Industrial Technology (OIT) of the U.S. Department of Energy (DOE) sponsors research and development programs focused on the U.S. materials processing industries. The goals of OIT programs are to develop technologies that have the potential for reducing raw materials and energy use, reducing waste generation, and increasing the productivity and global competitiveness of these industries.

OIT selects research projects based on the needs and priorities identified by the materials processing industries. OIT has developed partnerships with a number of energy-intensive and waste-intensive industries to determine their needs and priorities. Groups representing these industries, composed of chief executive officers, trade associations, and others, have agreed to develop documents describing their common vision of the future of the industry and identifying their highest priority needs, strategic goals, and research areas. To date, eight materials processing industries have produced vision documents in partnership with OIT. These are the agriculture, aluminum, chemical, forest products, glass, metal casting, mining, and steel industries. One additional industry, petroleum refining, is in the process of developing a vision document. OIT has dubbed these industries the "Industries of the Future" (IOF).

Of the eight industries that have developed vision documents, six have completed "road maps" describing how their industries will achieve their visionary goals. Based on these documents, industry groups have developed research agendas, devised implementation strategies, and committed resources to conduct and manage research projects. Table 1-1 shows the status of the vision documents and road maps for the IOF.

OIT's selection of research projects is based on a competitive process that includes a request for proposals and proposal reviews. The costs of selected projects are shared by OIT and the industrial participants, with the industry portion of the funding increasing over the course of the project.

TABLE 1-1 Status of Vision Documents and Road Maps for the Industries of the Future

Industry Sector	Vision Document (Date Released)	Road Map (Date Released)
Forest Products	November 1994	December 1996
Steel	May 1995	March 1998
Metal Casting	September 1995	January 1998
Glass	January 1996	November 1997
Aluminum	March 1996	May 1997
Chemicals	December 1996	December 1997 Computational Fluid Dynamics (draft) Catalysis (draft)
Agriculture	January 1998	not available
Mining	September 1998	not available
Petroleum Refining	not available	not available

NATIONAL RESEARCH COUNCIL INDUSTRIAL TECHNOLOGY ASSESSMENTS

Prior to 1993, OIT followed a "technology push" strategy, in which research projects were selected and prioritized according to their generic potential for reducing energy consumption and waste generation. In 1993, OIT changed to its current "market pull" strategy, in which the technology needs and priorities identified by the IOF industries are used to determine project selection. In 1995, OIT asked the National Research Council, through the National Materials Advisory Board, to evaluate their research and development program strategy; provide guidance during the transition to the new "market pull" strategy; and assess the effects of the change on OIT's cross-cutting technology programs, i.e., programs that apply to several industries. The National Research Council's Committee on Industrial Technology Assessments (CITA) was established in response to this request.

The CITA was asked to establish and oversee three topical panels on various aspects of the OIT program as part of its overall program review. The three topical panels were the Panel on Intermetallic Alloy Development (National Research Council, 1997), the Panel on Manufacturing Process Controls (National Research Council, 1998), and the Panel on Separation Technology for Industrial Recycling and Reuse. This report presents the work of the third panel.

PANEL ON SEPARATION TECHNOLOGY FOR INDUSTRIAL RECYCLING AND REUSE

Separation technologies play an important role in the chemical, petroleum refining, and materials processing industries. Several of the IOF industries identified separation technologies as important areas for research in their vision documents and road maps. The Panel on Separation Technology for Industrial Recycling and Reuse was established to identify the needs of the IOF industries and to recommend high priority areas for the OIT research program. The panel included the seven IOF industries that were involved in the program at the beginning of this study: chemicals, petroleum refining, aluminum, steel, metal casting, glass, and forest products.

Specifically, the panel was charged with the following tasks:

- to identify key separation process needs in the seven industries and to identify separation technologies that can be applied to meeting these needs
- to review OIT's current and planned research concerned with separation technologies for the materials processing industries
- to identify technology areas that are broadly applicable to two or more of the seven industries

- to suggest criteria for identifying and coordinating research and development in separation technologies

The panel held two working sessions. At the first session on October 9, 1997, the panel met with representatives of industry groups to discuss their needs for separation technologies and to identify potential cross-cutting needs. At the second session on December 2, 1997, the panel met with experts on cutting-edge separation technologies to identify the ones that might meet industry needs. This report is a summary of the panel's findings and recommendations for areas of future research.

ORGANIZATION OF THE REPORT

The report is organized into three parts. Part I is focused on the needs of the chemical (Chapter 2) and petroleum refining (Chapter 3) industries and their cross-cutting issues (Chapter 4). Part II focuses on the needs of the five materials processing industries, aluminum (Chapter 5), steel (Chapter 6), metal casting (Chapter 7), glass (Chapter 8), and forest products (Chapter 9); cross-cutting issues are discussed in Chapter 10. Please note that it is beyond the scope of this study to provide an in-depth or comprehensive analysis of separation processes for each industry. The report is based on information gathered at the two workshops and on the expertise of panel members and the focus is on cross-cutting issues. The basic issues in each industry are provided as background information in support of the panel's conclusions and recommendations on cross-cutting research in Part III (Chapter 11).

I

SEPARATION IN THE CHEMICAL AND PETROLEUM REFINING INDUSTRIES

2

Chemical Industry

The U.S. chemical industry includes producers of industrial gases, large-volume commodity chemicals and polymers, chemical products for agricultural and medicinal uses, and performance-targeted chemical and polymer specialties. The industry produces more than 70,000 products, including raw and basic materials, intermediate materials, and finished products (OIT, 1997a). The industry shipped $375 billion worth of products in 1996, comprising 10 percent of the value-added for the U.S. manufacturing sector and 1.9 percent of the U.S. gross domestic product. The chemical industry is the nation' s largest exporter, with exports totaling $61 billion in 1996. The industry employs more than one million workers (OIT, 1997b).

The chemical industry obtains raw materials from the petroleum refining, natural gas, and mining industries, as well as from biological sources. In 1994, the chemical industry consumed 5.8 quadrillion Btus, or 7 percent, of the total energy consumed in the United States. Air emissions for that year included 4.3 million metric tons of sulfur dioxide (SO_2), nitrogen oxides (NO_x), volatile organic compounds (VOCs), carbon monoxide (CO), and particulates.

TRADITIONAL CHEMICAL ENGINEERING SEPARATION PROCESSES

Chemical products are made by a combination of processes that include synthesis, separation, and purification. The traditional chemical engineering methods of separation and purification include distillation, crystallization, adsorption, membrane processes, absorption and stripping, and extraction. These technologies are briefly described below.

Distillation

Distillation and its companion processes, azeotropic and extractive distillation, are by far the most widely used separation processes for mixtures that can be vaporized. Distillation is a process for isolating components from a mixture based on differences in boiling points. Vapors are generated from liquids or solids by heating and are then condensed into liquid products. In azeotropic distillation, a compound is added to form an azeotrope with at least one of the components of the mixture. That component can then be more readily separated from the mixture because of the increased difference between the volatilities of the components. Extractive distillation combines continuous fractional distillation with absorption. A relatively high-boiling solvent is used to selectively scrub one or more of the components from a mixture of components with similar vapor pressures. Distillation processes are widely used for the separation of organic chemicals and for the separation of gases, usually at cryogenic temperatures, as in the production of oxygen and nitrogen from air.

Crystallization

Crystallization is one of the oldest unit operations in the portfolio of separation techniques used for industrial and laboratory processes. Crystallization is used to achieve several functions: separation, purification, concentration, solidification, and the production of a crystal that can be used to determine molecular structure. Because the heat of crystallization is typically much lower than the heat of vaporization, considerable energy savings can be realized in applications where crystallization is an effective means of separation.

Solutes can be recovered from solutions by reducing the solubility through cooling, heating, evaporation, chemical reaction, or by adding a nonsolvent to the mixture. Alternatively, separation of a chemical species from a mixture of similar compounds may be achieved by melt crystallization. In such operations, the mixture is cooled and the species allowed to solidify differentially according to their melting points. Melt crystallization is an important means of separating *para*-xylene from *ortho*-and *meta*-xylene. An example of the purification of a chemical species is the manufacture of L-isoleucine, in which the material crystallized from a fermentation broth that has been filtered and subjected to ion exchange may contain undesirable impurities. The crystals are then redissolved and recrystallized to enhance purity. Concentration of a solution can be accomplished by crystallization of the solvent. For example, fruit juice is concentrated via the crystallization of ice.

Product requirements are the criteria for determining the success of the crystallization process. These requirements are based on how the product will be used and the processing steps between crystallization and the recovery of the final product. Key determinants of product quality are size distribution (including mean and spread), morphology (including habit and polymorphic form), and purity. Crystal size distributions determine several important processing and product properties, including appearance, the separation of crystals from liquor, reactions, dissolution, and other processes and properties involving surface area, transportation, and storage.

Adsorption

Adsorption is a method of fractionating mixtures using microporous solids (adsorbents) that have strong affinities for one or more of the components in the mixture (adsorbates). The adsorbates held by the adsorbent solid are subsequently desorbed and the adsorbent freed for further adsorption. The process is necessarily cyclic, alternating between adsorption and desorption. Desorption involves weakening the bonds between the adsorbates and the adsorbent or reducing the driving force for adsorption. Desorption can be accomplished by increasing the temperature, reducing the pressure, adding another component that competitively adsorbs with the adsorbate, or a combination of these strategies.

Membrane Processes

Separation processes involving membranes require two bulk phases that are physically separated by a third phase, the membrane. In all membrane processes, the feed is separated into two phases: the permeate (the materials that go through the membrane) and the retentate (the portion of the feed retained by the membrane). The transport of materials between the permeate and retentate phases is controlled by the membrane and the operating conditions. One or more of the species in the feed mixture are allowed to pass through the membrane in preference to others, that is to say, the membrane is selective for these species. The permeate phase is enriched in these species as the retentate phase is depleted of them.

Most commercial membranes consist of thin, selective, active layers or skins (about 0.1 to 5μm) on porous support layers that provide mechanical strength. The active and support layers can be formed in a single operation from a given polymeric material. In the case of composite membranes, the active layer can be a coating on the support layer. The transport of any species across the membrane relies on one or more forces, such as those created by a gradient in chemical potential or electrical potential. Membrane processes typically do not involve a phase change and therefore do not involve a specific heat of vaporization (like distillation) or a specific heat of crystallization (like crystallization). Because there is no phase change, highly selective membranes can, in a number of circumstances, accomplish separations with considerably less energy than other methods.

In addition to gas separation, a number of membrane separation processes are used. Dialysis is the transfer of solute molecules across a membrane by diffusion from a concentrated solution to a dilute solution. In the electrodialysis process (e.g., the concentration of brine) a typical electrodialysis stack consists of a series of anion-exchange and cation-exchange membranes arranged in an alternating pattern between an anode and a cathode to form individual cells. A reverse osmosis membrane separates the various low-molecular-weight molecules and ions from the solvent by forcing the solvent or major component to pass selectively through the membrane by applying pressure greater than the normal osmotic pressure. Separation occurs based on the size, solubility, and/or charge of the various species. Ultrafiltration is another pressure-driven membrane process capable of separating somewhat larger solution components on the basis of molecular size and shape. Under an applied pressure difference across the membrane, the smaller molecules pass through the membrane and are collected as permeate while the larger molecules are retained by the membrane. The microfiltration process is similar to the ultrafiltration process, except its effective separation range is from 1,000 Å to 100,000 Å in molecular size whereas the ultrafiltration range is from 10 Å to 1,000 Å.

Absorption and Stripping

Absorption refers to the transfer of one or more components of a gas phase to a liquid phase in which the gas phase is soluble. Stripping is exactly the reverse, the transfer of a component from a liquid phase in which it is dissolved to a gas phase. There are three types of absorption processes: separation based on physical solution; separation based on reversible chemical reaction; and separation based on irreversible chemical reaction. Absorption processes require the generation of extensive areas of liquid surfaces in contact with gas phases.

Extraction

Liquid-liquid extraction is a separation technique involving two immiscible liquid phases. During liquid-liquid extraction, one of the two phases, the solvent phase, extracts the solutes from the other liquid phase. Solvent recovery and raffinate cleanup follow the separation. There is usually more than one possible method of purifying the solvent and raffinate phases, so process design is important. Solvent selection is based on liquid-liquid interfacial tension.

SEPARATION NEEDS

In the chemical industry, many separation technologies are already highly developed and more than one technology option is available for most processes. However, these separation technologies could be improved in terms of energy efficiency, raw materials use, or cost effectiveness. In addition, changing technologies and changing customer demands continually create new needs for the chemical industry. Opportunities for improving separation technologies for the chemical industry are identified and discussed later in this chapter.

Production of Industrial Gases

The chemical industry would benefit from more efficient and cost-effective separation methods for producing oxygen from air. Although oxygen is relatively inexpensive compared to typical organic compounds, current production methods are too expensive for it to be used in a number of production and combustion processes. Examples include hydrocarbon oxidation processes to produce materials like ethylene oxide, acrylic acid, and other oxygenated products. Inexpensive oxygen would benefit the chemical industry by providing a much-sought-after feedstock, especially in the production of synthetic fuels via the reforming of natural gas. Less expensive oxygen could also be used in a number of applications in other industries where, currenfiy, it is not always cost-effective. For example, oxygen could improve chemical and biological oxidative processes used for industrial production and waste remediation by increasing chemical efficiency, making recovery easier, and reducing investment. Finally, the use of oxygen would decrease energy use in combustion processes by eliminating the need to heat the nitrogen in air.

Nitrogen and the noble gases argon, krypton, and xenon are also produced by the separation of air (the noble gas helium is most often removed from natural gas). Nitrogen is used to produce inert atmospheres for industrial processes and storage facilities. A more efficient method for separation of air would also improve nitrogen production. Argon, krypton, and xenon are typically distilled from the residues in the fractionation of air, but more efficient methods of recovering these gases would be beneficial to the industry. A number of promising technologies under development could produce industrial gases, such as oxygen, nitrogen, and these noble gases, more efficiently and at lower cost.

Reactive Metal Complex Sorbents

Reactive metal complex sorbents may provide a means for producing oxygen more efficiently and at lower cost (see Chapter 4). A great deal of work has been done on the use of coordination complexes of cobalt (II), which reversibly bind oxygen for the separation of air (Ramprasad et al., 1995). Although this technology has been well demonstrated in a laboratory environment over relatively short periods of time, the economical production of oxygen by such means at the industrial scale has not yet been realized.

Polymer Membranes

Current commercial polymer membranes, mainly polysulfone, polyimide, ethylcellulose, and polycarbonate, can produce nitrogen-rich air with 95 to 99 percent, or more, nitrogen. However, the oxygen-rich air has only 45 to 50 percent oxygen. Membranes with higher selectivity and flux could decrease compression costs and membrane module size. Recently, an improved membrane based on polyaramide and polyimide has been developed with an O_2/N_2 selectivity of about seven (Koros and Walker, 1993).

Sorbents

Methods that utilize specific sorbents to recover noble gases efficiently would benefit the chemical industry. For example, argon might be recovered from O_2/Ar mixtures by using a sorbent to remove the oxygen. In addition, it may be possible to develop physical sorbents selective for shape or other characteristics for the recovery of krypton or xenon from liquid air fractions. Existing sorbents can be either reversible or irreversible and may provide avenues for the removal of trace contaminants in process streams. Specific sorbents could be used to remove contaminants from noble gases and to purify nitrogen for use as a production gas.

Production of High Purity Gases

With changing technologies, the demands for high-purity and ultra-high purity gases have increased. For instance, the progressive miniaturization of semiconductor devices has resulted in more stringent requirements in contaminant-free manufacturing, which in turn has increased the demand for ultra-high purity gases (see Table 2-1). The chemical industry needs more economical separation technologies for producing gases in ultra high-purity form, particularly oxygen, nitrogen, hydrogen, and argon. Demands for specific gas mixtures for use as analytical standards have also increased. One of the major challenges in this case is to maintain the composition of the prepared mixtures.

Dense Perovskite-Type Oxide Membranes

Inorganic polymer membranes, such as dense perovskite-type oxide membranes, may be developed to produce high-purity oxygen. This would require stable, thin (less than 2,000 Å) membranes with high oxygen productivity that can be operated at 800°C with common metallurgical hardware. The bismuth-based system with high oxygen ion conductivity and the thin-film coatings of $Bi_4V_2O_{11}$

on a porous ceramic substrate by the sol-gel technique are of particular interest (Pell et al., 1995).

TABLE 2-1 Projected Sizes of Semiconductor Devices and Gas Purity Requirements for Contaminant-Free Manufacturing

Year	1997	1999	2001	2003	2006	2009	2012
Device size (nm)	250	180	150	130	100	70	50
Bulk ambient gases Key impurity levels (ppt)	100–1,000	100–1,000	<100	<100	<100	<100	<100
Particles ≥ critical size (per liter)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Specialty gases POU particles ≥ critical size (per liter)	2	2	2	2	2	2	2

Source: Adapted from Semiconductor Industry Association, 1997.

Inorganic Membranes

Thin, nanostructured, dense metal and metal oxide membranes might be developed for the separation of gases, for example, high purity hydrogen, oxygen, and nitrogen. Indications are that membranes have been developed at Oak Ridge National Laboratories, but the work remains classified, and these membranes are, therefore, not available for commercial testing and exploration. Although highly H_2-selective palladium metal membranes are well known, problems, such as short lifetimes and poisoning by S, CO, and other substances, must be overcome. Future work in this area should be directed toward the development of molecular templale-directed synthesis of a nanostructured zeolite or inorganic material (Tanev and Pinnavaia, 1996; Yang et al, 1996) and the development of an economically feasible method of synthesizing a carbon molecular sieve with a uniform small pore size (Ioannides and Gavales, 1993; Trocha and Koros, 1994) for hydrogen or O_2/N_2 separation.

Polymer-Inorganic Hybrid Membranes

It may eventually be possible to produce high purity gases using high-selectivity polymer-inorganic hybrid membranes, such as polymer-zeolite membranes. The inorganic segment of the membrane could be used either to increase selectivity or to control membrane swelling (Ho and Ying, 1997). Other materials, like ceramics or silica, could be used. Future research should focus on tunable synthesis and the fabrication of low-cost membrane modules.

Removal of Acid Gases

The chemical industry would benefit from improved methods of separating out and removing unwanted acid gases, principally CO_2, H_2S, COS, and SO_2, from process streams. In the manufacture of ammonia and hydrogen, for example, carbon dioxide must be separated from mixtures with hydrogen, carbon monoxide, nitrogen, and steam. In some process streams, acid gases are present in large quantities as by-products that must be removed. In others, only low contaminant levels must be removed. Although many processes for carbon dioxide recovery are already in use, interest in the recovery of carbon dioxide has increased recently and the field is still open to innovation.

Polyimides, polyaramides, and polypyrrolones are among the polymers that are emerging or already in use (Baker et al., 1990; Zolandz and Fleming, 1992; Costello et al., 1994) and that could be used for the separation of acid gases from natural gas. Membranes made with polyvinylbenzyltrimethylammonium fluoride and polydiallyldimethylammonium fluoride have, uniquely, a high CO_2/H_2 selectivity (about 40 to 100) but low CO_2 fluxes due to thick active layers (Laciak, 1994; Quinn et al., 1995). Thinner membranes appear to lose this selectivity. In general, more novel methods will have to be developed to produce very thin membranes for a high flux of the permeating acid gases.

Distillation Technologies

In spite of the high energy required for distillation, this process is often chosen over other separation processes because of the relatively low initial capital investment required and because it can yield high purity products. Reducing energy costs for this separation process would yield great benefits. Other areas for research are the separation of substances with similar boiling points, separation processes where constant boiling azeotropes are formed (e.g., the separation of water from ethanol), and the concentration of mineral acids (e.g., HCI and HNO3) beyond their constant boiling mixtures. The separation of close boiling liquids will require new and improved methods of distillation.

Heat Cascading

One method of reducing energy consumption in distillation is to use the energy released in the condenser of one column as energy for the reboiler in another column, so-called "heat cascading." This process requires that the temperatures be adjustable (by manipulation of column pressures) so that the condenser temperature of one column is higher than the reboiler temperature of the other. One example of this approach is a seven-column commercial ethanol-refining distillation method in which steam is fed to just one reboiler, and the remaining column reboilers are fueled by condensers from the other columns (Humphrey and Keller, 1997). A second, more common, example is the double column used in air separation.

Vapor Compression

Distillation technologies based on vapor compression could be designed for more efficient use of energy. The high investment needed for the compressor will, however, limit the use of this technology to processes where energy costs are very high (e.g., cryogenic separation).

Coupled Chemical Synthesis and Distillation

Separation efficiencies could be improved by coupling distillation with chemical synthesis. One such combination is catalytic distillation where a solid catalyzed reaction and the distillation of its reactants and products occur simultaneously within a distillation column (Podrebarac et al., 1997). This method is used industrially in the synthesis of the fuel additive, MTBE, by the acid catalyzed reaction of methanol and isobutylene. The economic advantages of performing two unit operations in a single piece of equipment are obvious. In addition, the combination of separation and reaction, which allows the simultaneous selective removal of products, can lead to higher conversions in equilibrium-controlled reactions. This process has some limitations, however, such as the requirement that the reaction proceed in the liquid phase because the catalyst particles must remain wetted. Another way to facilitate the separation of a mixture in distillation would be to add a homogeneous selectively reactive component. This technique is referred to as reactive distillation (Terrill et al., 1985).

Membrane Separation and Distillation

Humphrey et al. (1991) have examined the possibilities of combining membrane separation and distillation. Although most membrane processes cannot produce high-purity products, it may be possible to take advantage of the energy efficiency associated with them to perform part of the separation. In one study, simulations were performed to identify systems with a high probability of using one-third less energy than current distillation operations. Table 2-2 shows the results of that study, which did not identify the specific types of membranes or process conditions that could be used to achieve the energy savings. Clearly, research on this and similar topics has the potential to yield significant benefits.

TABLE 2-2 Candidates for Energy Savings of 33 Percent through Hybrid Technologies Involving Membranes and Distillation

System	Potential Savings (10^{12} Btu)
Propane/propylene	13
Natural gas dehydration	12
Deasphalting of oil	10
Ethane/ethylene	6
Sour-water stripping	6
Inorganic acid dehydration	5
Acetic acid dehydration	3
Ammonia manufacture	2
MTBE manufacture	2
Urea manufacture	2

Drying Technologies

Drying, the removal of a solvent (such as water) from an existing solid body, is one of the most widely used separation techniques in the production of large-volume and specialty chemicals. For example, drying is used in the devolatilization of polymers, where unreacted monomers and solvents are removed. Drying is also used in the production of pharmaceuticals and bioproducts in powder form. Currently, drying processes are highly energy intensive. In fact, they are second only to distillation in terms of energy usage. Large capital investments are required for the equipment. Increased drying rates could lower equipment costs and, in some cases, increase energy efficiency. More energy-efficient drying processes would greatly benefit the chemical industry.

Production of Chiral Compounds

The chemical industry needs new separation technologies for the production of single-isomer chiral compounds. Chiral compounds are molecules that are mirror images of each other, or enantiomers. Some single-isomer chiral compounds are produced by selective chiral synthesis. However, the chemical synthesis of compounds that can form enantiomers usually leads to the production of racetalc, or 1:1, mixtures of the enantiomers. In these cases, specific enantiomers must be obtained by separation of the racemic mixtures.

Although enantiomers have identical chemical properties towards nonchiral substrates, their biological activities are usually very different from each other. Both single-isomer chiral compounds and racemic mixtures are increasingly in demand for pharmaceutical, agrochemical, and biotechnology applications. Drugs produced as single-isomer chiral compounds include antibiotics, anticancer agents, and analgesics (Chemical and Engineering News, 1997). An area for research is the separation of the single optical isomer from drugs that are currently marketed as racemic mixtures, for example, (S)-(+)-ibuprofen, the active single isomer of the familiar analgesic. Potential separation processes for chiral compounds include high-performance liquid chromatography, crystallization, and selective chiral permeation through membranes.

High-Performance Liquid Chromatography

High-performance liquid chromatography with chiral stationary phases is used on both an analytical and preparative scale to separate racemic mixtures of chiral compounds. A relatively recent innovation is the use of high-performance liquid chromatography columns consisting of resins that have been "imprinted" (much like fossilized leaves) with chiral molecules to make them selective toward the adsorption of those compounds. This technology could be further developed, as could other innovative, lower cost methods of optical isomer resolution, such as facilitated transport membranes that use chiral carrier molecules.

Crystallization

One technique for separating racemic mixtures of enantiomers is enantioselective crystallization of conglomerates or compounds that form mixtures of crystals of individual enantiomers. All other separation techniques for racemic mixtures rely on the interaction of the chiral component or its synthesis intermediate with another chiral substance. Thus, racemic mixtures may be resolved by reaction with a chiral reagent to form diastereoisomers, which are, in principle, separable by crystallization or other separation techniques.

Separation of Components from Dilute Streams

The chemical industry would benefit from better technologies for the separation of components from dilute product or waste streams. In some cases, the objective is the recovery of valuable components. In other cases, the objective is the removal of contaminants from an otherwise useful orrecyclable stream or from a stream that will enter the environment. The industry needs highly specified methods that can operate on minor components.

The commodity chemical and specialty chemical industries produce dilute effluent streams containing waste products that must be separated either for recovery and recycling or for destruction. Problems involving the separation of low concentration components, such as metal salts, inorganic compounds, and particulate matter, from aqueous streams are common. For example, the chemical commodity industry produces effluent streams containing low levels of valuable metal ions, such as copper, silver, mercury, gold, palladium, and platinum. Ideally, the effluent stream would be detoxified and the metals recovered simultaneously.

The chemical industry also needs better separation technologies to remove VOCs and nonvolatile organic compounds from effluent streams. The current method for the removal of VOCs involves purging the aqueous stream with air followed by the adsorption of the organic vapor in a carbon bed. The removal of nonvolatile organic compounds is often accomplished by biotreatment or by adsorption of the organics in carbon beds, followed by the regeneration of the carbon where practical.

Finally, the use of living organisms to synthesize chemical products (e.g., fermentation) is likely to increase. Biological processes often produce aqueous solutions with less than 10 percent of the desired substance. The recovery and purification of this substance presents unique challenges made more difficult by the potential fragility of the substance. Increasing the concentration of the solution could destroy the organisms that generate the products. In order for the bioprocessing sector of the chemical industry to grow, it needs separation technologies that enable the recovery of valuable compounds that differ only slightly in molecular structure from the other components in a dilute solution.

Promising research for the separation, removal, or recovery of components from dilute streams includes: reactive metal complex sorbents; gas separation membranes; the use of selective reducing/oxidizing agents; electrically aided membrane separation, such as electrodialysis; continuous adsorption processes; air oxidation combined with absorption; and the use of selective adsorbents to remove the products from bioprocessing streams.

Reactive Metal Complex Sorbents

Reactive metal complex sorbents may offer a means of separating out components of dilute effluent streams, such as recovering metals from dilute solutions by extraction with a liquid that contains a metal-ion specific ligand. Once the metal is recovered as the metal-ligand complex, it can be processed further (see Chapter 4).

Gas Separation Membranes

The removal of VOCs from air or industrial process gases is an emerging application for gas separation membranes. Current silicone rubber type membranes are sometimes only marginally permselective for VOCs. Thus, new membranes with higher selectivity, possibly achieved through the control of swelling, would lower costs and increase applications.

Reducing Agents

It may be possible to detoxify effluent streams containing low levels of valuable metal ions by reduction with a low-cost reducing agent, such as H_2. The metals could be recovered simultaneously.

Electrically Aided Membrane Separation

Materials might be recovered from dilute streams by electrically aided membrane processes. If the pressure driving force and electric fields are additive, the transport of a species across a membrane could be selectively enhanced or retarded. A combined-effect membrane could be constructed with sufficient strength to withstand a significant pressure field and with ionic transport capability (see Chapter 4).

Continuous Adsorption Processes

The vast majority of adsorption processes involve fixed beds of granular adsorbents that pass periodically through adsorption and desorption cycles. With the advent of polymer-based sorbents, combinations of moving and fluidized beds, in which the sorbent moves between sorbing and desorbing zones, have been developed. Thus, much of the process complexity associated with cycling fixed beds has been eliminated, but the physical stability requirements for the sorbent are now greater. The development of large, ceramic, monolithic adsorbent wheels has resulted in a new "moving sorbent" concept for recovering and concentrating small amounts of organic contaminants in gas streams. The wheel rotates at a rate of a few revolutions per hour, subjecting each part of the wheel alternately to adsorbing and desorbing conditions. Units have now been commercialized that can process several million cubic feet of gas per hour. This technology also eliminates much of the complexity associated with fixed-bed, cyclic operation.

Air Oxidation Combined with Absorption

A useful technology for the separation of constituents from dilute gas streams would be a combination of absorption and air oxidation of the collected organic contaminant. One technique is wet air oxidation, in which the whole liquid stream is heated in the presence of air or oxygen and the contained organic is incinerated. Problems to be overcome include the high energy cost and fouling of the reactors with inorganic residues. The former limitation could be mitigated by catalytic systems that enable wet air oxidation to take place at lower temperatures and pressures. Membrane pervaporation is an emerging technology for the isolation and recovery of VOCs from aqueous streams.

Adsorbent Specificity for Separation of Bioprocessing Streams

Affinity-based separation processes have grown more important in recent years because of their application in biological processes or on biologically produced species. The technique most often uses a chromatographic operation, which makes it possible to remove a specific species from solutions containing a number of other slightly different compounds (see Chapter 4).

Recycling Polymeric Materials

The growing number of consumer products manufactured from commodity organic polymer materials has led to problems in disposing of these materials. Recycling is one option for dealing with waste polymeric materials, such as polyethylene (PE), polypropylene, polyethylene teraphthalate (PET), and nylon. A substantial fraction of consumer polymer materials, such as PET bottles, are already being recycled. Some materials, such as polystyrene foam, are not economically recyclable in small quantities because of their low density. However, if these materials are used in sufficient quantities, the supply source is centralized, and local recycling facilities exist, they can be profitably collected and recycled. Recycling polymer materials (principally nylon) from used carpets is a promising new area that is currently being extensively investigated.

The physical similarities of commodity organic polymer materials poses problems in separating them for recycling and reuse. Mixtures of PE and PET can be separated by density, but problems arise if the polymers contain fillers. The identification and separation of polymer components will require more discerning separation techniques and instrumentation that can identify polymers to enable automatic sorting. The situation is complicated by the existence of a large number of polymer types and the fact that objects made out of polymers have a large variety of sizes and shapes. Further complications arise from the fact that polymers differ from each other not only in chemical composition, but also in more subtle respects, such as molecular weight, branching, order of monomer units in chains, and stereochemistry. These characteristics cannot be easily detected and can seriously affect the quality of the final product.

SUMMARY

Although the chemical industry already uses many highly developed separation technologies, they could be improved in terms of energy efficiency, raw materials use, and cost effectiveness. Areas for research include the following:

- more efficient and cost-effective separation methods for producing oxygen from air
- more efficient methods of recovering nitrogen and noble gases from cryogenic air separation fractions
- more efficient separation technologies for producing gases in high-purity form, particularly nitrogen, hydrogen, and argon
- improved methods of separating out and removing unwanted acid gases, principally CO_2, H_2S, COS, and SO_2, from process streams
- more energy efficient distillation technologies and practices
- more efficient distillation of substances with similar boiling points or when constant boiling azeotropes are formed
- more efficient use of energy in drying techniques for the production oflarge-volume and specialty chemicals
- separation technologies for the production of single-isomer chiral compounds
- technologies for the separation of components from dilute product or waste streams, including metal salts, inorganic compounds, and particulate matter from aqueous streams; valuable metal ions, such as copper, silver, mercury, gold, palladium, and platinum, from effluent streams; and VOCs and involatile organic compounds from effluent streams
- separation technologies for recycling chemically similar commodity organic-polymer materials

3

Petroleum Refining Industry

The U.S. petroleum processing industry refines 97 percent of the nation's transportation fuels and produces raw materials for other industries, such as the chemical industry. The petroleum refining industry has annual shipments worth $136 billion and employs 77,000 workers. This industry is extremely energy intensive, with an annual energy consumption of 6 quadrillion Btus, and produces 180 million tons of waste per year (OIT, 1997c).

SEPARATION NEEDS

The petroleum refining industry uses the same traditional chemical engineering separation technologies as the chemical industry, including distillation, crystallization, adsorption, membrane processes, absorption and stripping, and extraction. Like the chemical industry, the petroleum refining industry would benefit from separation technologies with improved energy efficiency, raw materials efficiency, and cost effectiveness.

Organic/Organic Separation

The petroleum refining industry would benefit from improved technologies for basic organic/organic separations, such as the separation of benzene from gasoline and the separation of aromatics from jet and diesel fuels. New membrane technologies are being developed for organic/organic separations, especially to address the problem of membrane swelling. Copolymers with hard segments for stability and soft segments for selectivity could overcome this limitation. Recently, a new pervaporation technology based on a polyimide/polyester copolymer membrane system was developed for the separation of heavy catalytically cracked naphtha into an aromatics-rich permeate for gasoline blending and an aromatics-lean retentate for distillate (jet and diesel fuel) blending (Ho et al., 1996). Current pervaporation membrane systems will probably be most effective in hybrid pervaporation/distillation processes where pervaporation performs a first, crude, low-energy, low-cost separation, leaving the polishing operation for distillation. Higher selectivity/flux membranes and modules that can withstand aggressive organic mixtures at relatively high temperature pervaporation conditions (about 120°C to 250°C) would be more cost-effective and have more applications. Controlling membrane swelling is critical to improving selectivity. If high selectivity could be achieved with pervaporation, it could replace distillation in many separation processes.

Olefin/Paraffin Separation

Currently, the separation of olefins (ethylene, propylene) from paraffins (ethane, propane) on a commercial scale is accomplished almost exclusively via cryogenic distillation. These two separation processes are very energy intensive and, in 1988, accounted for 6.3 percent (about 0.15 quadrillion Btus) of the total distillation energy used by the chemical and petrochemical industries (Humphrey et al., 1991). A less energy-intensive method for separating olefins from paraffins would therefore be extremely beneficial.

The separation of olefins from paraffins could be accomplished with less energy if selective facilitated transport membranes were used. Facilitated transport membranes with a high olefin/paraffin selectivity of about 200 include cross-linked polyvinylalcohol-containing $AgNO_3$ membranes (Ho and Dalrymple, 1994) and Ag+-exchanged perfluorosulfonic acid membranes (Koval et al., 1992; Davis et al., 1993). Both have the potential to save large mounts of energy from hydrocarbon feeds that do not contain poisonous sulfur compounds. Silver and cuprous complexing agents could also be incorporated into inorganic membranes in ways similar to those described for adsorbents. Olefin-complexing adsorbents, including an Ag+-exchanged polymer resin and a near-monolayer of CuCl dispersed on -Al_2O_3, might also be used to separate olefins from paraffins (Yang et al., 1997). For feeds containing sulfur compounds, a new membrane with a sulfur-resistant complexing agent and high selectivity will have to be developed.

Recently, polyimide membranes showing moderate selectivities of about 20 have been reported (Tanaka et al., 1996). A complete olefin/paraffin separation with membrane processes alone would require membranes with considerably higher selectivities, however, perhaps by an order of magnitude. A propylene/

propane separation of 100 using a carbon molecular sieve membrane has also been cited (Suda and Haraya, 1997), indicating that these membranes have potential for olefin/paraffin separations.

Methane Conversion

The conversion of methane to higher-value products is important for the petroleum refining industry and is essential for the development of remote natural gas reserves. Higher-value products that can be produced from methane include hydrocarbon liquids (methanol), synthetic lubricants and fuels, and olefins (ethylene).

Liquid hydrocarbons can be prepared from the synthesis gas generated from the partial oxidation of methane. Ethylene can be synthesized from the oxidative coupling of methane (Wang and Lin, 1995; Ramachandra et al., 1996; Zeng and Lin, 1997). All of these reactions require high-purity oxygen, however. Therefore, a source of inexpensive, high-purity oxygen would be an enabling separation technology. The alternative, using air, eventually requires a separation (e.g., of nitrogen from the synthesis gas product), which is as difficult as producing high-purity oxygen in the first place.

Inexpensive oxygen for use in the conversion of methane to higher-value products could be produced from air by the use of dense perovskite-type oxide membranes. High-purity oxygen could also be produced via a polymer-inorganic (zeolite) hybrid membrane, a zeolite molecular sieve membrane, or a carbon molecular sieve membrane.

Isomer Separations

Improved isomer separations could significantly reduce the energy consumption required for the manufacture of certain chemical products. One method uses molecular sieve membranes, including zeolite, carbon molecular sieve materials, and the (currently classified) metal and metal oxide membranes being developed at Oak Ridge National Laboratory. The isomer separations that could be achieved by this method include the separation of *p*-xylene from other xylenes and the separation of linear olefins (e.g., 1-butene) and paraffins (e.g., n-octane and n-dodecane) from their corresponding branched olefins (e.g., isobutylene) and paraffins (e.g., 2,2,4-trimethylpentane [iso-octane] and 2,3-dimethyldecane). Molecular sieve membranes could also be used in the membrane reactor configuration for the manufacture of *p*-xylene and linear olefins and paraffins if their corresponding isomerization reactions were enhanced. In this case, a chemical synthesis would be performed in conjunction with a closely coupled, but separate, membrane separation device. For example, *para*-xylene could be selectively produced by an equilibrium redistribution of mixed isomeric xylenes coupled with a selective transport of the product through a membrane (Scouten, 1997).

Separation of Asphaltenes from Petroleum

A lower energy method for separating asphaltenes from petroleum liquid would be useful to the industry and would significantly decrease the energy required for deasphalting with solvents (e.g., propane). The separation of asphaltenes from petroleum liquid could be achieved via high-temperature ultrafiltration. The removal of waxes from petroleum liquid could be accomplished either through ultrafiltration or microfiltration. Microfiltration via a membrane with 300 Å pores could be used to catch catalyst particles in a residual hydrotreater blowdown at about 450°C. In this microfiltration process, colloidal asphaltenses and some metals might also be captured and recycled to the hydrotreater with the catalyst particles. These applications will require the development of thinner nanostructured inorganic membranes (about 2,000, Å or less) to increase flux/productivity and to reduce module size. The industry would also benefit from lower cost fabrication of high-temperature membranes and modules, as well as fouling-resistant membranes and/or effective fouling control techniques, such as compositional doping, hydrodynamics, shear rate, and pressure (Ho and Ying, 1997).

Dehydrogenation of Ethylbenzene and Paraffins

Currently, the dehydrogenation of ethylbenzene to produce styrene and the dehydrogenation of paraffins to produce olefins are highly energy-intensive processes. Less energy-intensive separation methods would be useful for the petroleum refining industry.

Membrane reactors have the potential to significantly reduce the energy required for the dehydrogenation of ethylbenzenes and paraffins. High-temperature H_2-selective membranes could be used as membrane reactors, including palladiumbased, zeolite, ceramic, silica, glass, and carbon molecular sieve membranes. These membranes could be prepared using several techniques: synthesis of thin, nanostructured, dense palladium-based films (Bryden and Ying, 1996; Mardilovich et al., 1996); molecular template-directed synthesis of nanostructured materials; novel procedures to plug large pores or reduce pore size in ceramic and other membranes; and the sol-gel technique using uniform nanosized sol particles (Chu and Anderson, 1996).

Direct Conversion of Hydrogen Sulfide to Hydrogen and Sulfur

Hydrogen sulfide (H_2S) is produced along with methane from many natural gas fields, as well as from the hydrodesulfurization of crude oils containing sulfur compounds (e.g., thiophene, benzothiophene, and dibenzothiophene). Currently, the typical technology is to partially oxidize H_2S and convert it to elemental sulfur

(S) and water in the Claus process, which recovers the elemental sulfur but loses the valuable hydrogen (H_2). It would be advantageous to recover both the H_2 and S through the direct conversion of H_2S to these two products because the demand for H_2 is increasing, and crude oils are getting more sour with higher sulfur content. A method for separating H_2S into H_2 and S with some input of energy would be of great benefit to the petroleum refining industry.

The recovery of both H_2 and S through the direct conversion of H_2S to these two products could be accomplished using a high-temperature, H_2-selective membrane. A high-temperature (about 800°C) membrane reactor containing a molybdenum sulfide catalyst and a H_2-selective membrane could effect the catalytic decomposition of H_2S to H_2 and S (Ma et al., 1994).

Hydrogen Gas Separation

The petroleum industry has a growing need for the separation of hydrogen from other gases. Examples include H_2 recovery from refinery purge gases, such as hydrodesulfurization purge streams or H_2/CH_4 separation; H_2 recovery from ammonia purge gases or H_2/N_2 separation; synthesis gas H_2/CO ratio adjustment or H_2/CO separation; and the recovery of H_2 from gas containing H_2 and H_2S in coal gasification.

New membrane materials are promising technologies for hydrogen separation, including polyimides, polyaramides, and polypyrroldones. Thinner membranes (< 500 Å), which will decrease costs and increase flux/productivity, could reduce overall costs and expand markets. One potential application is the purification of a reformate gas to produce high-purity H_2, which would require a high H_2/CO_2 selectivity membrane. If CO_2 is the minor component in H_2, a membrane with a high CO_2/H_2 selectivity that would allow the retention of H_2 at feed pressure would be desirable. The recovery of H_2 from gas containing H_2 and H_2S in coal gasification will require a high-temperature H_2-selective membrane. This membrane would have the same requirements, e.g., high-temperature stability and high H_2/H_2S selectivity, as the membrane for the direct conversion of H_2S to H_2 and S described above.

Removal of Acid Gases

The petroleum refining industry needs better separation methods for the removal of acid gases from natural gases, such as the removal of CO_2 and H_2S from natural gas containing between 15 and 50 percent acid gases and 50 percent or more CO_2. Potential applications include the recovery of CO_2 from large-scale enhanced oil recovery projects.

The efficient separation of H_2S from petroleum refinery and coal gasification process streams represents a continuing challenge. Amine-based acid gas scrubbers for removing H_2S from petroleum hydrodesulfurization streams are currently used. As noted above, it would be desirable to recover the hydrogen value from the extracted H_2S. In coal gasification, where the removal of H_2S and COS in a continuous process directly from the hot product gases is still a major unresolved technical challenge, considerable economic benefits could be achieved.

For the removal of acid gases from other gases, thinner membranes (< 500 Å) and new membrane materials with high selectivity for CO_2 and H2S separation from CH_4 would reduce costs by increasing productivity and reducing methane loss to the permeate. Potential applications for natural gas containing 50 percent CO_2 (about 400 psi) or more will require a new membrane material with low plasticization by CO_2. This could be achieved via new polymer-inorganic hybrid materials, in which the inorganic would control plasticization and swelling of the highselectivity polymer, or via copolymers. A CO_2/CH_4 selectivity of 80–100, or higher, would be desirable.

Removal of Volatile Organic Compounds from Gases

One important separation need in the petroleum refining industry is the removal of VOCs from various gases. Examples include the removal of gasoline vapor from storage-tank vents in distribution stations (Ohlrogge et al., 1995); the removal of chlorinated and chlorofluorinated hydrocarbons from air; and the removal of solvents from air streams originating from coating and finishing processes and other operations involving the vaporization of solvents. More efficient and cost-effective methods for the removal of VOCs from these gas streams would be extremely beneficial to the industry. Gas separation membranes with higher selectivity could reduce costs and would have a wide variety of applications.

Removal of Organics from Wastewater

The removal of organic compounds from process wastewater represents another challenge for the petroleum refining industry. Examples include the removal of hydrophobic solvents, such as 1, 1, 2-trichloroethylene, chloroform, and ethylene dichloride; and the removal of hydrophilic solvents, such as methanol, ethanol, isopropanol, acetic acid, formic acid, and acetone. The industry needs better and more cost-effective separation technologies to recover solvents and to remove organics from waste streams that might otherwise be released to municipal wastewater systems.

Pervaporation is the most promising membrane process for the removal and recovery of organics from wastewater. Baker and Wijmans (1992) have commercialized this technology for the removal of organic solvents, such as acetone, from wastewater. Currently, silicone robber type membranes are sufficiently permselective to remove hydrophobic solvents, but they cannot remove hydrophilic solvents sufficiently, partly because of excessive membrane swelling. Thus, the industry needs new membranes that are selective for hydrophilic solvents.

Removal of Particulates

The petroleum refining industry needs better methods for removing particulates from gas streams, such as flue gases from traditional combustion units. In addition, the industry needs methods of removing submicron-sized particulates from coal liquefaction liquids.

High-temperature microfiltration is a promising approach for the removal of submicron particulates from coal liquefaction liquids (Baker et al., 1990), as well as from heavy crudes, shale oils, and tar sands. In addition, this separation technology could also be used for the treatment of used lubricating oil, particularly automotive crankcase oil, in which most of the contaminants are particulates. The membrane requirements for this application include high temperature stability, thinness, low-cost modules, and fouling resistance.

The removal of particulates from gas streams, such as flue gases from traditional combustion units, could be achieved via microfiltration membranes (e.g., modules composed of cordierite honeycomb monoliths coated with an inorganic microfiltration membrane, such as -Al_2O_3). Removal efficiencies of greater than 99.9 percent can be achieved with this method (Bishop et al., 1994). However, the thickness (< 2,000 Å) of the nanostructured microfiltration membrane will have to be decreased to increase flux/productivity, and the costs associated with the fabrication of the membrane module will have to be reduced. Another emerging application is the microfiltration of particulates from hot gases generated from advanced coal conversion technologies (e.g., the pressurized fluidized bed combustor). Although alumina-mullite has sufficient stability for this application, nanostructured microfiltration membranes with uniform pore size would be extremely useful.

SUMMARY

Like the chemical industry, the sophisticated separation technologies that the pertoleum refining industry uses could be improved to increase energy efficiency, raw materials efficiency, and cost effectiveness. Specific areas for improvement include the following:

- technologies for basic organic/organic separation processes, including the separation of benzene from gasoline and aromatics from jet and diesel fuels
- methods for separating olefins from paraffins

- methods of producing lower cost oxygen for methane conversion to synthesis gas
- processes for isomer separations, including *p*-xylene from the other xylenes and linear olefins and paraffins from their corresponding branched olefins and paraffins
- methods for separating asphaltenes from petroleum liquid
- methods for the dehydrogenation of ethylbenzene to produce styrene and the dehydrogenation of paraffins to produce olefins
- methods for recovering H_2 and S from H_2S with some input of energy
- methods for separating hydrogen from other gases, such as refinery purge gases, ammonia purge gases, and synthesis gas; methods for producing high-purity hydrogen
- methods for removing acid gases from natural gas
- methods for removing VOCs from air and various industrial process gases
- methods for removing organic compounds from wastewater and contaminated groundwater
- methods for removing particulates from gas streams and for removing submicron-sized particulates from coal liquefaction liquids

4

Cross-Cutting Issues for the Chemical and Petroleum Refining Industries

INTRODUCTION

The panel identified five issues that were common to the chemical and petroleum refining industries: the availability of lower cost oxygen; methods for removing acid gases and hydrogen separations; improved distillation technologies; the development of isomer separations; and methods for recovering components from dilute gaseous and aqueous streams. The panel also identified two technology areas with the potential to meet these needs and three enabling technologies.

COMMON NEEDS

Both industries need lower cost oxygen, which is an important product for one segment and an important feedstock for other segments of the chemical industry and an important feedstock for methane conversion in the petroleum refining industry. Technologies of interest include reactive metal complex sorbents, polymer membranes, and dense, perovskite-type oxide membranes. Because oxygen is already quite cheap, however, economic analyses of research projects in this area are essential. The potential cost reduction should be determined, as well as the extent to which industries would be impacted.

The removal of acid gases and hydrogen separation processes are important to both industries. The chemical industry requires methods for removing acid gases from process streams. The petroleum refining industry requires improved methods for removing acid gases from natural gas and process streams, for recovering hydrogen from gaseous waste streams that are currently burned for fuel, and ultimately for the recovery of hydrogen from hydrogen sulfide. Potentially applicable technologies include very thin, high-flux membranes, such as polyimides, polyaramides, and polypyrrolones, as well as various polymer-inorganic hybrid materials and inorganic membranes.

Improved distillation technologies would benefit both industries by reducing the amount of energy consumed in separation processes where distillation is still the best method. Technologies of interest include heat cascading, vapor compression, combined chemical synthesis and distillation, and combined membrane processes or other processes, such as adsorption, and distillation.

Improved isomer separations would benefit both industries. The chemical industry needs new separation technologies for the production of single-isomer chiral compounds. The petroleum refining industry needs improved isomer separations, such as the separation of *p*-xylene from other xylenes. Technologies of interest include high-performance liquid chromatography, crystallization, and zeolite and carbon molecular sieve membranes.

The separation and recovery of valuable components, such as metal ions, and the removal of contaminants, such as VOCs or particulates, from dilute gaseous and aqueous waste streams presents important problems for both industries. Technologies of interest include reactive metal complex sorbents/chemically facilitated transport membranes, reducing agents, electrically aided membrane separation, continuous adsorption processes, air oxidation combined with absorption, highselectivity gas separation membranes, and pervaporation.

SEPARATION TECHNOLOGIES

The panel identified two technology areas with the potential for addressing some of the needs described above: separation processes associated with chemical reactions and separation methods with multiple driving forces.

Separation Processes Associated with Chemical Reactions

Traditional chemical engineering separation methods rely mostly on differences in physical properties (e.g., boiling point, size, solubility) between the components of a mixture. If physical properties are similar or if a high specificity is required, separation methods that rely on chemical differences, rather than physical differences, may be useful.

Reactive Metal Complex Sorbents/Chemically Facilitated Transport Membranes

Reactive metal complex sorbents have been used extensively for the separation and recovery of metal ions. Activated carbons, widely used for purifying water, are mainly physical adsorbents. Greater selectivity is achievable by using sorbents with strong chemical interactions, such as metal coordination complexes. Metal complexes in solution or immobilized on solid surfaces for the separation of small molecules, such as Cu(I) complexes for the recovery of carbon monoxide from process gases and Ag(I)+ complexes for the separation of olefins from hydrocarbons, are increasingly being used (Doyle, 1981; Ho et al., 1988). In order for specialty membranes using complexation to be economical, however, either the market must be large enough to justify development costs or the base technology must apply to a broad range of problems with only minor modifications.

The high specificity of metal coordination complexes is exploited in chemically facilitated transport membranes, which allow for continuous, noncyclical, separation processes (O'Hara and Bohrer, 1989). In a chemically facilitated transport membrane, a reversible coordination complex or other reversibly binding species essentially acts as a highly specific mobile "carrier" for the desired component of the mixture. In ideal situations, highly selective separations are possible. Existing chemically facilitated transport membranes consist largely of supported liquids or emulsions containing carrier species (Way et al., 1982). Recently, solid-state chemically facilitated transport membranes using immobilized carriers have been suggested (Nishide et al., 1994). Although their transport rates are generally lower than for liquid systems, solid-state membranes should be easier to incorporate into commercial modules. Because of the potential variety and architecture of coordinating ligands, the scope is considerable for the design and synthesis of metal complexes for use in highly specific chemistry-based separation processes.

Separation Processes Coupled with Chemical Synthesis

The "separation" process can be a synergistic combination of usually separate processes, such as chemical synthesis and physical separation. Important combinations include catalytic distillation and reactive distillation. In addition, the extent of conversion in equilibrium-controlled reactions can be increased by the reversible absorption of one of the products. This type of "sorption enhanced process" (Carvill et al., 1996) is illustrated in the water-gas shift reaction:

$$CO_2 + H_2 \xrightleftharpoons{\text{CAT}} H_2O + CO$$

By using a solid zeolite adsorbent for water, at 250°C, the equilibrium shifts to yield almost completely carbon monoxide until the adsorbent is depleted. Continuous production of carbon monoxide is possible by a combination of reaction, sorption, and sorbent regeneration steps.

Chemical synthesis could also be combined with a closely coupled, but separate, membrane separation device. This would be most useful for equilibrium processes and would require a membrane selective for the particular product. An example is the selective production of *para*-xylene by an equilibrium redistribution of mixed isomeric xylenes coupled with selective transport of the product through a membrane. Synergistic processes that combine chemical synthesis with distillation, sorption, and membranes can, in principle, lead to more energy-efficient and materialsefficient chemical processing, especially for equilibrium-controlled reactions. For each of these hybrid systems, however, significant challenges will have to be overcome to achieve selectivity with the individual catalytic synthesis, distillation, sorption, or membrane separation steps.

Membrane Reactors

The most intimate combination of a separation process with chemical synthesis occurs in a membrane reactor, in which the membrane and catalyst are one and the same. Membrane reactors can potentially increase the efficiency of chemical synthesis because the reaction and separation steps are combined into a single process. These devices can improve efficiency by biasing equilibria to produce the desired product.

The potential benefits of membrane reactors include, for example, the reduction of the formation of coke in dehydrogenation reactions and improved separation of homogeneous catalysts from reaction product mixtures. Membrane reactors that use immobilized enzyme catalysts have been used for synthesis, as in the conversion of sucrose to glucose. Gryaznov (1986) pioneered the concept of membrane reactors with inorganic systems utilizing H_2-permeable palladium spiral membranes for hydrocarbon hydrogenation/dehydrogenation reactions. This method is particularly advantageous for the equilibrium-limited dehydrogenation reaction of alkanes, where the removal of H_2 by permeation can increase product yield. Recent research has been focused on porous inorganic membranes, which offer better transport rates than palladium or other dense systems but have lower selectivities. The inorganic membranes usually consist of porous alumina, glass, or other oxides impregnated with the appropriate catalysts, such as platinum for the dehydrogenation of hydrocarbons to olefin and molybdenum sulfides for the dissociation of H_2S to sulfur and hydrogen.

One of the most enticing developments is the use of dense oxide, high-temperature (800°C to 900°C) oxide ion transport ceramic membranes in a membrane reactor for the selective oxidation of methane to synthesis gas with air (Balachandran et al., 1997). These O_2-permselective membrane systems will most likely be used to conduct other *in situ* selective oxidation reactions, such as the synthesis of olefin oxides. These applications will, however, require the development of O_2-transport membranes that can operate at much lower temperatures (< 500°C) at which selective oxidation catalysts can effectively be used.

Oxygen could potentially be produced from air at lower cost by the use of dense, perovskite-type oxide membranes. The membranes could be used in the membrane reactor configuration for these reactions (see Figure 4-1). The state-of-the-art membrane materials are focused on the perovskite structure (ABO_3) with alkaline earth cations as the A site and transition metal cations as the B site (Lin and Zeng, 1996). The major outstanding issues include membrane stability and thickness and the high-temperature requirement (> 800°C). Changes in thermal expansion and defect structures have been observed even at low oxygen pressures (below 10^{-6} atm).

The implementation of membrane reactor technology has been limited by the availability of membranes with the required properties. For a membrane to work in the reactor configuration shown in Figure 4-1, it must be stable in the reaction environment, selectively transport desired species at high rates, and be easily incorporated into modules.

Separation Methods with Multiple Driving Forces

The driving force in a separation process can be enhanced by coupling different physical and chemical phenomena. Separation processes involving a phase change or molecular diffusion rely on a thermodynamic driving force defined by the difference between the chemical potential of the transferring species in the source and the chemical potential in the recipient. In most instances, the driving force is approximated by the difference in concentration of the species. Multiple driving forces exist either when a naturally occurring driving force for a specific operation is enhanced by an intervention that changes the system thermodynamics or when two or more separation techniques are combined. An example of the first category is the addition of an electrical potential across a membrane to facilitate the transport of a species through the membrane. An example of the second is using an adsorption step to break an azeotrope formed by one of the products of distillation.

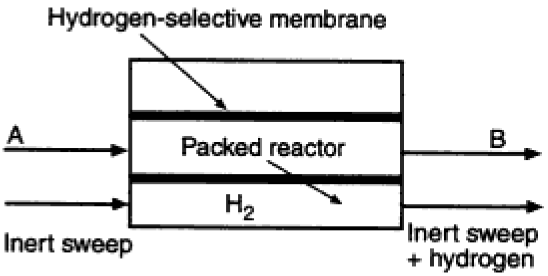

Figure 4-1
Membrane reactor configuration used in dehydrogenation technology.

Adsorbent Specificity

Affinity-based separation has become more important in recent years because of its application to biological processes and biologically produced species. The technique most often uses a chromatographic operation and makes possible the removal of a specific species from solutions containing a number of other slightly different compounds. This method uses alternations in the thermodynamics of the separation process to remove the affinity materials (i.e., reverse the sorption).

The principles of affinity chromatography are illustrated in Figure 4-2, where a specific substance has been attached to a solid support, and the attached compound (receptor) is a companion to the one to be separated from a mixture of species that are similar in all respects but the one used as the basis of separation, which might be chemical functionality, steric hindrance, or a combination of the two. The companion compounds might be an enzyme and an enzyme inhibitor, an antibody and an antigen, a nucleic acid and a nucleic base, a hormone and a receptor, or a vitamin and an appropriate carrier protein. In the operation, mixture conditions are adjusted, and the solution is fed to the chromatographic column. The desired species attach to the receptor while the undesired species pass through the column. After the undesired species have been purged, conditions in the column are altered, for example by adjusting pH, to release the desired species from the receptor. This highly selective process should be investigated for use with separation techniques other than chromatography.

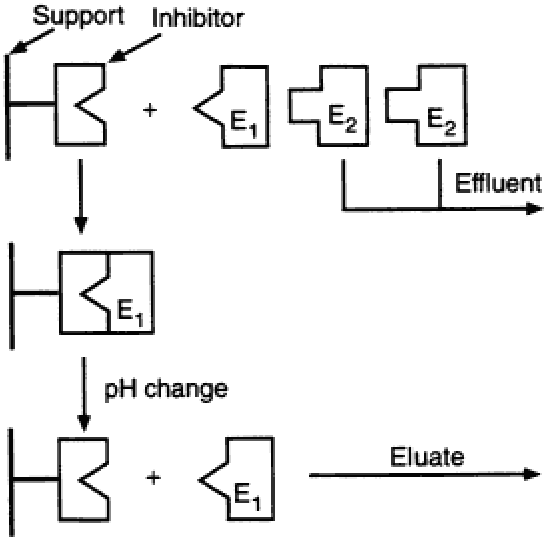

Figure 4-2
Schematic illustration of affinity chromatography.

Electrically Aided Separation

Electrochemistry has the potential to combine reaction and separation into a single process step. Traditional chemical engineering unit operations are often described as a reaction, a separation of products from unreacted material, and a recycling of unreacted materials back to the reaction step. With electrochemical methods, the splitting of a salt into an acid and a base, for example, can be done in a single bipolar electrodialysis unit that combines the separation of the anions and cations with the production of the needed protons and hydroxyl ions (Mani, 1991). Other examples include the production of hydrogen iodide without by-products (Weinberg, 1997); electrochemical separation in gas separation technology (Winnick, 1990); and electrodialysis for the separation of ions from liquids (Strathmann, 1979).

Pressure and electric fields could be additive to selectively enhance or retard the transport of a species across a membrane. A combined-effect membrane could be constructed with both sufficient strength to permit the application of a significant pressure field and ionic transport capability. Electrode material could be applied to either side of the membrane. The promise of electrochemical synthesis/separation methods is that they will be able to synthesize pure products under moderate conditions and with high energy efficiency, while simultaneously performing separation processes. Electrochemical synthesis/separation methods will require advances in materials and the basic understanding of physico-chemical phenomena in electrochemical processing.

Reversible Complexation of Organics with Organic Agents

Reversible complexation of organics with organic agents is a promising new separation technology that is currently being researched. Acetylenic inclusion compounds (organic molecules that can trap a specific component of a mixture in their crystal lattice) can be used for the recovery of NaOH from aqueous solution (Toda, 1987). In addition, some classes of organic compounds (e.g., cyclodextrins and calixaranes that are porous at the molecular level) can function as size-selective hosts in separation processes.

Chemical Reactions

In a number of cases, chemical reactions can be used to enhance the driving force for separation. One example is the synthesis of methyl acetate from acetic acid and methanol. Reactive distillation is used to separate the methyl acetate from the reactants and products resulting from the synthesis. Successful application of these technologies could make separation easier or even unnecessary.

ENABLING TECHNOLOGIES

Membrane Materials

No single membrane material will have all of the desired characteristics for membrane separation technologies. Important properties for emerging membrane materials include impact strength, flexibility, and thermal stability, as well as the properties required for a particular separation (i.e., flux and selectivity). The development of materials for specific applications will only be economical if the application is widely used, so research should be focused on membranes that will be useful for a variety of applications.

Currently available commercial polymer membranes include polysulfone, polyimide, ethylcellulose, and polycarbonate. These materials are easy to form, have high flux rates and efficiencies, and have been used successfully. However, they also have several limitations. First, they degrade in harsh chemical or high-temperature environments. Polymers that are stable in these environments are brittle and difficult to process. Second, applications, such as the production of oxygen-rich air and the removal of acid gas from natural gas, will require membranes with higher selectivity and higher flux. Polyimides, polyaramides, and polypyrrolones are among the polymers that are emerging or already in use, but membranes made of these polymers tend to have high selectivity but a low flux due to their thick active layers. Thinner membranes have been produced to try to increase flux, but these membranes could lose their selectivity due to imperfections. Finally, swelling is a problem for polymer membranes in some applications, such as organic separations. Swelling problems can potentially be overcome by combining hard segments for stability with soft segments for selectivity.

Inorganic materials are also being used to construct membranes. Membranes made out of microporous inorganics and nonporous metals also have significant limitations, however. Emerging applications include the use of thin, nanostructured, dense metal membranes for the separation of gases, such as hydrogen. Other applications include the use of molecular sieve membranes, such as zeolite and carbon molecular sieve materials, for the separation of isomers and dense, perovskite-type oxide membranes to produce high-purity oxygen.

Sorbent Materials

Sorbent materials separate components by three methods: the formation of stronger bonds with certain components than with others; the exclusion of some components and inclusion of others based on their relative geometries (molecular sieving); and separation based on differences in intraparticle diffusion rates. Sorbent materials in the first category represent by far the largest tonnage of sorbents sold; sorbents in the third category are by far the smallest. Most sorbents are inorganic (adsorbents), although a few are polymeric with selectivity based on the relative solubilities of components in the polymer.

In order for a sorbent to be regenerated for further use, the bonds formed between the sorbent and the sorbate (the material being sorbed) must be reversible. The degree of reversibility is a critical factor for the economic viability of sorption processes. The few adsorbents that bind components irreversibly can only be used to remove relatively small amounts of components (about 100 kg/day) or less because of the high cost of removing and replacing the spent adsorbent.

So-called hydrophobic sorbents, such as activated carbon, silicalite, and various resins, tend to be selective for less polar components and tend to select among hydrophobic species based roughly on boiling points. Hydrophilic adsorbents (e.g., activated alumina, silica gel, and zeolite molecular sieves) are selective for polar compounds and form relatively strong bonds with water as compared to a wide range of organic species.

The number of adsorbent types, not including a variety of irreversible adsorbents, is relatively small (less than 10), but most have many variations. Thus, activated carbons can be produced from various carbon-containing sources and can be heat-treated in various ways to produce differences in inherent bond strengths with sorbates, different pore sizes, and different particle shapes. As a result, hundreds of separate activated-carbon products are being produced commercially.

The newest class of sorbents consists of special shapes that facilitate movement between adsorption and desorption zones. One example consists of small, spherical, uniformly-sized particles of polymer sorbents that are used in processes that combine fluidized and moving beds and that conceptually resemble a conventional absorption/desorption process. A second example consists of large, monolithic shapes of metal ioxides or activated carbon usually in the form of a large wheel. The wheel rotates several times per hour through adsorbing and desorbing zones.

On-line Diagnostics and Sensors

On-line detection of the composition of material streams in separation processes would benefit the chemical and petroleum industries. Carefully controlling reaction conditions is an effective strategy for minimizing undesired side reactions, and hence reducing the need for subsequent separation or purification steps. Much of the technology for the fine control of reactions is commercially available, including excellent means of controlling key parameters, such as flow, temperature, pressure, and mass. Feedback algorithms are often well known, and there is ample computing power and memory to implement these on a real-time basis.

More often than not, the limiting components for controlling reactions are the sensors. The chemical and petroleum refining industries need accurate, selective chemical sensors that can maintain performance in harsh or extreme manufacturing environments. In distillation processes, sensors that could determine compositions on-line at various points within a distillation column would be an enormous help in controlling and optimizing performance by allowing distillation columns to operate as close as possible to minimum reflux. These rapidly responding sensors would have to be capable of detecting minor differences in the structure of chemical compounds or fractions in a potentially harsh environment.

The growing need for sensors is apparent when product specifications are strict. Uncertainties in the distillation column are usually dealt with by operating the column very conservatively, which often leads to product purities that exceed specifications. The consequences of this practice are shown in Figure 4-3, which plots energy costs as a function of product purity. Note that the slope of the plot increases as purity increases, meaning that the incremental energy cost associated with increasing purity by a fixed amount increases as the base value increases. The figure also shows the effect on energy costs of high and low process variability for the same mean operating value of product purity. The mean operating value has

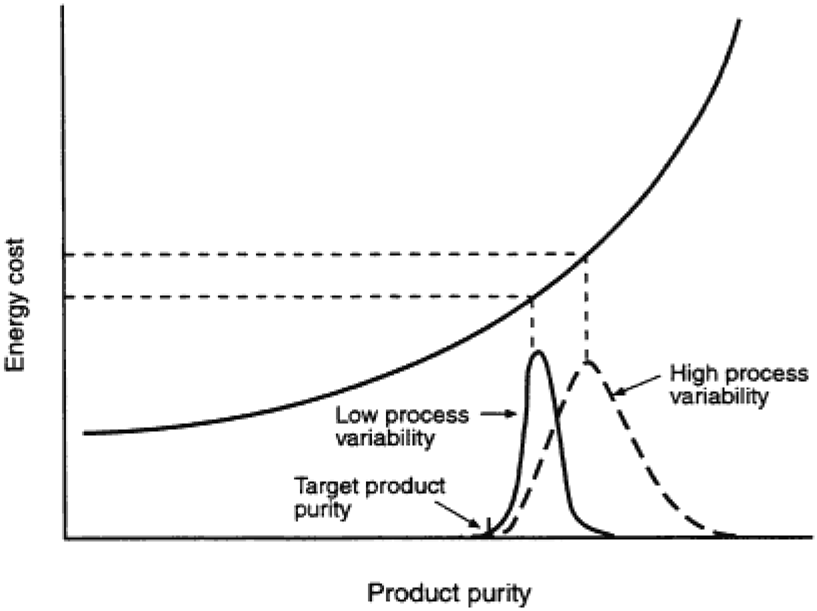

Figure 4-3
Schematic illustration of the relationship between energy costs, product purity, and process variability. Energy costs increase with increased product purity. Increased process variability results in increased energy costs with no increase in product purity.

been selected so that no portion of the product is below purity specifications. Processes that can be tightly controlled to lower the uncertainty in terms of purity have significantly lower energy costs than processes that cannot be tightly controlled. Columns operated in the mode just described often become bottlenecks in the production process.

Improvements in control technology are likely to occur as the result of improved sensors, control algorithms that improve feed-forward, capabilities, and artificial intelligence and fuzzy logic methodologies to update process models and controller operations. However, industrial experience has shown that frequent maintenance and calibration of sensors is important. Fouling is likely to occur, as well as interference from minor contaminants. Early research and development should include the use of realistic industrial process streams and contaminants. Although the cost of a sensor is clearly important, a robust solution to a challenging detection problem may be worth significant capital expenditures. Finally, the interest in using biological sensors to detect chemical composition has increased significantly.

Improved Understanding of Thermodynamics

The ability to separate a mixture as efficiently as possible is closely related to making the best possible use of the driving forces. In most separation processes, the thermodynamic description of equilibrium between two phase is an indispensable tool in understanding driving forces. Research in phase equilibrium is hardly new, and extensive information is available. Nevertheless, some aspects of phase equilibrium have been so little researched that some separation processes cannot be optimally designed. The negative consequences of suboptimal designs include excessive energy use, less-than-maximum separation or recovery, and high investment costs.

Several aspects of phase equilibrium are lacking data and correlations. One of these areas is mixtures in which one or more components of importance are at very low concentrations (e.g., parts per billion). These are the same conditions encountered in the removal of already small concentrations of pollutants from waste streams, as well as in the purification of final products. This near-infinite dilution is difficult to quantify because, not only do we not have analytical-chemistry techniques for accurately determining extremely low concentrations, but also the maximum deviation from ideal-phase behavior almost always occurs at these concentrations. As a result, phase-equilibrium correlations derived from data at less extreme compositions often yield vapor-liquid and liquid-liquid equilibrium estimates that can be wrong by a factor of at least two or more in the near-infinite dilution range. This degree of error can cause substantial departures from the optimal design. Systems that involve, for example, liquid-solid equilibria are also subject to major problems in the very-low-concentration range. Accurate activity coefficient data for molecules in near-infinite dilution, and use of this data in modeling and design, are critical.

A second area for research is systems in which reaction accompanies the attainment of equilibrium. A typical example is the absorption of H_2S into amine and other basic solutions. Ionization of the H_2S can occur in the liquid phase, and, in some systems, reaction kinetics can be slow enough that a combined reaction rate/phase equilibrium design model must be derived. High-quality models are rarely available in these cases. A third research area might be called extreme condition equilibria. Extreme conditions include temperatures well above 100°C or well below 0°C and pressures in the supercritical-fluid range. Supplying the critical thermodynamic information for separation processes in the areas described above will require combining advanced analytical-chemistry technology with phase-equilibrium equipment and deriving correlations that accurately describe and generalize the experimental data.

II

SEPARATION IN THE MATERIALS PROCESSING INDUSTRIES

5

Aluminum Industry

The United States is the world's largest consumer and producer of aluminum. In 1995, the primary smelting sector of the industry produced 3.375 million metric tons of aluminum, constituting 17.3 percent of world production. In addition, the secondary refining sector recovered 3.188 million metric tons of recycled aluminum. Imports made up the rest of the 9.265 million metric tons of aluminum consumed in the United States that year (Aluminum Association, 1997). Total annual shipments of aluminum in 1993 were valued at $21 billion, and the industry employed 134,000 workers (OIT, 1997c).

Aluminum is an energy-intensive industry, with an annual energy use of 1 quadrillion Btus and energy expenditures of $2 billion, or 8.6 percent of the total value of shipments in 1993 (OIT, 1997c). Production of aluminum from recycled materials requires only 5 percent as much energy as primary production and thereby decreases the total energy consumption of the industry.

SEPARATION NEEDS

Various sectors of the aluminum industry, from primary smelters to producers of finished products, have diverse separation needs. In terms of basic processes, the industry needs improvements in separation processes that increase metal purity. The industry as a whole has a need for innovative separation technologies to improve the sorting, and thereby the quality, of scrap. The recycling of scrap reduces energy use, reduces costs for the purchase of raw materials, and reduces the impact of waste on the environment. The separation needs of the aluminum industry are shown in Figure 5-1.

Figure 5-1
Separation issues for the aluminum industry.

Separation Processes for Improving Metal Purity

Separation processes are an important part of the aluminum manufacturing process. The three basic processes used in making aluminum are the Bayer process, for the conversion of bauxite into alumina, the Hall-Heroult process, for the electrolytic smelting of alumina to aluminum, and the alloying, casting, forging, and fabrication processes for making products. These basic processes are relatively straightforward. The industry has an overriding, constant need to maintain the purity of material flows because most other metals are more noble than aluminum. Once an impurity is introduced into the aluminum melt, it is practically impossible to remove it. Therefore, the industry's standard practice is to avoid impurities as much as possible.

The Bayer process is the principal method for producing alumina feedstock. In this process, bauxite ore, a mixture of aluminum, iron, titanium, and silicon oxides, is crushed and milled and then mixed with a concentrated solution of sodium hydroxide. This mixture is fed into autoclaves where the alumina in the ore is dissolved to form sodium aluminate at temperatures of up to 270°C. Silica reacts to form sodium aluminum silicate, which precipitates out of solution, and the other oxides remain as solids. The sodium aluminate is recovered separately and converted to alumina. The solid-rich residue, known as red mud, is washed to recover sodium hydroxide and then disposed of.

Because of the retention of sodium oxide in the Bayer process, aluminum fluoride must be added to the electrolytic cell, which results in the generation of excessive cryolite. Minor impurity levels of other oxides, such as iron, zinc, and silica, are reduced in the electrolytic cell and become major impurities in the metal. Calcium oxide, if retained, is a major impurity in the electrolyte. The aluminum industry would benefit from improved separation technologies to remove these impurities from the metal and the electrolyte, or to avoid them altogether.

During the Hall-Heroult process, the electrolytic cells generate solid and gaseous fluorides, as well as CO_2 emissions. All smelters use scrubbing systems to treat the off-gases. Dry scrubbers, which are designed to put the gases in contact with alumina in dispersed phase or fluidized bed reactors, are the preferred technology because unreacted alumina is used to capture hydrogen fluoride and electrolyte compounds that can be returned to the cell. Elemental impurities (e.g., fluorine, vanadium, lithium, iron, phosphorus, and nickel) concentrated in the scrubber alumina are subsequently returned to the cell. Once in the cell, iron reduces metal quality, phosphorus reduces current efficiency, and vanadium reduces both. Therefore, better separation technologies for removing iron, phosphorous, and vanadium from the scrubber alumina would be of considerable interest to the industry.

During cell tapping, electrolyte is inevitably removed along with the metal and ends up in casting centers as a dross contaminant. It can have an additional detrimental effect through back reaction with aluminum to produce elevated levels of light metals in the melt, which in turn creates a need for additional chlorine fluxing.

Chlorine gas fluxing is used in combination with argon or nitrogen to remove light metal impurities, such as sodium and lithium, hydrogen gas, and oxide inclusions, from molten aluminum. Chlorine fluxing is also used extensively in the secondary, or recycling-based, sector of the industry to selectively remove unwanted magnesium from casting alloy melts. The magnesium is present in the melt because a mixture of scrap, including both cast and wrought alloys, is used for the melt, and the wrought alloys contain magnesium levels that exceed the cast alloy target specification. The industry would benefit from alternatives to removing impurities via chlorine fluxing, which is expensive and creates environmental problems.

Filtration of molten metal is a complementary technique to fluxing for removing oxides and nonmetallic inclusions from the melt. Filtering is designed to provide consistent metal quality for a wide range of casting requirements. The techniques employed are ceramic foam filters (which use replaceable filter cartridges), packed beds, and sedimentation. A better understanding of filtration mechanisms would increase the efficiency and reliability of this technology, as well as lower the costs. The industry also needs new techniques for sensing inclusions in metal.

Primary Smelting

In the Hall-Heroult process, a direct current is passed through a current-conducting bath of molten cryolite (Na_3AlF_6) in which alumina is dissolved. The bath is contained within an insulated cell. Carbon anodes are suspended above the cell and are dipped into the bath. The cathode is the molten aluminum. Under the influence of the applied current, aluminum is deposited at the negative electrode and collects at the bottom of the cell. Oxygen is released at the carbon anodes where it reacts to form CO and CO_2 at the expense of the anode material. Approximately two tons of alumina and one-half ton of carbon are required for the production of one ton of aluminum. Hence the primary smelters are significant emitters of CO_2. The carbon anodes are produced in a separate plant from a mixture of calcined petroleum coke and coal tar pitch, which has been prebaked.

Avoiding CO_2 emissions and the search for nonconsumable electrolytic anodes are linked. CO_2 is created by the current practice of using consumable carbon anodes in reduction cells, and the aluminum industry is searching for alternatives. The ideal electrode would be a nonconsumable inert material with the required current conducting properties and the ability to withstand the aggressive environment in the cell. Improvements in this Hall-Heroult method of reacting and separating out aluminum would reduce CO_2 emissions.

After the electrolytic cell is taken out of service, spent potlining (the insulation and containment material of the electrolytic cell) remains. This material often contains fluoride compounds and sodium cyanide, which must currently be processed as hazardous waste. The industry would welcome better ways of dealing with spent potlining, such as methods of separating out components before processing to reduce process costs and volume. Therefore, a method of removing hazardous materials from spent potlining would benefit the industry.

Upgrading Scrap

Identifying and sorting scrap was cited as a major need by every sector of the aluminum industry because of the diversity of aluminum alloy specifications and because of the restrictions imposed by those specifications on the chemistry of scrap remelts. The quintessential example is the recycling of secondary foundry alloys compared to the recycling of used beverage cans. Secondary foundry alloys are generally quite liberal in their tolerance for alloying elements, especially elements such as iron and silicon, which are routinely picked up during the recycling process. Silicon is a major component of foundry alloys because it improves melt fluidity needed for casting. Therefore, many secondary foundry alloys are able to accept wrought alloy scrap as melt ingredients. Magnesium levels in wrought alloy specifications often exceed foundry alloy specifications, but magnesium can be readily removed from the melt by chlorinating or by specific fluxes. In contrast, wrought alloys (with the exception of alloys such as 3105 utility sheet designed specifically to be made from recycled metal) are usually intolerant of impurities, and, except for the 4XXX series, are necessarily low in silicon. Therefore, although mixed wrought alloy scrap may be used to make secondary foundry alloys (with the use of fluxing where necessary to reduce magnesium), foundry alloy scrap cannot be used to make wrought alloys. The degree of tolerance among wrought alloys is entirely dependent on the chemistry of the target alloy. Used beverage cans, which are a mixture of 3104 (an aluminum alloy containing manganese) and 5182 (an aluminum alloy containing magnesium), are compatible for remelting because the combined melt chemistry is compatible with fresh 3104, allowing for the removal of excess magnesium through oxidation.

The global scrap aluminum balance is maintained today because of the healthy growth of the secondary foundry alloy business, particularly for automotive casting applications. Indeed, this industry consumes not only all of the old scrap castings and automobile scrap, which are a good mix of cast and wrought alloys, but also mixed wrought and cast alloy white goods, such as refrigerators and other household appliances. In the absence of this healthy demand, the mixed alloy scrap would have to be segregated to find a recycling outlet. The aluminum industry has targeted the automotive sector for significant growth, especially in the area of wrought alloy applications for structures and closures. If this growth is realized, aluminum intensive vehicles will contain as much, or more, wrought alloy as foundry alloy. The recycling of these vehicles will create a demand for separating component alloys into wrought and cast alloys, and subsequently into individual alloy streams, to satisfy recycling and material supply criteria. This will require improved methods for separating aluminum scrap.

Solid Residues

Dross is the oxide-rich by-product of aluminum melting operations. White dross from smelting or clean remelt operations may be rich in metal, with the balance aluminum oxide, whereas so-called black dross or salt cake contains salt flux, which is used to facilitate the wetting of aluminum scrap, as well as oxide and reduced amounts of metal. Salt cake, which is reactive, contains aluminum nitride, aluminum carbide, and fine aluminum and is a candidate for recycling to recover the entrained metal and salt flux. These recycling methods have yet to be developed.

Gaseous and Aqueous Emissions

The aluminum industry, in particular the remelt and recycling sector, is regulated for the emission of typical gaseous effluents, such as HCl, NO_x, SO_x, VOCs, and fine particulates in gaseous streams. Emissions are controlled via incinerators, acid gas neutralizers injected into the exhaust stream, and bag house filters with neutralizing precoats. As regulations become tighter, the industry is looking for more efficient methods for separating or treating these emissions. Improved dewatering methods (i.e., more efficient removal of water from process and effluent streams), especially in the Bayer process, is another area for research.

SEPARATION TECHNOLOGIES

The panel identified a number of separation technologies with potential to meet the separation needs identified by the aluminum industry. For example, ceramic foam filters show promise for removing impurities from molten metal, and the industry would benefit from a better understanding of this technology. In addition, the search for alternatives to carbon anodes should focus on nonconsumable inert materials with the required current conducting properties that are capable of withstanding the aggressive environment in the cell (note that this may lead to a greater consumption of electricity).

Upgrading Scrap

With an ideal separation technology, closed-loop recycling of scrap metal could be achieved for complex products like automobiles. The metallurgical value of scrap would be maximized by eliminating the wasteful practice of using chlorine to remove valuable alloying elements like magnesium. Some of the separation could be done by hand, using component database tools and hand-held analytical devices. However, for complex product forms like automobiles, much of the old scrap will probably be processed by shredding, the objective of which is to reduce the size of the scrap pieces and liberate the desired material from impurities. Unfortunately, the size reduction results in material that requires very high-speed sorting for the process to be economical. High-speed noncontact techniques have been identified that would be capable of differentiating all alloys of interest.

The successful separation of different types of aluminum alloys will require continued work on the fundamental mechanics of high-speed conveying, the positioning scrap pieces in sequential arrays before they enter analysis, and methods of physically sorting analyzed pieces by alloy type. Separation technologies for upgrading scrap include sorting methods based on physical properties, such as magnetic and electrical properties, densities, and melting points (see Chapter 10).

Recycling Salt Cake

In Europe, disposing of salt cake is prohibitively expensive because of the high costs of landfills, so it is substantially recycled. In some countries, the presence of salt cake in landfills has been banned by legislation. In established recycling practices, the salt cake is crushed and milled to recover recyclable aluminum, which is returned for melting, and the residue is dispersed in water to dissolve the salt. The solids are removed by filtration, and the salt is recovered from the brine by flash evaporation. The recovered salt is returned to aluminum smelters for reuse as flux, but the evaporation process is energy-intensive and costly. The solid nonmetallic by-products, which contain oxides together with aluminum metal and aluminum nitride, will form hydrogen and ammonia in the presence of moisture and heat if unreacted. Applications for reacted or stabilized nonmetallic byproducts have been found in the cement industry, but there may be other opportunities for further separation and upgrading of these by-products. Other by-products from aluminum processing, such as bauxite residue, red mud, and bag-house dusts, could also be separated into useful streams.

Gaseous and Aqueous Emissions

Inorganic membrane modules composed of cordierite honeycomb monolith coated with a microfiltration membrane (e.g., Al_2O_3) and vanadium-based catalysts could be used for removing SO_2 from flue gas. Oxy-fuel burners are used in some sectors of the aluminum industry, chiefly in recycling furnaces. The principal attraction of oxy-fuel is its intrinsic low NO_x attributes compared with conventional fuel-air burners. However, the high cost of oxygen remains a significant barrier to the use of this technology. Lower-cost, hot oxygen would enable the implementation of additional oxy-fuel systems. In addition, the use of oxygen, as opposed to air, for combustion results in energy savings because the energy used to heat the nitrogen component of air, the thermal value of which is lost in the flue gas, would be saved.

SUMMARY

The aluminum industry has a broad array of separation needs that affect all production processes, from primary smelting to the manufacture of finished products. Specific areas for improvement include:

- the separation of impurities from alumina feedstock
- the separation of impurities from dry scrubber alumina
- alternatives to chlorine fluxing for the removal of light metals and magnesium molten metal filtration
- methods for sensing inclusions
- decreasing or eliminating CO_2 emissions by the development of nonconsumable electrodes
- methods of reducing and recycling spent potliner
- methods for segregating/sorting scrap by alloy
- separation/uses for nonmetallic by-products
- salt/water separation for efficient recycling of salt cake
- treatment of dilute gas streams
- lower cost oxygen for oxy-fuel burners
- efficient removal of excess water in the Bayer process

6

Steel Industry

The U.S. steel industry produces about 100 million tons annually. In 1994, this constituted 12.6 percent of world production. In addition, the United States imports about 25 million tons of steel each year. The value of U.S. steel production is approximately $50 billion per year, and the industry employs about 170,000 workers (AISI, 1997).

Steel is the fourth largest energy-consuming industry in the United States, using 1.944 quadrillion Btus in 1994. This was 2.3 percent of the energy consumed in the United States and 20 percent of the energy consumed in U.S. manufacturing. Also in 1994, the industry produced 32 million tons of solid waste and by-products. In general, the industry recycles 95 percent of the water used in steel production and processing (AISI, 1997).

SEPARATION NEEDS

The steel industry comprises two major parts. The first is called the "integrated" segment because iron ore and coke (made from coal) are combined in blast furnaces to produce molten iron (called hot metal), which is then refined and alloyed to produce various types and grades of steel. The oxygen-based refining process, which is the one most widely used today, is sometimes called the basic oxygen process and may be carried out in a basic oxygen furnace (BOF) or a basic oxygen converter. Oxygen-based steelmaking accounts for about 60 percent of the steel produced in the United States each year.

The second, and fastest growing, part of the U.S. steel industry is based on the electric arc furnace (EAF), which can melt steel scrap to make liquid steel without going through the ore-coke-blast furnace cycle. Fluxes and oxygen are used to further refine the EAF output, usually by ladle treatment. Facilities that use EAF steelmaking are popularly known as "minimills" because they are cost-effective and much smaller than integrated plants. Minimills now produce about 40 percent of U.S. steel output.

Although there are broad similarities between integrated steel mills and minimills, each have unique requirements. Among integrated steel mills, there are also broad similarities between separation processes for raw materials and for products that are recycled and reused.

Coke Production

Traditional integrated steelworks use iron ore, coal, limestone, and oxygen or air to produce steel. The first step in this process is the conversion of coal to coke, a porous, strong, carbon-rich material used in blast furnaces to provide most of the reducing power and heat required to reduce iron from iron oxides. Coke also maintains porosity in the furnace charge while the iron and slag are being melted.

Coke is produced by the destructive distillation of coal, and valuable organic compounds are separated as by-products. When the coke is finished, however, it is a red-hot mass that must be pushed from the coke oven and quickly quenched with water, which emits copious amounts of gases, steam, and particulates that pose severe air and water pollution problems. Although the industry has tried to solve these problems for many years, better methods of separation are continuously being sought, particularly for the removal of particulates from gases and water. Methods of treating quench water so it can be recycled and reused are also of interest to the industry. Over the years, the industry has tried to cut down or even eliminate the use of coke, and today the "coke rate" (pounds of coke per ton of hot metal) is much lower than it was even a few years ago. Steelmakers have also lowered coke rates by adding fuel oil or powdered coal through the blast furnace tuyeres. Anything that lessens coke requirements lessens the environmental problems associated with coke production.

Ironmaking

As supplies of the best natural ores (ores that do not require beneficiation) dwindled, the chemistry and physics of ironmaking in the blast furnace were becoming better understood. By the time the industry was forced to turn to much lower grade ores, which had to be finely ground, beneficiated, and reconstituted as pellets, increased productivity in the blast furnace had more than redressed the balance. Today, the production records belong to sintered ores (partially agglomerated ores strong enough to permit efficient gas flow in the blast furnace). Sintering also provides opportunities to incorporate fluxing agents into the mix to make their use more efficient and to reintroduce mill scale (the iron oxide waste produced during rolling). The sintering machine can take ore as coarse as 10mm and as fine as "all passing through 100 mesh," provided that efficient air flow through the bed is maintained. Although some iron ore producers are still motivated to increase product grades, ironmakers must take other factors into account. For example, a high grade iron oxide pellet would not be acceptable unless it could stand up to reduction in the blast furnace.

The process of ironmaking takes place in the blast furnace, a highly productive unit capable of turning out several thousand tons daily of molten iron, known as "hot metal" or "pig iron" (if cast). Inside the blast furnace, a high-temperature reducing atmosphere is maintained while fuel and ore are fed into the furnace, more or less continuously, through the top. Pressurized preheated air is blown in near the bottom, providing oxygen for coke combustion and carbon monoxide formation. In the shaft (stack) of the furnace, the mix of coke, limestone, and iron-bearing material progresses downward as solid-state reduction proceeds. Near the bottom of the stack, temperatures reach 1,000°C and slag formation commences, involving the added limestone, silica, and alumina from the ore, as well as other impurities from both the ore and coke. In the fusion zone, temperatures reach 1,200°C to 1,600°C. This portion of the furnace, called the bosch, terminates at the tuyere line, where everything except coke is molten. Near the tuyeres there is a limited oxidation zone in which coke can still be burned, raising the temperature to 1,900°C. In the hearth of the furnace, below the tuyere line, hot metal and slag can collect. Some separation of impurities may still take place, but the molten layers are relatively quiescent and are frequently tapped. Some formation of refractory compounds (e.g., TiN) may take place above the hearth. These are solids and may be troublesome in the downstream steelmaking operations.

As a separator, the blast furnace is only effective for removing silica, alumina, and other gangue minerals and the oxygen in iron minerals. The burden of removing impurities is therefore placed on the steelmaking process. Blast furnace hot metal is far too high in carbon to be directly useful except as pig iron in certain foundry operations. The various processes for making steel are fairly effective for separating impurities, and so are used for this purpose.

Oxygen Steelmaking

The integrated steelmaking industry relies almost entirely on oxygen processes to make steel from hot metal. A typical heat yields about 200 tons of finished steel in about 38 minutes from a charge of 80 percent carbon-saturated hot metal and 20 percent heavy steel scrap. About 10 tons of flux, mostly lime, is also added to the furnace to form a slag for the capture of impurities. During the "blow," large quantities of oxygen forced through the molten bath oxidize carbon, silicon, and other impurities.

Although oxygen steelmaking is a mature process, improvements could still be made in the removal of nitrogen and phosphorus, a requirement for many higher-quality steels. Nitrogen can only be swept out as a gas by carbon dioxide generated in the process, and phosphorus must be oxidized to the slag. Neither separation is very efficient as presently practiced. The furnace slag itself contains recoverable metallic iron, but its separation requires that the slag be crushed and magnetically separated, an inefficient, labor-intensive process. Finally, the oxygen furnace produces a fine dust that must be separated and collected. This dust has a very low bulk density, is difficult to handle, and is usually deposited in a landfill, even though it may contain potentially valuable constituents, such as zinc.

Further refining downstream of the oxygen process may be required to control residual impurities and prevent inclusions. Better knowledge of the relationships between steel properties and the specific costs and benefits of better separation technologies could help prioritize research.

Electric Arc Furnace Steelmaking

A typical EAF produces 150 to 200 tons of steel from scrap in a heat (about one hour). Fluxes and oxygen may be used, but to a lesser degree than in an integrated shop. These may be used in the EAF itself, but it is more likely to be done in a ladle. Because of the relative purity of the scrap charge, less slag builds up in the EAF operation than in a BOF, but the EAF still has the same problems with the removal of nitrogen and phosphorus. Improved separations here would benefit both segments of the industry.

Dust from the EAF is a serious problem, partly because 1 to 2 percent of the charge by weight appears as dust, but mostly because the EAF dust contains substantial quantities of iron oxide, zinc oxide, and lime, as well as smaller, but very troublesome, quantities of lead oxide, cadmium oxide, and other materials. Like the BOF dust, EAF dust is very light and difficult to handle. For EAF dust to be economically attractive, separation technologies must be found to remove the zinc oxide from the iron oxide, which also contains some zinc ferrite. It is possible that, if a zinc-rich fraction could be separated, zinc could be produced from it. The iron-rich fraction could then be recycled.

Ladle or Secondary Refining

After oxygen or EAF steelmaking, the steel is further refined prior to casting. Ladle, or secondary, refining processes include deoxidation, desulfurization, and vacuum degassing. The primary purpose of secondary refining is to produce clean steels from which second phase inclusions, such as alumina (Al_2O_3) and other oxides, have been removed. These inclusions are small (1 to 100 μm) and are usually captured in a slag on top of the steel. Little is known about the separation mechanism from liquid metals. The problem includes the transport of the inclusion to the interface and its dissolution in the liquid top slag. A better understanding of these separation processes would be useful to the industry.

Scrap Separation

Both segments of the steel industry have trouble obtaining enough clean scrap of known composition. The integrated steel industry is probably in somewhat better shape because it controls its own "home" scrap, but it also needs heavier scrap as a coolant in the BOF. The minimills, obviously, would suffer quality problems as well as growth constraints if they could only use obsolete scrap, especially automotive shredder scrap.

Like the integrated mills, the EAF plants try to use any home scrap they produce because it is heavy to transport and its composition is known. They also compete for prompt industrial scrap generated in the manufacture of steel products, such as automobiles, because this is also quality steel with low residual impurity levels. However, the advent of continuous casting has reduced the quantities of home scrap available, and more efficient manufacturing methods are reducing the availability of prompt industrial scrap.

Postconsumer scrap can be in almost any form. Typically, it is shredder scrap contaminated with both metallic and nonmetallic impurities. For example, automobiles contain significant quantities of nonferrous metals, alloying elements, such as nickel and chromium, and combustibles, mostly plastics. Because these impurities are hidden in the automobile's structure, they cannot be recovered before shredding, and magnetic separation after shredding is only partially effective. Scrap is usually washed to separate nonmetallics, but shredder scrap is relatively coarse, and the remaining metallic contaminants cannot be effectively removed by highintensity magnets (for paramagnetic materials) or eddy current separators (for conductive nonmagnetics).

The most troublesome impurities in EAF steelmaking today are copper and, to a lesser extent, zinc. For higher-quality steel products, such as flat rolled sheet and bar-quality steels, copper and other residual elements must be below specified levels in the EAF feed because they are not removed in the process and their presence may make it impossible to achieve the desired properties. A flat rolled steel, for example, may have a maximum allowable copper level of 0.1 percent, as opposed to 0.25 percent copper in typical automobile shredder scrap. Some plants that run on scrap try to use dilution with other lower-copper scrap, and some do not attempt to produce certain grades of steel, but competitive pressures are forcing EAF operators to expand into a broader spectrum of products. Obviously, better separation methods for removing copper and other residual impurities from scrap is one of the most critical problems facing the steel industry today. In the future, however, changes in the design of automobiles and the materials that go into them, such as the use of plug-in electrical components that can be recovered before shredding, may have a greater impact than improved methods for separating shredder scrap.

Direct Reduced Iron

From the beginning of the "minimill revolution" more than 30 years ago, a great deal of consideration was given to direct reduced iron (DRI). The various processes that were studied were all aimed at removing oxygen from iron ores in the solid state. By the 1960s, a few plants had been built using coal-based and natural gas-based processes. Some of these were in locations where a small steel mill could be justified, and the scrap for a more conventional EAF plant was not available (New Zealand, for example). In the United States, scrap was preferred for reasons of cost, both capital and operating. In the 1970s, reformed gas became the fuel/ reductant of choice, although some coal-based plants were in operation and some process development involving coal continued.

There is a strong positive incentive for using high grade feed for direct reduction because slag-forming gangue minerals in the DRI impose additional burdens on the EAF. Suitable feeds ideally contain no more than 3 percent silica plus alumina, but very few natural ores approach this level of purity. Therefore, the feed is usually finely ground, beneficiated by magnetic separation, flotation, or both, and reconstituted as fired oxide pellets before reduction. After reduction, the product typically contains 88 percent or more metallic iron, 8 percent or less unreduced iron oxide, and about 2 percent silica and other constituents.

A finished DRI pellet is very reactive. It has a large internal surface area, will reoxidize in contact with moist air, and may even burn if it contacts water. DRI pellets obviously present problems for storage and shipping, for which producers have tried many different remedies. The most widely used remedy today is hot briquetting, a process in which the DRI pellets, under a protective atmosphere, are briquetted to reduce their surface area and seal off internal surfaces. The DRI briquettes can be handled, stored, and shipped, even across the oceans.

A more recent alternative that has its own advantages is producing iron carbide (Fe_3C). The raw materials for this method must also be high-grade ore or pellets, and the fuel is reformed natural gas, but the product is stable and does not require briquetting. The first carbide plants are now being established, but it remains to be seen how well iron carbide will fare in competition with more conventional DRI.

DRI (and carbide) have several advantages over scrap. First, they can dilute impurities, such as copper. Second, they are steady, predictable sources of highquality feed. Third, they are a means of "importing" low-cost energy from places where natural gas is readily available. Finally, they can act as hedges against rising scrap prices. They do, however, require a capital investment that is not incurred by using scrap.

Many EAF plants in the United States are located where they are because of the availability of scrap, and cheap natural gas may not be available at the same sites. The circumstances for DRI plants are entirely different. Very few U.S. ores are suitable as DRI feeds, and DRI plants in the United States must therefore subsist on imported pellets. The trend toward overseas sites, where cheap gas is available and high-grade pellets can be brought in easily, is probably irreversible. By the same token, gas-based DRI technology has moved ahead so far and so fast that coal-based processes will probably be relegated to areas where available coal can be used or where only incremental quantities of DRI are needed. Therefore, it is doubtful that a DRI process using coal would be of great value to the U.S. steel industry. Just as the iron ore industry became internationalized several decades ago, the DRI industry as a whole will develop according to the supply of ores, the availability of natural gas, and transportation. The cost of DRI will be the summation of these costs.

Given the reactivity of fresh DRI, removing impurities from this product is out of the question, so impurities must be excluded from the feed. Therefore, ore beneficiation would be a better target for research related to DRI. The coal separation needs identified here are the same as those for coal that is intended for coke production. Whether for coke or DRI, there are physical requirements (i.e., size and moisture) that make it difficult to consider flotation as a separation method for improving the grade of coal. Liquefaction works on the coal rather than ash and sulfur.

Gaseous and Aqueous Emissions

In coke production, gases are produced and large volumes of liquids are used. These gases and liquids carry particulates that complicate separation and treatment. Even so, major amounts of VOCs, which are valuable by-products, are routinely recovered from coke operations. Water is partially recovered and recycled, decreasing the use of fresh water. Although the coke ovens are one of the most obvious sources of gaseous and liquid emissions, all iron and steelmaking processes produce similar emissions. Therefore, research on the separation of fine particulates from gases and liquids could yield broad benefits for the industry as a whole.

SEPARATION TECHNOLOGIES

Removal of Impurities from Molten Metal

Currently, phosphorus is removed from molten metal by oxidation to the slag, and nitrogen (N_2) and residual gases are removed in the large quantity of CO gas generated in the process. These processes could be improved. Considerable research has been done on methods of refining copper from liquid iron using various fluxes. The sulfidation of copper, where the Cu_2S is dissolved into a sulfide matte, has been investigated in detail by a number of researchers. These studies have shown that it is impractical and uneconomical to refine copper from molten iron and that it is best to separate copper out in the scrap stage.

Scrap Separation

Separation technologies for upgrading scrap include sorting methods based on physical properties, such as magnetic and electrical properties, density, and melting point (see Chapter 10). Copper should be removed from solid steel scrap before it goes into solution. Promising techniques include cryogenic fragmentation of the scrap into small pieces followed by magnetic or visual separation. Dissolution of the solid copper into a sulfide matte, or even liquid aluminum, is another promising technique, but difficulties include sulfides or aluminum being attached to the scrap and high costs.

Improved Ore for Direct Reduction of Iron

Separation methods based on gravity or density can be used to improve the quality of ore for DRI. Particles of different densities are separated in a medium of intermediate density, such as a suspension of fine heavy particles in water; in a solution of a salt, such as calcium chloride and various bromides; or a in a true "heavy liquid," such as a thallium malonate/formate solution. For separation of particles heavier than water, suspensions of fine solids can be used, such as magnetite and ferro-silicon. For separation of coarse particles, such as metals from the nonferrous product of shredded automobiles, relatively quiescent vessels can be used. For separation of finer particles, the application of a second force (e.g., centrifugal force) may be required to hasten the process and sharpen the density difference.

Gaseous and Liquid Emissions

Inorganic membrane modules composed of cordierite honeycomb monolith coated with a microfiltration membrane (e.g., Al_2O_3) and vanadium-based catalysts could be used to remove SO_2 from flue gas. The use of oxygen, as opposed to air, for combustion could decrease gaseous emissions. The principal attraction of oxy-fuel is its intrinsic low NO_x attributes compared with conventional fuel-air burners. However, the relatively high cost of oxygen remains a significant barrier, and lower-cost, hot oxygen would greatly facilitate the implementation of oxy-fuel systems. In addition, the use of oxygen for combustion results in energy savings because it eliminates the need to heat the nitrogen component of air.

SUMMARY

The separation needs identified for the steel industry are as follows:

- more efficient recovery of VOCs and better separation of fine particulates from gases in coke production
- better recovery and reuse of quench water in coke production
- separation processes for improving the chemical and physical quality of iron-bearing materials for blast furnace feed
- improved methods of removing impurities, particularly nitrogen and phosphorus, from steel in both oxygen and EAF steelmaking
- improved methods for handling, recycling, and recovering valuable materials from BOF dust
- improved methods for recovering metallic iron from BOF slag
- improved methods for handling EAF dust and technologies for partially recovering the zinc portion and recycling the iron-rich portion of the dust
- improved understanding of the mechanisms that separate inclusions from liquid steel, including transport of the inclusion to the metal-slag interface and dissolution or incorporation of the inclusion into the liquid slag
- better separation methods for dealing with copper and other residual impurities in scrap
- separation processes to produce very high grade DRI feeds
- better understanding of the behavior of fine particulates in gaseous or liquid media

7

Metal Casting Industry

The U.S. metal casting industry ships approximately 13 million tons of castings annually, valued at more than $23 billion (OIT, 1997c). Ferrous metal castings account for 85 percent of the tonnage (valued at $12.2 billion), and nonferrous metal castings, primarily of aluminum, account for the remaining 15 percent (valued at $7.8 billion) (American Metal Casting Consortium, 1995). The metal casting industry, which employs approximately 210,000 workers, is dominated by small businesses. Of the 3,100 metal casting establishments in the United States, 80 percent employ fewer than 100 workers (OIT, 1997c). The metal casting industry uses 0.25 quadrillion Btus of energy per year.

SEPARATION NEEDS

Mould Production

The use of sands to make moulds and cores is nearly universal in the metal casting industry. A pattern (often made of wood) is used to make the mould, which establishes the external shape of the metal casting. To make a sand mould, clean sand is mixed with small amounts of hydrophilic clay, usually bentonite, and pulverized coal. Water is added to facilitate handling, and the mixture is placed in two boxes called the "cope" and the "drag." The pattern is then used to transfer the desired external shape of the metal casting in the packed sand in the cope (top of the casting) and the drag (bottom of the casting). The two boxes with the pattern impression constitute the mould.

The core is the interior piece of the mould needed to make hollow castings. In the core room of a metal casting facility, new sand is mixed with resin and sometimes a catalyst and formed into the core. The core is then placed in the mould, and the two mould boxes are assembled into a "flask" ready for casting.

In the mould production process for investment casting, a wax pattern is repeatedly dipped into ceramic slurry and coated with dry ceramic grit until the mould is of adequate thickness. The mould is then dried via water evaporation before it can be used. Drying is the rate-limiting step for this kind of mould production, and the metal casting industry would benefit from a separation technology that reduced drying time in investment casting mould production (Carter, 1997).

Casting Production

During casting, molten metal is poured into the mould. The flask is then set aside to cool. In the shake-out house, when the metal casting is solid but still hot, it is removed from the mould. After further cooling, the casting is transferred to the cleaning room where remnants of the core are removed. The metal casting that comes out of the mould includes metal that was cast into the "gates" (openings through which molten metal reaches the mould and through which gases are vented) and "risers" (reservoirs from which metal flows into the casting as it cools and contracts). The gates and risers are excess metal and comprise between 5 and 50 percent of the casting. They must be removed either mechanically or by hand.

During the mould production and casting production operations, dust is created. Most metal casting operations have dust control facilities to maintain high-quality ambient air, but disposal of the captured dust is a problem. Better dust removal technologies would benefit the industry as a whole.

Removal of Impurities from Molten Metal

Both ferrous and nonferrous metals are melted in furnaces prior to casting. Removal of impurities from the molten metal is an important separation issue for the metal casting industry. Technologies currently used include the addition of deoxidants, usually silicon or aluminum, and the addition of magnesium to certain alloys for the removal of oxygen and sulfur. Improved, cost-effective technologies to remove impurities from molten metal would be of great interest to the metal casting industry.

Gas inclusions, caused by gases given off during casting, are often found in the gates and risers removed from mould castings. These impurities increase the difficulty of recycling foundry-generated scrap. Methods for preventing or minimizing gas inclusions in castings would be beneficial to the industry.

Upgrading Scrap

Separation issues for the metal casting industry include the handling of foundry and nonfoundry scrap. Gates and risers removed from metal castings can sometimes be cleaned and returned directly to the furnace, but gas inclusions often limit their recyclability. Specific impurity levels determine which pieces can be reused directly and which pieces must be diverted to other products or re-alloyed and refined. Methods for efficiently and cost effectively separating gate and riser scrap by impurity level would be beneficial to the industry.

With few exceptions, foundries must have a reasonable idea of the composition of scrap in order to use it. Limitations are imposed by the scrap required quality and the cost of scrap separation. Each foundry would prefer to use only scrap produced in that foundry, but this is not generally possible.

Scrap separation is accomplished in a number of ways. The best and most cost-effective method is segregation of different scrap types by the scrap generator. With this method, different types of scrap are never mixed together in the first place, and foundries have clean scrap of known composition to reuse. Some facilities, such as large iron foundries and smaller specialty foundries, have on-site scrap separation facilities. Others, such as smaller metal casting operations that compete in more generalized markets, do not have the financial resources to operate their own separation facilities. These operations depend on intermediary scrap processors who separate and segregate scrap for resale. Separation processes used at these facilities include hand sorting, identification by visual or chemical means, magnetic separation, and eddy current separation. Currently, only the most valuable metals are separated (Carter, 1997). More economical and efficient means of separating nonfoundry scrap would increase the industry's ability to recycle scrap.

Sand Reclamation

Sand is the material most commonly used for making moulds in the metal casting industry. More than 10 million tons of sand are used for this purpose annually in the United States. The reclamation of spent sand is a function of the type of sand, its relative value, the additives mixed in with the sand, and the process it has undergone. The most widely used sand is silica, and high-silica sand is easy to reclaim. "Lake sand" from the Great Lakes region can be cheap, if locally available, but it contains carbonates and other minerals that make it more difficult to reclaim. High-value sands, such as zircon and chromite, are almost always reclaimed.

The core room of a metal casting facility is the source of about 20 percent of spent sand, which originates from rejected cores and spillage. This sand poses a serious separation problem because it is often contaminated with resins and other chemicals. Some core room sand is currently reclaimed using dry attrition scrubbing with dust removal and thermal treatment to burn or volatilize the organic binders. Wet scrubbing, although more efficient, is used less frequently because of the difficulty and cost of drying the sand and dewatering the scrubber sludge prior to disposal. Improved technologies for drying sand and dewatering sludge would increase the metal casting industry's ability to reclaim core room sand (Wood, 1997).

The shake-out house, where castings are removed from moulds, is the source of approximately 50 percent of spent sand from metal casting operations. This spent sand is a mixture of clay-bonded mould sand and resin-bonded core sand. During the casting process, most mould sand is dried but otherwise remains unchanged. The thin layer of clay in contact with the molten metal, however, is calcined from the heat. Spent mould sand that has undergone casting therefore contains calcined clay that must be removed before reuse. Like core room sand, spent mould sand can be reclaimed using dry attrition scrubbing with dust removal. Wet scrubbing is used less frequently because of drying and dewatering problems.

Core sands are typically mixed with resins that act as binders to ensure that the shape of the core is maintained during casting despite pressure from the molten metal. Many different binders are used, and these are generally oxidized or volatilized by the heat of the casting process. If the binders are not destroyed during casting, they leave behind adherent residues that can complicate core sand reclamation. Better methods for reclaiming spent sand from the shake-out house would be beneficial to the industry.

Most sand that is reclaimed originates in the shake-out house. Shake-out sand is first subjected to lump-breaking. Metals and coarse pieces are removed using magnets and screens. Some of this sand is reused directly. Because spent mould sand cannot be used to make cores, however, reclaimed sand from the shake-out house combined with sand from the core room gradually results in a build-up of excess spent sand. Some spent sand, whether contaminated or not, must therefore be discarded to a landfill.

The remaining 30 percent of spent sand from the metal casting industry originates in the cleaning room. Currently, reclamation of this sand is not attempted. Sand is removed from metal castings primarily by shot blasting. During this process, metal flashing is removed along with sand, and some metal is smeared onto sand surfaces. In addition, metal may be abraded from the casting and become mixed in with the spent sand. Finally, sand grains may be broken into finer particles, sometimes changing the size distribution of the sand from that desired. Available sand reclamation technologies still leave too much contaminated material, which must be discarded. Cost-effective and efficient methods for reclaiming cleaning room sand would, therefore, be beneficial to the industry.

Gaseous and Aqueous Emissions

The metal casting industry faces problems of gaseous and aqueous emissions similar to those faced by the aluminum and steel industries, but on a lesser scale.

Because most foundries are small businesses, the volume of emissions is lower. However, the industry needs improved methods for removing specific components from melting and refining process emissions, for separating fine particulates from gases and liquids, and for dewatering sludge.

SEPARATION TECHNOLOGIES

Sand Reclamation

Better characterization of the surface chemistry of sand and additives would improve the industry's ability to reclaim sand. Methods for low-temperature oxidation or separation of binders would improve the industry's ability to reclaim core room sand that has not been through the casting process. Methods of curing or solidifying organic binders would also be beneficial.

Gaseous and Aqueous Emissions

As for the aluminum and steel industries, inorganic membrane modules composed of cordierite honeycomb monolith coated with a microfiltration membrane and vanadium-based catalysts could be used for removing SO_2 from flue gas, and oxygen-based combustion could lower emissions of NO_x. Advances in membrane technology and lower-cost oxygen production would therefore benefit the metal casting industry.

SUMMARY

The following separation needs were identified for the metal casting industry:

- technologies to reduce the drying time of investment casting mould production
- better dust removal technologies
- improved technologies to remove impurities from molten metal
- methods for preventing or minimizing gas inclusions in gates and risers
- methods for efficiently and cost-effectively separating gate and riser scrap by impurity level
- economical and efficient means of separating nonfoundry scrap
- better methods for reclaiming core room sand (contaminated with resin and other chemicals), including improved sand drying and sludge dewatering technologies

- better methods for reclaiming shake-out house sand (contaminated with calcined clay and metal pieces)
- cost-effective and efficient methods of reclaiming cleaning room sand (sand with metal smears and a changed size distribution)
- lower cost oxygen for oxy-fuel burners
- better methods for removing specific components from gaseous and liquid emissions

8

Glass Industry

The glass industry has four major segments. The container glass segment produces glass packaging products, such as bottles and jars. The flat glass (or float glass) segment produces windows for residential and commercial construction, automobile windshields, mirrors, instrumentation gauges, and furniture, such as tabletops and cabinet doors. The fiberglass segment is composed of two distinct subindustries: building insulation (glass wool); and textile fibers used to reinforce plastics and other materials for the transportation, marine, and construction industries. The specialty glass segment produces handmade glass, tableware and oven-ware, flat panel display glass, light bulbs, television tubes, fiber optics, and scientific and medical equipment. Much of this segment relies on high technology research to create new and profitable materials.

The U.S. glass industry annually ships 21 million metric tons of products worth more than $20 billion. Container glass accounts for 12 million tons, flat glass for 4.3 million tons, pressed and blown glass for 3.5 million tons, and glass wool insulate for 1.7 million tons. The industry employs 250,000 workers nationwide (OIT, 1997c). Energy consumption by the glass industry is approximately 0.4 quadrillion Btus per year.

SEPARATION NEEDS

Melting and Fining

All commercial glasses are based on silica. Other major oxide constituents include boric acid, alkali, alkaline earths, and aluminum oxide. Depending on the characteristics of the finished product, numerous other oxides may be added. For many types of glass, 20 to 40 percent cullet (waste glass) is added. Cullet requires approximately 10 percent less energy to heat to the molten state (compared with virgin raw materials) and increases the efficiency of the melting process, thereby conserving energy. The use of cullet also reduces waste and raw material costs.

During the melting and fining process, raw materials are melted, gaseous impurities are removed from the molten glass, and chemical reactions occur to form the final glass compound. The major separation issue for this process is air emissions. As raw materials are fed into the furnace, volatile compounds in the raw materials and molten glass are released, and gases, such as nitrogen oxides, are formed. These gases entrain sulfur oxides and alkali ions, which are vaporized and carried out of the system. Fine particulates, ranging in size from 0.1 to 5 μm, are generated from raw material dust and volatile condensates (e.g., sulfates and borates). Approximately 0.5 to 2 pounds of particulates are produced per ton of glass.

These gases and fine particulates are difficult to collect, especially the fine particulates at higher temperatures. Methods currently in use include aqueous emission control devices, electrostatic precipitators, high energy scrubbers, baghouse filters, and selective noncatalytic reduction. Unfortunately, these air pollution control devices produce solid waste residue, wastewater, and/or require large amounts of energy. Some captured material (e.g., sulfates, borates) can be processed for recycling into the batch charge. Better methods for the separation and capture of gases and fine particulates at high temperatures would benefit the glass industry.

Another separation problem associated with the melting and fining process is the removal of glass from spent refractory materials. This is of particular concern when a high-lead glass has been melted in the furnace. An economical method of removing glass from furnace refractories would facilitate the recycling of these materials.

Recycling of Cullet

After leaving the furnace, molten glass for producing containers is mechanically formed by mold blowing, pressing, or casting. Once the glass is shaped, it is placed in an oven for controlled cooling or annealing, after which it is inspected and prepared for shipment. Damaged or defective glass is reused as in-house cullet. Lubricating oils used during the forming process, however, can cause problems with the quality of in-house cullet. These oils may leach from cullet piles, thus contaminating water, or they may increase particulate formation in the furnace. A method of separating lubricating oils from in-house cullet would be beneficial to the glass industry.

Manufacturers of glass containers are large users of postconsumer cullet; more than 2.5 million tons were purchased in 1996. The quality of postconsumer cullet is a problem because most municipal collection systems do not sort glass by color, and the cullet contains numerous contaminants, such as dirt, gravel, paper, plastic, metal, and ceramics. Noncontainer glass, such as window panes, mirrors, light bulbs, drinking glasses, ovenware, and glass ceramics, is also a problem because it cannot be used to make container glass. Even a small percentage of contaminants can result in defective glass and can damage glass manufacturing equipment (GPI, 1997). The glass industry needs more efficient and cost-effective methods for sorting contaminants from postconsumer glass and for sorting different glass compositions from each other.

Once cullet has been sorted by composition and contaminants have been removed, the cullet must be sorted by color. The color purity required depends on the color of the glass being produced. For example, cullet used to produce green glass must contain less than 4 percent mixed glass, cullet used to produce brown glass must contain less than 2 percent mixed glass, and cullet used to produce clear glass must contain less than 1 percent mixed glass (GPI, 1997). The glass industry needs more efficient and cost-effective methods for separating cullet by color. Cullet is generally crushed before it is mixed with raw materials for melting. Separation methods to remove grinding media from ground glass particles would facilitate the recycling of cullet and the reuse of grinding materials in finishing and polishing operations.

Fiberglass Recycling

Fiberglass manufacturers can use glass cullet that has not passed inspection for the container recycling industry. Currently, between 10 and 40 percent of the raw materials used by fiberglass insulation manufacturers is recycled glass. The fiberglass sector is the largest secondary market for postconsumer and industrial waste glass, using approximately 870 million pounds in 1993. Research is needed, however, to facilitate the recycling of fiberglass itself. An important separation issue for this segment is the removal or dissolution of organic coating materials on glass insulation fibers, which interferes with traditional melting technologies.

Specialty Glass

The production of specialty glasses often requires the use of solvents, such as acetone or acrylics, that end up in wastewater streams. Methods of separating solvents from wastewater would be beneficial to the specialty glass industry.

The reuse of cullet is also problematic for the specialty glass industry because the low volume of many specialty products does not justify recycling. Nevertheless, some parts of the industry are looking into the possibilities of recycling. The television glass industry, for example, is making efforts to recycle glass from used television sets and computer monitors. For this segment of the industry, separation issues include techniques for economically separating lead frit and lead funnel glass from nonlead panel glass.

SEPARATION TECHNOLOGIES

Cullet Sorting and Recycling

The optical properties of materials, such as their color, induced fluorescence, and refractive index, can be used as a means of separation. A number of technologies already exist for improving the quality of cullet. Contaminants, such as paper, plastic, and metals, can be removed by hand picking, screening, and nonferrous metal separation techniques. Ceramics can be identified by an optical ceramic sorter, which uses infrared light to detect the ceramic's opacity, and separated from the cullet by air jets. A similar technology is used for separating cullet by color. Once materials are identified, the identification can be used to trigger pulsed air jets and physically separate them. Improvements to this technology would include increasing the hourly volume to make the process more cost-effective.

Gaseous Emissions

Oxygen has replaced air in a growing number of commercial combustion applications. Oxygen burns without producing significant amounts of nitrogen oxides, generates substantially fewer particulates, and can lower the quantity of natural gas used by as much as 25 percent. However, oxygen is more expensive than air and can cause hot spots in the melt, possibly damaging refractory materials. Oxygen is also more reactive than air and, therefore, more difficult to preheat. Research on lower cost methods of producing pure oxygen, methods of avoiding hot spots, waste heat recovery, and pretreating technologies would reduce emissions.

Better Understanding of Glass Processes

According to OIT's glass industry road map, cleaner processing will require improved sensors, measurement devices, instrumentation, and control technologies. Improving the environmental performance of current technologies will also require a better understanding of the fundamental mechanisms and chemistries of the glass manufacturing process. For example, the industry needs a better understanding of the formation and fate of emissions in current melting and refining technologies (Energetics, Inc., 1997).

SUMMARY

Separation needs for the glass industry include:

- better methods for the separation and capture of gases and fine particulates at high temperatures
- economical methods of removing glass from the surface of furnace refractories
- methods of separating lubricating oils from in-house cullet
- more efficient cost-effective methods for sorting nonglass contaminants from postconsumer glass
- methods of separating different types of glass, such as flat glass (e.g., soda lime) and container glass (e.g., borosilicate, pyroceramic)
- more efficient and cost-effective methods for separating cullet by color
- technologies to separate ground glass particles from grinding media
- techniques for the removal/dissolution of organic coating materials on glass insulation fibers to allow glass to be recycled
- techniques for separating solvents from wastewater streams
- techniques for separating lead frit and lead funnel glass from nonlead panel glass

9

Forest Products Industry

The U.S. forest products industry comprises both the pulp and paper industry and the wood products industry. In 1993, pulp and paper industry products were valued at $247.4 billion, and wood products were valued at $103.6 billion (U.S. Department of Commerce, 1994). The forest products industry as a whole employs more than 1.4 million people and is one of the top 10 manufacturing employers in the United States (AFPA, 1994a). The annual energy consumption of the forest products industry is about 3 quadrillion Btus, and its hazardous waste production is about 219 thousand tons (U.S. Environmental Protection Agency, 1993).

SEPARATION NEEDS

The pulp and paper industry is highly capital intensive, with a new integrated mill costing about $1 billion (AFPA, 1994a). Research and development on new separation processes must, therefore, be targeted to overcoming the barriers of capital investment and required return on investment. This industry would benefit greatly from the optimization of existing processes. Natural products, such as the wood used for papermaking, are very complex and variable. Fundamental research on the physico-chemical properties of the materials and waste streams of the forest products industry could improve existing processes with significantly less capital investment than would be required for the development of new separation processes. The multicomponent nature of all streams and materials in pulping and papermaking must be kept in mind when concepts for separation are investigated.

Pulping

Of the several pulping processes used in the United States today, the kraft pulping process is used for producing the largest volume of wood pulp (more than

80 percent) (AFPA, 1994b). The presence of contaminants at different stages of the pulping process results in a number of separation requirements. Inorganic materials not needed for the pulping process (i.e., nonprocess elements [NPEs]) include potassium, chloride, calcium, phosphorous, metals, and transition metals. An accumulation of NPEs in the pulping process can cause problems, such as scaling, corrosion, plugging of heat exchanger passages, increased use of bleaching chemicals at later stages, and problems with filtration. The forest products industry would benefit from technologies to separate NPEs from the pulping stream.

Brown-Stock Washing

During the digesting process, wood fibers are liberated from other wood components, such as lignin (Kocurek, 1983). A filtration step, called "brown-stock washing," is subsequently used to separate the wood fibers from inorganic chemicals and dissolved wood components. This is an important step for minimizing the carryover of pulping chemicals and NPEs into the subsequent bleaching operation. A better understanding of the fundamental science behind the brown-stock washing process would benefit the forest products industry. Areas of interest include fluid dynamics during washing and the mechanisms and kinetics of absorption and adsorption of organics and inorganics on wood fibers. The goal of this research would be to predict the path that a given organic or inorganic material would take under different process conditions, which could lead to optimized operation protocols for existing washers and presses; new, more efficient, low-cost washing processes; and a better understanding of how the behavior of NPEs is affected by changes in process conditions, such as temperature and concentration.

Black Liquor

Black liquor is the effluent stream that contains the unwanted components of wood (mostly lignin) and the majority of spent inorganic chemicals. This effluent must either be disposed of or reused. Currently, the inorganic components of black liquor are recovered via thermal oxidation in a kraft recovery furnace. The organic components are burned and their fuel value is recovered in the production of electrical energy and steam. The recovery furnace is an example of a separative reactor where sulfates are reduced to sulfide and discharged as an inorganic smelt, together with carbonates. Organic carbon is simultaneously oxidized to CO_2 and discharged with the flue gas.

Alternatives to the kraft recovery furnace are under development. These alternatives, which involve adding incremental black liquor processing capacity to existing operations, may ultimately replace the kraft recovery furnace with more efficient technology. A major challenge for some of these alternative technologies is the removal of sulfur and other compounds from hot gases that are to be used in the gas turbines (Larson and Raymond, 1997).

A better understanding of crystallization and precipitation from multicomponent aqueous inorganic solutions, or from mixtures of inorganics and organics in water, could increase the efficiency of NPE removal. Black liquor, for example, is an aqueous organic/inorganic mixture with multiple interactions between the organics and inorganics. One significant area for research is the highly complex scaling behavior of black liquor as it is concentrated in evaporators to obtain solids for firing in the recovery furnace (Frederick and Grace, 1979). As a result of recent changes in digester technology, scaling problems in multiple-effect evaporators have increased. Scaling problems could potentially be controlled if the physical chemistry of the system were understood better. The goal would be to achieve benign NPE purge streams with NPEs in a form that could be discharged directly to the environment, sold as by-products, or used as raw material for other industries (e.g., potassium for fertilizers).

Low Effluent Conditions

The pulp and paper industry is facing new challenges as a result of the need to recycle, rather than discharge, water. Inorganics, replacement chemicals, and recycled effluents from the bleaching and papermaking processes increase in concentration in the liquor cycle unless selective purges are used (Ulmgren, 1997). Figure 9-1 illustrates the path of one NPE, chlorine, in the liquor cycle. If efforts are made to decrease water use by minimizing or eliminating the effluent streams that serve as purges, this concentration may be increased. For example, reducing the effluent from kraft pulping has led to significant problems in controlling sulfidity (the sulfide/hydroxide balance in the wood-digesting liquor). The solution to this problem will require robust methods for separating sulfur compounds from liquor streams. The same technology would be useful for obtaining liquors with different sulfidities for the kraft cooking process. Some alkali-insoluble elements (green liquor dregs) in the liquor cycle can be purged with existing purge streams if the settling process currently used is executed efficiently or if one of the newer available technologies, such as pressure filters, is implemented. However, the removal of alkali-soluble elements, such as potassium and chloride, will require new selective purge methods.

Bleaching

Some types of wood pulp undergo bleaching processes to remove additional lignin and brighten the pulp. These bleaching processes produce effluent that can be detrimental to the environment. In an effort to reduce effluent from bleaching processes, wastewater is recycled countercurrently through the process and reused for brown-stock washing. One problem with this, however, is that bleach effluent is thus introduced into the kraft chemical recovery process where it can cause problems.

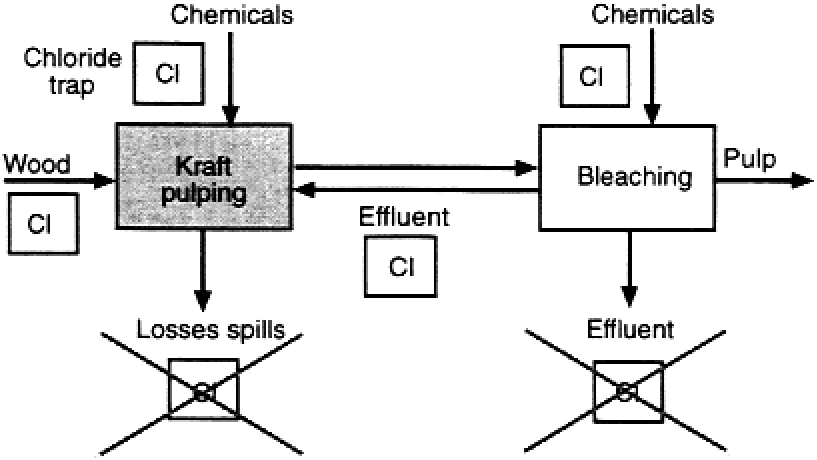

Figure 9-1
Schematic illustration of bleached pulp production emphasizing chlorine, a nonprocess element (NPE).

Currently, the high-pH portion of the bleach effluent, which carries some dissolved inorganics and the majority of organics extracted during the bleaching process, can be recycled successfully and the organics incinerated in the kraft recovery furnace. In newer systems, the bleach effluent with the highest content of inorganics is produced after the first bleaching stage, which uses chlorine dioxide (Vice and Carroll, 1998). This effluent is acidic and contains substantial amounts of dissolved organics, NPEs (e.g., chlorides, metals, and transition metals), and small amounts of suspended solids (e.g., fibers). The industry would benefit from methods for removing inorganic contaminants from bleach effluent before it is recycled to the brown-stock washing and kraft chemical recovery processes. The organic contaminants could then be thermally destroyed in the recovery furnace and problems arising from inorganics entering the recovery process could be avoided.

Methods for dewatering bleach effluent, other than evaporation, would also be beneficial. If the organics in the effluent could be concentrated, they could be incinerated in the kraft recovery furnace and the remaining effluent could be treated and discharged directly to the environment.

Hazardous Air Pollutants

The forest products industry would benefit from separation technologies to decrease emissions of methanol and other VOCs from pulping and bleaching processes (Pinkerton, 1998). Methods of separating VOCs listed as hazardous air pollutants from both wet air streams and aqueous streams are of great interest to the industry. If environmental regulations regarding gaseous and vapor emissions are significantly tightened in the future, hazardous air pollutants will have to be separated from the pulp before it reaches the paper machine to avoid releasing them in dilute form via gaseous or aqueous streams, from which they will be much more difficult to remove. Research is therefore needed on the basic behavior of VOCs in process equipment and on separation methods that can be combined with modifications to existing pulping and bleaching processes (Rezac, et al., 1996). If hazardous air pollutants could be removed earlier in the bleaching process, when they are highly concentrated, the high cost of installing systems to remove these pollutants from dilute effluent streams could be avoided.

Papermaking

In the papermaking process, a thin layer of cleaned, bleached, and diluted wood pulp is applied to a rapidly moving fine mesh belt. Water is removed from the wood pulp, first by mechanical means and then by evaporation. The mechanical means used for water removal include application of a vacuum by various means, and pressing. These processes extract most of the water and interlace the fibers to form a paper sheet (Sell, 1992). The resulting wastewater stream contains dissolved organics, papermaking additives, and inorganic salts. When the rate of water discharge is high, dissolved materials are continuously removed from the system and do not cause problems. Efforts to reduce water discharge can result in both organic and inorganic contaminants building up in processing equipment and causing problems, such as scaling, corrosion, and poor product quality. The industry would benefit from separation processes to remove dissolved organics and inorganics continuously from papermaking process water under low effluent conditions. Because mechanical water removal methods cannot remove water to the low level needed, the final stage of papermaking includes water removal by evaporation. Evaporation, however, is a slow process, and more efficient methods for removing water would be welcomed by the industry.

Paper Recycling

Currently, 40 percent of the paper used in the United States is recovered for recycling (AFPA, 1994a). In-house waste paper and postconsumer paper can both be recycled. Postconsumer paper, which must be collected and transported to recycling plants, has a higher level of contaminants than virgin wood pulp and must be more thoroughly cleaned before it can be reused for papermaking. After the initial, coarse cleaning, an aqueous stream is produced containing wood fibers, small amounts of dissolved organics and inorganics, and suspended contaminants, such as adhesive residues, waxes, inorganic fillers, and the polymeric inks used in xerography and laser printing. If these suspended contaminants remain in the recycling stream, they can cause deposits, scaling, and faults in the final paper product. Centrifugal cleaning, screening, and flotation are all currently used to improve the quality of the recycled fiber furnish.

Removal of suspended contaminants from recycled fiber furnish is challenging. Fiber loss must be minimized to avoid problems with sludge disposal and recycling efficiency. Density-and size-based separation processes are of limited use because the density difference between contaminants and fibers is insignificant and the size distribution of the contaminant is too broad. Flotation is sometimes used, but the fluid dynamics and physical interactions of gas bubbles and suspended and dissolved materials often result in high fiber losses (up to 20 percent). Research into methods of optimizing the removal of suspended contaminants in recycled fiber streams, as well as efficient and cost-effective separation processes to separate contaminants from wood fibers, would be of great interest to the forest products industry.

Lumber

The main output of the wood products sector of the industry is lumber. Lumber is typically dried in kilns using steam as a heat source. A significant quantity of VOCs is released from the wood during this drying process. The industry would benefit from technologies for the cost-effective capture of VOCs for disposal or reuse and from drying strategies that either minimize the release of VOCs or generate waste streams sufficiently concentrated so that they can be treated easily.

SEPARATION TECHNOLOGIES

Pulping Streams

The technologies that would be most effective for separating NPEs from pulping streams are based on physical or physico-chemical methods. Technologies with the potential to remove inorganics and alkali-soluble elements, such as potassium and choride, from pulping streams include ion exchange, electrodialysis, and crystallization. Gas separation membranes and absorption or adsorption technologies are promising methods for removing sulfur and other compounds from black liquor gasification effluent gases intended for use in gas turbines.

Bleach Effluent

Potential technologies for separating organics from bleach effluent streams include recent advances in membrane materials, which may be able to separate and concentrate the organics so that they can be incinerated and the remaining effluent discharged to the environment. Alternatively, if inorganics were removed from the bleach effluent, the remaining effluent could be incinerated. Ion exchange, electrodialysis, and crystallization are separation technologies with the potential for removing inorganics from bleach process effluent streams.

Inorganics and Organics in Effluent Streams

Membrane vapor permeation, adsorption, and biological remediation are promising technologies for the removal of VOCs from wet air streams and aqueous effluent streams. Filtration, membrane filtration, electrodialysis, and precipitation could be developed for the continuous removal of dissolved organics and inorganics from paper machine process water.

Removal of Contaminants from Recycled Fiber Streams

Research into flotation mechanisms, surface chemistry, and custom chemistries for specific contaminants may improve the removal efficiency for suspended and dissolved contaminants in the recycled fiber stream. Overall, a focus on underlying principles, rather than on optimized solutions for special cases, would be most effective.

Drying

Impulse drying has the potential to be a more efficient at removing water from the papermaking process than evaporation. Biological beds represent a potential technology for the cost-effective capture and disposal or use of organics from lumber drying processes. In addition, the industry would benefit from drying strategies that minimize the release of organics or generate concentrated streams that can be treated easily.

SUMMARY

The forest products industry has a variety of separation needs including the following:

- separation of inorganics in pulping streams
- separation of alkali-soluble elements, such as potassium and chloride, from the kraft liquor cycle

- improvements in the basic understanding of crystallization and precipitation from multicomponent aqueous inorganic solutions and mixtures of inorganics in water
- fundamental research on brown-stock washing, including fluid dynamics and the kinetics of absorption and adsorption of organics and inorganics on wood fibers
- separation of sulfide compounds from liquor streams (sulfidity control, split sulfidity, kraft cooking)
- removal of contaminants (e.g., sulfur compounds) from hot gases from black liquor gasification
- removal of inorganic contaminants from bleach effluent
- removal of VOCs from wet air streams and aqeous streams
- research into the basic behavior of VOCs in process equipment (equilibrium and nonequilibrium)
- separation processes to remove dissolved organics and inorganics continuously from closed-cycle paper machine process water
- separation concepts for VOCs that may combine separation processes with modifications of existing pulping and bleaching processes
- optimization of the removal efficiency for suspended and dissolved contaminants from the recycled fiber stream
- cost-effective capture and disposal or use of organics from lumber drying processes or drying strategies that minimize release or generate concentrated streams

10

Cross-cutting Issues for the Materials Processing Industries

INTRODUCTION

The materials processing industries have extremely diverse needs for separation technologies. However, the panel identified seven issues that are common to two or more of the materials processing industries described in this report. These are: removal of impurities from feedstock; metal purification; separation of scrap; prevention of gas inclusions; separation of components from dilute gaseous streams; separation of components from dilute aqueous streams; and water remoral. In addition, the panel identified one technology area with the potential to meet some of these needs and three enabling technologies.

COMMON NEEDS

The removal of impurities from feedstock is an important issue for the aluminum and steel industries. The removal of impurities from alumina feedstock minimizes the need for metal purification at later processing stages. Improving the quality of iron-bearing materials for blast furnace feed and DRI feed is important to the steel industry.

Metal purification is important for the aluminum, steel, and metal casting industries. The purity of molten metal is important for the aluminum industry because almost all other metals are more noble than aluminum, and once an impurity is introduced into the melt, it is almost impossible to remove it. Removal of nitrogen and phosphorus from steel during steelmaking is an important separation issue for the steel industry. The metal casting industry would benefit from improved methods of removing impurities from molten metal.

Sorting scrap materials is important for the aluminum, steel, metal casting, and glass industries. For the aluminum industry, energy savings can be obtained by melting scrap instead of raw materials. Improved scrap sorting can also lead to improved metal purity. The steel industry needs better methods for removing copper and other impurities from shredded automobile scrap. The metal casting industry would benefit from efficient and cost-effective methods of separating gate and riser scrap, as well as nonfoundry scrap. Recycling by the glass industry would be improved by better methods of sorting nonglass contaminants from postconsumer glass, different types of glass from each other, and different colored cullet. The glass industry would also benefit from technologies for separating glass particles from grinding media and technologies for separating lead flit and lead funnel glass from nonlead panel glass for recycling.

The prevention of gas inclusions is important for the steel and metal casting industries. The steel industry would be helped by a better understanding of the mechanisms of separation of inclusions from liquid steel. The metal casting industry would benefit from improved methods for preventing or minimizing gas inclusions in gates and risers.

Separation of components from dilute gaseous streams are important for all of the materials processing industries. For the aluminum industry, increasingly stringent regulations on emissions from several processes used to produce aluminum have made this a necessity. In the steel industry, the recovery of VOCs and particulates from gases in coke production is an important separation issue. Better methods for capturing gases and fine particles at high temperatures would benefit the glass industry. The forest products industry needs separation technologies for better separation of the contaminants from the hot gases produced in black liquor gasification and of VOCs from wet air streams.

Separation of components from dilute aqueous streams are an issue for all of the materials processing industries. The aluminum industry needs better separation methods, particularly for the Bayer process. In the steel industry, the recovery and reuse of quench water from coke production is an important consideration. The glass industry would benefit from methods of separating solvents from wastewater streams. The forest products industry needs improved technologies for the separation of inorganic contaminants from bleach effluent streams, VOCs from aqueous streams, and dissolved organics and inorganics from paper machine process water.

Water removal is an important issue for the aluminum, metal casting, and forest products industries. Improvements are needed in water removal from the Bayer process used by the aluminum industry. In the metal casting industry, reducing the drying time of investment casting moulds is an important consideration. In addition, the reclamation of core room sand would be improved by better drying of sand and dewatering of sludge. The forest products industry would benefit from technologies to optimize the removal of suspended and dissolved contaminants in the recycle fiber stream, better paper drying methods, and lumber drying strategies that minimize the release of organics or generate concentrated streams of organics that can be treated easily.

SEPARATION TECHNOLOGIES

Methods of Separating and Sorting Solids Based on Physical Properties

The panel identified one separation technology with the potential for meeting a number of the cross-cutting needs of the materials processing industries. The aluminum, steel, metal casting, and glass industries each identified separation needs that could be classified as materials handling and sorting or separation methods based on the physical properties of components. In many cases, the analytical technology has already been developed, and scrap separation processes are in place. In order to make these processes more economical, a higher speed sorting technology, such as the current air jet and conveyer belt technology, must be further developed. In other cases, the analytical technology has not been developed yet. Separation based on physical properties is an area of research and development where similar technologies could benefit these four industries.

This family of separation methods is based on the classical physical properties of solids, such as magnetic and electrical properties, densities, and melting points. A number of these techniques are already being used, and refinements of existing techniques are commonplace. These processes are often part of the process flow of an industrial operation.

Separation Processes Based on Melting Points

Separation processes based on melting points are one example of separation methods based on physical properties. Sweat furnaces have been used in the scrap processing industry for many years for separating metals according to their melting points. The sweat furnace operates at a temperature at which one metal is selectively melted from a component, leaving the metal with the higher melting point, usually a ferrous metal, as a recoverable solid. Incipient melting of one phase in an alloy mixture has also been used as a means of separation.

Separation Processes Based on Gravity

As the name implies, the force of gravity comes into play in all gravity separations, but only one relies entirely on gravity. In this case, particles of different densities are separated in a medium of intermediate density. Depending on the densities of the particles, the medium can range from water to solutions denser than water to suspensions of fine, heavy particles in water. In practice, solutions of salts, such as calcium chloride and various bromides, have been used to a limited extent because of recovery problems and the consequent costs. Water is used as the medium if one of the particles floats; many useful separations are actually done in this way. True "heavy liquids," such as thallium malonate/ formate solutions, are used for analytical separations, but they are much too expensive and toxic to be used industrially.

For separations of particles heavier than water, suspensions of fine solids can be used: magnetite and ferro-silicon are commonly used because their suspensions can be reconstituted by magnetic separation. In use, these suspensions must be agitated to prevent or limit settling of the medium. For separations of coarse particles, such as metals from the nonferrous components of shredded automobile scrap, large, relatively quiescent vessels can be used, but finer separations may require a second force, often a centrifugal force, to hasten and sharpen the density difference. Coal cleaning is probably the largest and most highly developed use for this "dense media" technology.

Air separators take advantage of the fact that very light particles, even though they are heavier than air, can be swept aside by a current of air flowing normally to the suspended stream. Ancient farmers took advantage of this phenomenon to winnow their grain; highly developed machines are now available that can effect a wide variety of air-induced separations, including heavy from light metals (e.g., lead from aluminum in scrap processing). Obviously, materials to be air-separated must be dry.

Throughout history, water has been the most common separation medium, even though the particles being separated may be heavier, sometimes much heavier, than water. When an assemblage of particles is allowed to settle freely in water, they tend not to separate cleanly according to density because mass and shape come into play. When the settling assemblage reaches a certain density, a condition of "hindering settling" is reached, and separation according to mass and shape then becomes possible. If the bulk material is then shaken or dilated rapidly, it is possible to segregate particles and separate the coarse and fine particles of the denser constituent in a single product. This principle was known in antiquity; today the machines that do it are called "jigs."

Another phenomenon observed and used in ancient times was the behavior of particles being carried in traction by a flowing stream. Early peoples developed smooth stone tables on which fine particles of metal-bearing ores could be separated in a thin film of flowing water, and, in due course, they learned to flit the tables and direct some of the water across the flowing stream. Eventually, impediments to the flow called "riffles" were introduced to protect very fine heavy particles from being washed away. Ninety years ago the modern shaking table was introduced; an asymmetrical lengthwise forward and backward shaking action was added to adjustable tilt and water controls. At this stage, gravity or density differences were still operative but were not sufficient to effect a practical separation.

Flowing film separations can be made using devices that are simpler than shaking tables and have higher capacities per unit capital investment and operating cost. One of these devices, the "spiral," is essentially an open half-cylinder in a spiral shape. The device has no moving parts; particles and water flow down the spiral and are influenced by gravity flow, wash water introduced along the inside edge of the spiral, and centrifugal force, which spreads the flow out and up the curved surface. Ports located along the spiral "cut" and divert heavier materials as they are separated.

Perhaps the ultimate development of flowing film separators is the "pinched sluice," a device even simpler and cheaper than the spiral. The sluice is a simple inclined tray, wider at the bottom than at the top. Particles and water introduced at the top flow down the surface; the film spreads out and slows as it nears the bottom where cutters intercept the separated products. The sluice is usually "pinched" along its length so that the change in width is not uniform from top to bottom. This design feature accentuates the separation, but the efficiency of a single sluice is usually low, so that a succession of sluices must be used. This is not a great impediment because sluices are usually made of fiberglass or fiber-reinforced plastic and are inexpensive. An important variant of the sluice is the cone separator, which is essentially a sluice integrated through 360 degrees. Cones have very high capacities and are often used ahead of spirals or sluices to make rough, highrecovery separations.

Separation Processes Based on Magnetic and Electric Forces

Solids can be classified as ferromagnetic, paramagnetic, or diamagnetic. Relatively few are ferromagnetic, but those that are respond to magnetic force so strongly that magnetic separation is the most common and efficient method for separating them. The ferromagnetic class includes iron and most steels, some other metals, and a few minerals, such as magnetite. The separation environment can be wet or dry, and the equipment is designed to lift the ferromagnetics out of mixtures. Permanent magnets can be used, but most industrial processes employ electromagnets.

Paramagnetic materials exhibit some susceptibility to magnetic force, but it is much weaker than for ferromagnetics. This difference dictates that much stronger magnets be used and that equipment be designed to minimize the "air gap" over which the field must operate. Capacities would also be lower because the weaker forces require longer separation times. Nevertheless, paramagnetic separations are very widely used, and major advances have been made in both magnet strength and equipment design. Cryogenic magnets are being used more widely, and equipment is designed for optimally configured field gradients. A vivid example is provided by the machines used to separate paramagnetic iron minerals from kaolin slurries intended for use in making very high quality paper. The magnetic force is so weak that time must be allowed for the iron-bearing particles to overcome the drag forces of water. High gradients are achieved by using stainless-steel wool as a secondary magnet in a field generated by a powerful cryogenic magnet.

Magnetic separation does not depend on the electrical conductivity of the material being treated; in fact, many conductors are diamagnetic. Because they are conductors, some materials experience a force when passed through a variable magnetic field due to the generation of eddy currents, which are induced in conductive particles as a result of time dependent variations of a magnetic field. Eddy currents, in turn, interact with the magnetic field to generate repulsive forces, the magnitude of which are related to the conductivity, shape, mass, and size of the particles and the intensity of the magnetic field. Eddy current separators are based on either rotating disc permanent magnets or linear motor electromagnets for the generation of time dependent magnetic fields. The particles are passed through the magnetic field and physically separated according to the degree of thrust exerted on individual particles by the magnetic field. This method is now used for certain industrial separations, the separation of various nonferrous metals from the product of shredding old white goods and automobiles, for example, and the separation of aluminum cans from mixed packaging materials.

Electrical separations take advantage of charges, either natural or induced, on solid particles. In a simple form, particles passed between two oppositely charged plates are attracted or repelled according to their own charges and can thereby be separated. This technique is called electrostatic separation because the charge relationships are not changed. In electrodynamic separation, however, charged particles brought into contact with a grounded drum lose their charges at different rates and are repelled more or less strongly, which is the basis for the separation. The natural differences between discharging rates can sometimes be accentuated by treating the particles with chemical reagents or by heating, but the material being separated must be dry. Dust is also a problem, but the principal limitation of the method is that the particles must usually be fed to the drum in a layer only one particle deep.

Tribo-electrification is based on the fact that two dissimilar materials contacted or rubbed together will become charged. If one material is an insulator, it will retain its charge; if both are insulators, the retained charges will be in the order of the dielectric constants of the two. Separators based on this phenomenon are now being developed.

Separation Processes Based on Optical Properties

Optical properties of materials, such as color, induced fluorescence, or reflectivity can be used as a means of identification for separation. For example, certain metals in a mixed stream can be identified by their reflectivity and the identification used to trigger pulsed air jets that physically separate the elements of the stream. Glass can be identified by type using optical sorting based on color, coupling the identification signal to a physical method of particle separation.

ENABLING TECHNOLOGIES

The panel identified three enabling technologies that would help the materials processing industries meet their separation needs: lower cost oxygen; particle characterization; and on-line diagnostics and sensors.

Lower Cost Oxygen

Several industries, including the aluminum, steel, and glass industries, have stated that inexpensive, high-purity oxygen would be beneficial in combustion processes. As noted in Chapter 5, oxy-fuel burners are already being used in some sectors of the aluminum industry, chiefly in recycling furnaces. The attractions of oxy-fuel include low NO_x emissions compared with conventional fuel-air burners and energy savings from not having to heat the nitrogen component of air. Currently, the relatively high cost of oxygen remains a significant barrier to wider use of this technology.

Particle Characterization

Particles are ubiquitous in industrial processes and can be found as raw materials, products, by-preducts, and contaminants. The materials processing industries would benefit from improved characterizations of particles in terms of size, shape, and composition. Because of the wide range of particles, conditions, and parameters to be monitored, particle characterization encompasses a wide range of technologies.

The properties of the particle that must be characterized depend on the process and the nature of the particle. In some cases, such as precipitation reactions, the size, shape, and density of the crystals are important. Size determination, however, is exceptionally difficult when the shape of the particle varies substantially from spherical. In other cases, characterizing the particle's chemical composition may be necessary for determining its source. For settling operations, particle density becomes important. For other separation processes, surface area, electrostatic charge, surface energy, and chemical characteristics may be important. In sorting operations, for example, in the recycling of cullet for glass manufacture, particle color is critical. Finally, an enormous number of separation processes are based on crystallization or precipitation processes, many of which operate with little or no control on particle size because it is impossible to measure size or transitions in size on line.

Particle characterization has many uses for in process applications. Characterization methods must, therefore, be rugged and have response times that are appropriately rapid for the system. In some cases, such as the monitoring of particulates in stack gases, the characterization device must either withstand a harsh environment or function via remote sensing.

On-line Diagnostics and Sensors

On-line detection of the composition of material streams in separation processes would benefit all of the materials processing industries. For example, knowing the composition of molten glass in a tank would allow for real-time adjustments in composition and would increase product yield. On-line detection of inorganics, such as dissolved metals and transition metals in aqueous systems, would benefit the forest products industry.

In fact, the on-line detection of the amount, size, and shape of particles is a significant challenge for all of the IOF industries (Klimpel, 1997). Some examples are the composition of papermaking furnishes and the control of particle emissions from manufacturing and combustion. On-line detection of the composition of process streams and the makeup of individual objects in these streams is essential to the sorting and reuse of materials, such as glass and aluminum (Kenny, 1997).

Sensitive analytical procedures that can detect new species in process emissions have stimulated efforts to eliminate them. For example, recent detections of chlorinated wastes in the aqueous streams leaving pulp and paper processes have stimulated research and development on nonchlorine-based bleaching.

III

CROSS-CUTTING SEPARATION ISSUES

11

Conclusions and Recommendations

Separation processes are essential elements of the technological foundations of the seven IOF industries included in this report. For the chemical and petroleum refining industries, separation processes are used to separate and purify the products of reactions. For the aluminum, steel, and metal casting industries, separation processes are used, among other things, to purify molten metal and to sort scrap. For the glass industry, separation processes are essential to the recycling of preand postconsumer cullet, and for the forest products industry, separations are involved in nearly all process steps of pulping and papermaking. In addition to the importance of separation technologies in industrial processes, separation processes also present opportunities for waste reduction and more efficient use of energy and raw materials. New developments in separation technologies are, therefore, critical for the continued productivity and global competitiveness of these industries.

KEY SEPARATION PROCESS NEEDS

In its analysis of key separation process needs, the panel included the seven industries involved in the OIT research program at the time of the panel' s inception. These seven industries are the chemical, petroleum refining, aluminum, steel, metal casting, glass, and forest products industries. Although the panel identified a number of areas where separation issues affect more than one of these industries, the panel also concluded that they are highly diverse in terms of their separation needs and technologies and warrant individual treatment. In fact, the panel found that many important separation problems are industry-specific.

RESEARCH OPPORTUNITIES

Although separation technologies are essential to all seven industries, there are few cross-cutting research opportunities. Because of the diversity of raw materials, product forms, and processing conditions in these industries, research opportunities are mostly industry-specific. The panel, therefore, does not believe that the OIT program would be significantly more efficient if a single cross-cutting research program in separation technology were established.

However, a relatively well developed separation technology in one industry might be transferable to another industry, and a few technology areas are relevant to some, if not all, of them. The panel, therefore, recommends that the technical program managers at OIT coordinate separation research among the IOF industries, and monitor and disseminate the results. The panel identified five opportunities for coordinated programs: improved separation processes for the chemical and petroleum refining industries; bulk sorting technologies for the materials processing industries (especially aluminum, steel, metal casting, glass, and polymer recycling); separation technologies for dilute gaseous and aqueous waste streams; drying and dewatering technologies; and lower cost oxygen production. These five areas are described further below.

Separation Processes for the Chemical and Petroleum Refining Industries

The chemical and petroleum refining industries have a number of separation issues in common. In addition to general improvements in process efficiency, the panel identified two separation technology areas with the potential to meet some of the needs of both industries:

- **separation methods that use multiple driving forces**, including processes in which a naturally occurring driving force for a specific operation is enhanced by an intervention that changes the system thermodynamics or in which two or more separation techniques are coupled (combined membrane separations and distillation; affinity-based adsorbent separations; and electrically aided separations)
- **separations associated with chemical reactions**, in other words, methods that combine reaction and separation in one process step (reactive metal complex sorbents and chemically facilitated transport membranes; coupled chemical synthesis and separation processes; membrane reactors; and electrochemical methods of separation)

Bulk Sorting Technologies for the Materials Processing Industries

A number of the materials processing industries (aluminum, steel, metal casting, glass, and the polymer-recycling sector of the chemical industry) identified separation needs that can be classified as materials handling and sorting issues, specifically, high-speed scrap separation. Examples include separation of wrought from cast aluminum alloys, separation of aluminum scrap from other metals, separation of copper and other contaminants from solid steel scrap, and separations of polymers for recycling.

Research and development in this area should focus on making processes more economical. Higher speed sorting technologies, such as air jet and conveyer belt technology systems, could be developed and implemented. This is an area where several industries could benefit from research and development of the same technology, including:

- **on-line sensors for high-speed analysis** of the composition of streams and the makeup of individual objects in these streams
- **physical separation techniques,** including gravity separations (e.g., air jet separations, flowing film separations), magnetic separations, and electrical separations (e.g., electrostatic separation and tribo-electrification)
- **high-speed sorting technologies,** including the fundamental mechanics of high-speed conveying, techniques to position individual scrap pieces in sequential arrays before analysis, and methods for physically diverting the analyzed pieces by material type

Dilute Gaseous and Aqueous Streams

The panel identified the separation of components from dilute gaseous and aqueous streams as an opportunity for cross-cutting research in separations technology. All of the IOF industries identified one or both of these areas as important. Examples of separation needs regarding dilute gaseous streams include the removal of VOCs from various gases in the petroleum refining and steel industries; the removal of NO_x, SO_x, VOCs, and particulates from aluminum effluent streams; and the removal of CO_2 from O_2 combustion product exhaust streams. Examples of separation needs regarding dilute aqueous streams include: the separation of metal salts, inorganic compounds, and particulate matter from aqueous streams in the chemical industry; the removal of organics from wastewaters in the petroleum refining industry; and the removal of contaminants, such as inorganics and alkali-soluble elements, from pulping streams in the forest products industry. Potential areas for cross-cutting research include:

- **methods for separating components from dilute gaseous streams**, such as adsorption, high-selectivity membranes, inorganic membranes, and advanced-particle-capture technologies for the removal of submicron (< 2.5 micron) and micron-sized particles

- **methods for separating components from dilute aqueous streams**, such as reactive metal complex sorbents, reducing agents, air oxidation combined with absorption, membranes, steam and air stripping, electrically facilitated separations, destructive-oxidation techniques, electrodialysis, ion exchange, and crystallization

Drying and Dewatering Technologies

Another cross-cutting area for research is drying and dewatering technologies. Several industries, including the chemical, petroleum refining, metal casting, and forest products industries, have identified separation needs that could be met by improvements in drying and dewatering technologies. Examples include: the removal of solvents from polymers (devolatilization) in the chemical industry; the removal of entrained water from crude oil and the drying of natural gas in the petroleum refining industry; the drying of ceramic casting materials and reclamation sand in the metal casting industry; the drying of paper in the papermaking process of the forest products industry; and the drying of sludges from waste gas scrubbing and wastewater treatment.

Lower Cost Oxygen

The chemical, petroleum refining, aluminum, steel, and glass industries have stated that inexpensive, high-purity oxygen would be beneficial to them in combustion (oxy-fuel) and other processes. The attraction of oxy-fuel is lower NO_x emissions compared to air and significant energy savings from not having to heat the nitrogen in air. Although the cost of oxygen is relatively low compared to many other chemical products, it is currently high enough to be a significant barrier to the implementation of many new, energy-saving applications.

RESEARCH OPPORTUNITIES IN ENABLING TECHNOLOGIES

The panel identified five enabling technologies that, although they are not separation processes, would promote improvements in industrial separations. These are membrane materials, sorbent materials, on-line diagnostics and sensors, an improved understanding of thermodynamics, and particle characterization. The panel recommends that OIT focus its long-term, fundamental research on these areas.

Membrane Materials

No single material can have all of the desired characteristics for membrane separation technologies. Important properties for emerging membrane materials include impact strength, flexibility, thermal stability, and transport properties. The development of materials for a specific application may be economical if the application is sufficiently widely used. In general, however, research should be focused on membrane materials that are useful for a variety of applications. Promising areas of research include the following:

- **polymer membranes** with improved selectivity and flux
- **inorganic membranes,** including thin, nanostructured membranes for gas separations (research should be focused on molecular template-directed synthesis of nanostructured zeolite or inorganic materials and an economical synthesis of carbon molecular sieve membranes with uniform and small pore sizes)
- **polymer-inorganic hybrid materials** for high-selectivity applications (research should be focused on tunable synthesis and the fabrication of low-cost membrane modules)

Sorbent Materials

Sorbent materials could enable the development of several separation technologies. The newest class of sorbents can now be moved between sorbing and desorbing zones, much like the typical absorption/desorption cycle. A form of continuous processing has thus been commercialized. This process is currently being used to remove small concentrations of organic contaminants from gas vent streams.

On-line Diagnostics and Sensors

On-line characterization of material streams in separation processes would benefit all of the IOF industries. Much of the technology to control key parameters, such as flow, temperature, pressure, or mass, are commercially available. Many feedback algorithms are well known, and ample computing power and memory are available to implement these on a real-time basis. In many cases, the limiting components are process sensors, especially accurate and selective chemical sensors that can maintain their performance in harsh or extreme manufacturing environments.

Specific opportunities for improving on-line sensor technology are listed below:

- sensors to determine compositions on-line at various points within a distillation column so it can operate as close as possible to minimum reflux
- sensors that can detect inorganic compounds, such as dissolved metals and transition metals, in aqueous systems
- sensors that can characterize the amount, size, and shape of particles

- sensors that can characterize the composition of streams and the makeup of individual objects in these streams for sorting

Four factors that must be considered in the development of new sensors for manufacturing are: the potential for fouling, interference from minor contaminants, ease of maintenance and replacement, and cost.

Improved Understanding of Thermodynamics

The ability to separate a mixture efficiently is closely linked to the best possible use of the driving forces available for the separation. In most separations, the thermodynamic description of equilibrium between two phases is an indispensable tool for characterizing driving forces. Research in phase equilibrium is hardly new, and the volume of information available to researchers is extensive. Nevertheless, several areas of phase equilibrium relevant to separation processes have been sparsely researched. Opportunities for fundamental research in phase equilibrium include the following:

- mixtures in which one or more components of importance are at very low concentrations (e.g., parts per billion)
- systems in which reaction accompanies the attainment of equilibrium (e.g., the absorption of $H2_{S}$ into amine and other basic solutions)
- "extreme-condition" equilibrium (e.g., temperatures well above 100°C or well below 0°C and pressures in the supercritical-fluid range)

To supply the critical thermodynamic information for many separations in these areas, advanced analytical-chemistry technology must be combined with phaseequilibrium equipment, followed by the derivation of correlations that accurately describe and generalize the experimental data.

Particle Characterization

Particles are ubiquitous in industrial processes. The properties of particles that are important to characterize depend on the process and the nature of the particles. Particle characterization has many significant process applications. Characterization methods must, therefore, be robust and have appropriately rapid response times for the system. For some applications, such as the monitoring of particulates in stack gases, the characterization device must either withstand a harsh environment or function via remote sensing.

RECOMMENDED CRITERIA

Based on the opportunities identified by the panel for each industry and the maturity of separations technologies, the panel has identified some general criteria for OIT to select research and development projects. The panel determined that the following selection criteria should be used:

- **Time Scale.** Projects should focus on high-impact technologies that have been demonstrated in the laboratory and will be ready for commercial application in five to seven years.

Although the industry vision statements focus on goals for 2020, moving as quickly as possible toward new, practical, and economically viable technologies is imperative because of the long commercialization times for the large-scale processes used by the IOF industries. Five to ten years may easily pass between laboratory demonstration of a concept and its subsequent first commercialization. Widespread commercialization can take several more years. Also, revolutionary technologies naturally take longer to commercialize because of higher risk of failure. Technologies that take longer than five to seven years to develop will have an insignificant effect on energy consumption and raw-materials utilization by 2020.

A portfolio designed to meet the five to seven year time frame will limit the projects OIT should consider funding. First of all, fundamentally oriented, diffuse projects will not be likely to have commercial applications by 2020, except in cases where the experimental data obtained can have a significant impact on the large existing capital-equipment base of the IOF industries. Second, each project should include process design and economics components, including the economics of the current technologies against which the proposed technology will be evaluated and reasonable economic targets. Every project in the portfolio should be evaluated annually to ensure that the work is progressing satisfactorily toward these targets.

- **Cross-cutting Criteria.** OIT should only support cross-cutting research in separation technologies that are either (1) embryonic technologies that could lead to major advances in several industries or (2) improvements in mature, high-use technologies where incremental improvements could have a substantial effect.

In some instances, a separation technology is well developed in one industry but not well known in another where it might be profitably used. In these cases, cross-industry conferences and other exchanges of information should be fostered and facilitated by OIT. Because of certain technological similarities among the IOF industries, significant technology transfers between industries may be possible. OIT should encourage this aspect of research.

- **Impact on Existing Processes and Equipment.** Proposed projects should be evaluated for the potential economic impact of a new separation method and for the potential effect of that new method on existing processes and equipment. OIT should consider funding the development of fundamental data when knowledge of such data can produce substantial improvements in existing separation processes.

- **New Technologies.** Projects for the development of new separation technologies should be multidisciplinary and should be potentially scaleable to production volume, both in technical and economic terms.

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APPENDIX A

BIOGRAPHIES OF PANEL MEMBERS

George E. Keller II (chair) recently retired as senior corporate research fellow for Union Carbide Corporation. He received a Ph.D. in chemical engineering from Pennsylvania State University and spent 36 years working for Union Carbide. He has experience in chemical and petroleum separation technologies, including distillation, membranes, adsorption, and extraction, and is co-author of a recently published book, *Separation Process Technology*. He chaired the Gordon Research Conference on Separations in 1985 and was a member of the National Research Council Committee on Separation Science and Technology in 1986. Dr. Keller is a member of the National Academy of Engineering.

R. Ray Beebe retired as senior vice president of Homestake Mining Company. He received an M.S. degree in metallurgical engineering from the Montana School of Mines. His areas of expertise include mineral processing, crushing, extraction, leaching, electrochemical separations, ore beneficiation and upgrading, and ferrous and nonferrous metals. Prior to his tenure at Homestake Mining, he held senior management positions with Marcona Corporation and Newmont Mining Corporation. Mr. Beebe is currently the chair of the National Research Executive Committee on Industrial Technology Assessments. He has previously served as a member of the National Materials Advisory Board and as vice chair of the National Research Council study on competitiveness of the U.S. minerals and mining industry. He is a member of the National Academy of Engineering.

Richard J. Fruehan is professor of metallurgical engineering and director of the Center for Iron and Steelmaking Research at Carnegie-Mellon University. He received a Ph.D. in metallurgical engineering from the University of Pennsylvania.

His areas of expertise include the physical chemistry of metallurgical reactions in steelmaking and other metals production. He has 14 years of experience with U.S. Steel Research and is associate editor of *Metallurgical Transactions*. Dr. Fruehan has previously served on two National Research Council committees, the Committee on Industrial Energy Conservation and the Panel on International Cooperation and Competition in Materials Science and Engineering.

Norman N. Li retired as director of research and technology for AlliedSignal and is currently president of NL Chemical Technologies. He received a Ph.D. in chemical engineering from Stevens Institute of Technology. He has 18 years of experience with Exxon Research and Engineering and was director of separation science and technology at UOP (formerly Universal Oil Products, Inc.) for seven years. He is one of the developers of the liquid membrane separation technology, and his experience includes biochemical separation and purification, colloids and interfaces, metal removal processes, water treatment systems, leaching, and extraction. Dr. Li has published 73 papers in major technical journals, edited 13 books, and received 43 U.S. patents. He was a member of the National Research Council Committee on Separation Science and Technology in 1986 and has chaired two Gordon Research Conferences. He is a member of the National Academy of Engineering.

Eve L. Menger retired as director of characterization science and services at Corning, Inc. She received her Ph.D. in chemistry from Harvard University. She has expertise in characterization science, technology transfer, and industrial chemicals and processes, including nonsteady state effects in diffusion controlled processes, heterogeneous catalysis, and excited state reactions. She held senior research and management positions at AlliedSignal for nine years and has served on two National Research Council committees, the Committee on Industrial Competitiveness and Environmental Protection and the Committee on Diversity in the Naval Scientific Workforce.

Guido P. Pez is chief scientist, inorganic and organo-fluorine chemistry, at the Corporate Science and Technology Center of Air Products & Chemicals, Inc. He received his Ph.D. in chemistry from Monash University. His areas of expertise include inorganic chemistry, catalysis, and organo-fluorine chemistry. He has 17 years of experience leading a research group in these areas at Air Products & Chemicals and 12 years of prior experience with Allied Chemical Corporation. He has extensive expertise in separations based on chemical reactions and synthetic inorganic and organometallic chemistry as applied to catalysis.

Peter H. Pfromm is assistant professor at the Institute of Paper Science and Technology. He received his Ph.D. in chemical engineering from the University of

Texas at Austin. His expertise includes gaseous membrane separations, electrochemical separations, specialty separations, separation processes for closed-cycle manufacturing, paper recycling, and polymer science. Dr. Pfromm previously held positions at Membrane Research and Technology, Inc., and Fraunhofer Gesellschaft/IGB in Stuttgart.

Ronald W. Rousseau is professor and chair of the School of Chemical Engineering at the Georgia Institute of Technology. He received his Ph.D. in chemical engineering from Louisiana State University. His research interests include separation and purification via crystallization, with special emphasis on crystal nucleation and growth, and crystal morphology, purity, and size distribution. He received the American Institute of Chemical Engineers (AIChE) Gerhold award for his work in separations and has published more than 130 papers based on his research. He is editor of the *Handbook of Separation Process Technology* and co-author of *Elementary Principles of Chemical Processes*. He has served as chair of the Council for Chemical Research and is a Fellow of the AIChE.

Michael P. Thomas is director of technology and business development with Alcan Recycling. He received a Ph.D. in metallurgy from the University of Cambridge. He has expertise in metallurgy and materials processing, with 15 years of industrial experience in new product research and development, management of research and development, corporate strategy, and business management. He is chair of The Aluminum Association's Automotive and Light Truck Recycling Committee. He has published more than 40 papers and holds six patents.