FUTURE DIRECTIONS FOR SEPARATION SCIENCE
IN NUCLEAR AND RADIOCHEMISTRY

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Future Directions for Separation Science in Nuclear and Radiochemistry

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Abstract

Solvent extraction and ion exchange have been the most widely used separation techniques in nuclear and radiochemistry since their development in the 1940s. Many successful separations processes based on these techniques have been used for decades in research laboratories, analytical laboratories, and industrial plants. Thus, it easy to conclude that most of the fundamental and applied research that is needed in these areas has been done, and that further work in these "mature" fields is unlikely to be fruitful. A more careful review, however, reveals that significant problems remain to be solved, and that there is a demand for the development of new reagents, methods, and systems to solve the increasingly complex separations problems in the nuclear field. Specifically, new separation techniques based on developments in membrane technology and biotechnology that have occurred over the last 20 years should find extensive applications in radiochemical separations. Considerable research is needed in such areas as interfacial chemistry, the design and control of highly selective separations agents, critically evaluated data bases and mathematical models, and the fundamental chemistry of dilute solutions if these problems are to be solved and new techniques developed in a systematic way. Nonaqueous separation methods, such as pyrochemical and fluoride volatility processes, have traditionally played a more limited role in nuclear and radiochemistry, but recent developments in the chemistry and engineering of these processes promises to open up new areas of research and application in the future.

Introduction

Historically, the ties between separation science and technology and nuclear and radiochemistry have been very strong. It can be fairly stated that the needs of nuclear and radiochemistry have been one of the major driving forces behind the development of many modern separation techniques and processes. Conversely, the field of nuclear and radiochemistry would not have become an important, widely applied science without the rapid progress in separation science and technology that has occurred in the twentieth century.

Table 1 lists a few example that illustrate this close relationship. The isolation of polonium and radium from pitchblende, which marked the

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Table 1. Some Important Separations in the History of Nuclear and
Radiochemistry

Year	Development	Separation Method(s)
1898	Discovery of polonium and radium	Precipitation, electrolysis, distillation.
1913	Discovery of isotopes	Mass spectrometry, gaseous diffusion
1919	Discovery of non-integer isotopic weights	Mass spectrometry
1934	Separation of chlorine isotopes	Gas centrifuge
1940	Discovery of transplutonium elements	Ion exchange
1944	Macro-scale production of plutonium	Solvent extraction
1944	Macro-scale production of enriched U-235	Electromagnetic separation, gaseous diffusion
1965	Laser isotope separations	AVLIS, MLIS

beginning of radiochemistry, was carried out using the classical separation techniques of precipitation, electrolysis, and distillation. Later progress in nuclear and radiochemistry, such as the discovery of isotopes and non-integer isotopic weights, required the development of new separation methods such as mass spectrometry, gaseous diffusion, and gaseous centrifugation. This technology was later refined and scaled up by many orders of magnitude to find applications in other areas and to produce isotopically pure, macro-scopic samples of elements for a variety of uses in research, medicine, energy production, and weapons. Similarly, the need to separate and identify the newly-discovered transplutonium elements spurred the development of ion exchange and related chromatographic methods. The modern hydrometallurgical industry was founded on the technology that was developed in response to the war-time need for processes to purify multi-kilogram quantities of plutonium and enriched uranium.

This short table is by no means complete, but it is sufficient to illustrate the influence that nuclear and radiochemistry has had on the development of separation science and technology and vice versa. New separation methods were invented and old ones improved because of the important scientific, military, and economic needs that grew out of the evolving field of nuclear and radiochemistry.

Will this symbiosis continue? In all probability it will. The develop-ment of laser isotope separation methods and the need for improved separation methods for purifying radiopharmaceuticals may be cited as ongoing examples of nuclear and radiochemists working hand in hand with separation scientists and engineers. There is, however, a new driving force that will affect the direction of both separation science and nuclear and radiochemistry, and that is the increasing pressure to satisfy the ever more stringent regulations for

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environmental discharge, product purity, and related health, safety, and environmental considerations. Many of these regulations are aimed at the radioactive and hazardous wastes that are generated in the nuclear industry. Statutes are already in force that require purities at or below the analytical level of detection (1). Developing the separation and purification methods needed to achieve these limits is a great challenge for separation scientists and engineers. The remainder of this paper will examine some of the separation techniques that are especially important in nuclear and radiochemistry, and will explore what areas on research are likely to be most fruitful.

Solvent Extraction

The premier forum for reporting progress in solvent extraction science and technology is the International Solvent Extraction Conference (ISEC), which is held every three years. The proceedings of the most recent conference in this series (2), accurately reflect the research areas and applications that are of the greatest concern to workers in this field. The proceedings of a recent symposium sponsored by the Industrial and Engineering Chemistry (I&EC) Division of the American Chemical Society (ACS) are also a significant source of up-to-date information (3). Bravo et al. have also presented an excellent review of extraction technology (4).

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

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There is almost universal agreement that the major challenge in solvent extraction chemistry is the development of new, highly selective, solvent extraction reagents. Ideally, one reagent (or perhaps a pair of synergistic reagents) would be developed for each component of a mixture. Even though this goal may never be realized, it is the guiding principle behind much current solvent extraction research. Advances in our understanding of the kinetics and thermodynamics of coordination chemistry are being applied to the design of new solvent extraction reagents. These reagents are being designed by inorganic chemists, who are building more complex molecules to satisfy the specific coordination demands of a given molecule or ion, and by biochemists, who are working to determine the structure of the active sites in complex biological macromolecules (e.g., enzymes) in order to build simpler molecules that will retain the functionality of the active sites without the excess molecular structure of large biological molecules. Advances in coordination chemistry, structural chemistry (solid and solution), biochemistry, and quantum mechanics, all of which are needed, will also contribute to realizing the goal of producing "designer molecules" for solvent extraction. In addition to greater selectivity, these reagents should have higher resistance to chemical, thermal, and radiolytic degradation, as well as improved solubility and emulsification characteristics.

The chemical and physical properties of interfaces have been largely neglected in the study of solvent extraction processes relative to the vast amount of information that has been reported on the equilibrium thermodynamics of the bulk systems. The kinetics and mechanisms of interfacial transport have been particularly difficult to study and interpret, but progress is now being made (5). The results of excellent, detailed studies of drop-interface coalescence are becoming available (6). These and similar

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studies are of considerable importance to the solution of some of the long-standing problems in the application of solvent extraction, such as the origin, nature, and cleanup of interfacial emulsions (often referred to colloquially as interfacial "cruds"). As more information and improved theories of solvent extraction kinetics become available, separations based on kinetic effects rather than on equilibrium distributions are being designed. (A few separation methods based on kinetic effects are already in use, but the number is small.)

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

The effects of the application of external fields (electromagnetic, gravitational, etc.) on solvent extraction systems have begun to receive considerable attention (7). These studies are certain to lead to new separations processes and, at the same time, are being used to study the interfacial properties already discussed.

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

Modeling complex solvent extraction systems is difficult and will almost certainly require a sophisticated knowledge of applied mathematics beyond that of a typical chemist or chemical engineer. Collaboration between these two disciplines is currently quite rare, but it shows promise for advancing our ability to model separation systems and hence to optimize their design.

Ion Exchange

Much of what has been said about solvent extraction applies equally to ion exchange. Indeed, it is useful to think of ion exchange as a solvent extraction system in which the solvent extraction reagent has been immobilized on a solid support. Of course, this analogy may be somewhat misleading in some cases, but the techniques share more commonalities than differences. As in solvent extraction, the application of ion exchange will be enhanced and broadened by the development of improved, more highly selective, reagents. Details of the structure and reactivity of the solid-liquid

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interface are poorly understood, and new techniques are needed to study them. The kinetics of ion exchange processes and the parameters that govern it are not well understood.

An important area in ion exchange technology that is less clearly analogous to solvent extraction chemistry is the development of inorganic ion exchangers. A review of the status of inorganic ion exchange has recently been published (8). It is interesting to note that the early synthetic ion exchange materials were primarily inorganic. They were quickly replaced by synthetic organic resins, however, because of the difficulty in manufacturing a reproducible inorganic material and because of the instability of these materials in acid solution. Organic resins were found to have limitations as well, especially in applications that required exposure to high temperatures or radiation fields. Thus, research on potential inorganic ion exchangers continued at a low level until a breakthrough came in the mid-1960s when it was shown that the group IV phosphates and arsenates could be prepared in crystalline form. These materials show great promise not only as ion exchangers, but also as membranes and as catalysts or catalyst supports.

Membrane Separations

An excellent assessment of membrane technology and applications has recently been published (9). This assessment, along with the proceedings of a symposium sponsored by the Subdivision of Separations Science and Technology of the I&EC Division of the ACS (10), summarizes the current status and frontiers in membrane technology. A thorough review of the history of membrane technology has been published by Lonsdale (11). Bravo et al. have also reviewed the subject recently (12). The following comments draw heavily on these sources.

Membrane separation technology is relatively new, but its use has

expanded rapidly since the introduction of the first commercial electrodialysis and microfiltration units in the 1960s. The first high-efficiency reverse osmosis membranes were also introduced in the 1960s, but reverse osmosis and ultrafiltration did not become commercially successful until the 1970s. Today, a number of membrane processes are routinely used on both laboratory and industrial scales. These include electrodialysis, reverse osmosis, microfiltration, ultrafiltration, dialysis, electroosmosis, membrane extraction, pervaporation, and gas separation. Hwang and Kammermeyer (13) have prepared an excellent textbook describing these and other commonly used membrane separation unit operations. Such technologies, however, have been applied almost exclusively to the processing of aqueous streams. The application of membrane separation processes to nonaqueous solutions, gaseous systems, and gas-liquid systems is promising, but relatively unexplored.

It is important to note the close relationship between membrane separations, solvent extraction, and ion exchange. The most striking example is the case of liquid membranes (LMs) with facilitated transport, where a solvent extraction reagent (often called a "liquid ion exchanger" or a "carrier molecule" in this context, depending on the background of the investigator) is used to effect ion exchange or some other form of mass transport into or through the membrane phase. LMs may take the form of a discrete membrane layer, of an emulsion, or may be supported on a solid. They are among the most interesting classes of membranes currently under investigation, and much of the research is being done by scientists who were previously labeled "solvent extraction chemists" and who are reporting their work at solvent extraction conferences (14).

At first glance, this blurring of the lines between solvent extraction chemistry, ion exchange chemistry, membrane chemistry, and (as will be

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

Biomembranes (membranes made from biological material or synthetic membranes designed to mimic the structure and function of biological membranes) show enormous potential for a variety of applications, most notably in the photochemical generation of electricity. Two excellent reviews that detail these applications have recently been published (15, 16).

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

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fields are present) and pharmaceutical chemistry (where organic solvents are common).

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

The high costs of membrane separation processes are not so much an independent deficiency in the technology as they are a reflection of the problems with material limitations and the high degree of empiricism in the manufacture and application of membranes. It has been suggested (9) that the short operating life of many membranes is the most important factor contributing to membrane system cost, followed closely by the low flux that can be achieved in membrane modules. Both of these problems can potentially be solved by the development of improved membrane materials.

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

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Chromatography

For the purposes of this paper, the general term "chromatography" is used to include the techniques of gas, liquid, paper, thin layer, and affinity chromatography. A thorough review of progress in the development of each of these techniques is publisned in even numbered years in the journal Analytical Chemistry (17), and good discussions of the general theory of chromatography may be found in several texts (18). That many significant reviews of chromatographic techniques appear in a journal devoted to analytical chemistry points to a great deficiency in the field, namely, the difficulty in scaling up most chromatographic techniques to an industrial size. The speed, resolution, and ability to handle very small samples have made chromatographic techniques among the most useful in analytical separations. The application of chromatographic techniques to large-scale problems, however, has been frustrated by many of the same deficiencies that exist for the separation techniques already discussed. These include the need for technological advances that would allow the practical, cost-effective scale-up of analytical chromatographic systems, and the need for theoretical advances, especially in the areas of transport and interfacial phenomena, that would allow accurate modeling of the behavior of these large scale systems. Many hundreds of references to the theory of chromatography have been reported in recent years, and the development of new packing materials, supports, column designs, column materials, mobile phases, stationary phases, detectors, and instruments continues at an impressive rate. Still, such developments are more evolutionary than revolutionary, and one of the most exciting prospect in chromatography is for a breakthrough that will allow all of these advances to be applied on an industrial scale.

One form of chromatography that already operates on a scale consistent

with the industry to which it is most often applied is affinity chromatography. This is an interesting case in which the separation technique (affinity chromatography) is both an application of and is applied to the same science (biotechnology). Two recent papers review the development and status of this relatively new method (19,20). Affinity chromatography uses highly selective biological molecules immobilized on a solid support to effect the separation of a specific molecule or class of molecules from a mixture. This separation technique depends on the extreme specificity of enzymes, antibodies, and other biological molecules to approach the ideal of "one solute-one separation agent" discussed previously. It should be noted that immobilized inorganic ligands are used to effect the separation of biomolecules as well. The potential of this technique in the biological sciences is enormous and it represents an active area of research; the potential in inorganic systems is also large (the affinity of certain inorganic ligands for biomolecules works both ways), but is less developed.

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

Photon-Enhanced Separations

The development of the laser as a source of pure, monochromatic electromagnetic energy has brought about rapid changes in many fields of science and

technology. In general, exposing a mixture to laser light will not cause a separation, but the laser photons may be thought of as a tunable, highly selective "reagent" that can react with one component of a system and change (ionize, oxidize, or reduce) it to a species which can be easily removed from the mixture by some traditional separation technique.

Perhaps the best known examples of the application of laser technology to separations are the laser isotope separation (LIS) methods (21-23). Table 2 summarizes their development. The most developed LIS methods are Atomic Vapor Laser Isotope Separation (AVLIS) and Molecular Laser Isotope Separation (MLIS). While the isotopes of many elements have been separated by LIS techniques since the technology was developed in the early 1970s, most of the work has concentrated on the separation of the isotopes of uranium for use as fuel in nuclear reactors.

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

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Table 2. Progress in laser isotope separation*

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

*Adapted from ref. 21, Table I, p. 128.

Over a period of about 10 years the U.S. Department of Energy evaluated the potential utility of several MLIS and AVLIS processes for the enrichment of uranium. By 1985, a specific AVLIS process, currently being developed at Lawrence Livermore Laboratory (LLL) and the Oak Ridge National Laboratory, had been chosen over all competing LIS methods as well as gaseous centrifugation. Development of AVLIS as the primary enrichment technology in the U.S. will continue until it is ready for commercial implementation in the 1990s. Details of the key research needed to complete the development of AVLIS for this purpose are classified.

While a single LIS process has been chosen for uranium enrichment in the U.S., other processes of this type are being developed and used for a variety of applications (22). In addition, a substantial amount of what had been facetiously called "laser alchemy" has been reported in the literature (23). Unexpected behavior has been observed in a number of chemical systems when they are exposed to laser radiation, especially when the molecules involved are complex. Considerable research will be required before the details of these reactions can be explained. It is clear, however, that these laser-induced reactions have a large, if still somewhat ill-defined, potential as a key step in new separations processes.

In many cases, the highly monochromatic radiation of a laser may not be required to perturb a chemical system in such a way that a separation is feasible. Toth (24-25) and his co-workers have used radiation from a mercury lamp to selectively adjust the oxidation states of various actinides in solution in order to improve the separation of these elements from each other using solvent extraction.

The use of photons, whether from lasers or from conventional light sources, as a "reagent" in a separation system has a number of advantages,

including the ease with which they can be produced, high selectivity, minimal waste generation, and low cost. The potential of lasers as an integral part of new separation systems has begun to be explored only recently. It is reasonable to expect many new techniques and applications to be developed using these powerful tools.

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

Nuclear Fuel Reprocessing

The Purex process remains the only technology that is in widespread use for recycling spent nuclear fuel. Despite more than 40 years of experience, many problems with the process have not been solved. From an operational point of view, methods have been developed to minimize the effects of the most severe of these problems, but the fundamental causes and control of solvent degradation, the formation of interfacial precipitates, and marginal decontamination factors for troublesome fission products such as zirconium, technetium, ruthenium, and neptunium are still under investigation. While research in these areas is important, it will result in incremental, rather than revolutionary, improvements in the process. There are, however, a number of unresolved questions regarding the best method for handling the wastes and useful by-products that are generated in this process. Further, the decision to defer indefinitely the construction of any civilian reprocessing facilities creates an opportunity to explore radically new process chemistries for possible use in the twenty-first century.

When construction of the AGNS Reprocessing Plant at Barnwell, South Carolina, was halted and the Clinch River Breeder Reactor Program was

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

Thus, the status of nuclear fuel reprocessing technology in the United States is largely defined by efforts currently underway at existing facilities and projects that might be done in collaboration with other countries. A number of important separations problems have been identified at these facilities, and short-term research to improve separations technology in the reprocessing industry should be aimed at their resolution. Long-term research should be focused on developing an improved understanding of the base technology of the Purex process and closely related modifications, such as the use of alternative extraction reagents (e.g., tri(2-ethylhexyl) phosphate, sulfoxides, carbamoylmethylphosphonates, etc.). Moreover, the long interim between the present and the time when a new reprocessing facility will be constructed affords an excellent opportunity for developing alternative, radically different, reprocessing schemes to the point where critical evaluations can be made concerning the most desireable technology for deployment in the twenty-first century. Examples of such alternative technologies include several nonaqueous methods, such as pyroprocessing (26-27) and fluoride volatilization using dioxygen difluoride or krypton

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difluoride (28-31), as well as new aqueous methods employing membrane technology or the alternative extractants already mentioned. These novel separation methods were too undeveloped to consider for use in a facility to be built before the end of the century; however, there is now time for further development and evaluation of these technologies before a new reprocessing plant is likely to be built in the U.S. While the lack of vigorous reprocessing program based on Purex technology is regrettable, the opportunity for a head start in the development of twenty-first century reprocessing technology is an exciting one.

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

Nuclear fuel reprocessing generates large volumes of organic wastes that must be disposed of or destroyed. These wastes include both spent solvents (TBP, carbon tetrachloride, hydrocarbon diluents) and aqueous solutions of organic complexing agents. For example, about 4 million gallons of aqueous waste containing significant concentrations of tetraphenyl boron are

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

There is a general need in the nuclear industry for a process to separate the lanthanide elements from the trivalent actinides in a nitrate-based rather than a chloride-based system. The use of chloride complicates flowsheets by requiring nitrate-to-chloride and chloride-to-nitrate conversions, and by accelerating equipment corrosion.

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

A major research on the main part of the Purex flowsheet is not warranted. The Europeans and Japanese have active programs in this area, but the research is designed to fill the gaps in the data base and to address some of the remaining trouble spots, such as technetium, ruthenium, neptunium, or palladium chemistry, and valence adjustment. These efforts are worthwhile and should be a part of a continuing base-technology program in the U.S., but they do not form the basis for a large research program. The prototypic, high-burnup, mixed-oxide fuel that nas recently become available from the Fast Flux Test Reactor should, however, be thoroughly studied and used to test proposed reprocessing schemes of all types, including those that

are highly speculative (e.g., fluoride volatility processes based on dioxygen difluoride).

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

Waste Management

The problems presented by the hazardous material that have (or are being) discharged to the environment are enormous, and their solutions challenge the limits of separation science and technology on all fronts. Pollutants that must be separated from the environment may be solids, liquids, or gases; they may be simple anions or cations, organic or inorganic, natural or man-made, dilute or concentrated, radioactive or stable. They come from the smokestack industries, energy production, automobile exhausts, the health-care industry, and residential waste treatment units. Some of the problems are ongoing, while others are left over from an era when little thought was given to how waste materials were discharged to the biosphere. The news media are diligent at pointing out where hazardous and radioactive wastes are, were, or might one day be stored or discharged. Standards for what constitute an environmentally acceptable level of discharge to the environment are becoming increasingly stringent, and there is

every indication that trend will continue.

Such a litany of gloom may make the problem seem intractable, but that is far from the case. Great progress has been made, and the techniques and research needs discussed above point the way for even greater progress. The application of highly selective, more efficient solvent extraction, ion exchange, and membrane separation (chiefly reverse osmosis and ultrafiltration) techniques has successfully reduced the concentration of many of the pollutants that were once common in aqueous industrial effluent streams. Emissions of the oxides of sulfur from coal-fired electrical plants have been reduced substantially by pretreating the coal to remove inorganic sulfur and by scrubbing the flue gas after the coal is burned. Biotechnologists have developed remarkable microbes with the ability to decompose hazardous halogenated compounds (32), nitrates (33), and cellulosic materials (34) in the soil, solid wastes, aqueous waste streams, and waste ponds. Supercritical water has been used to destroy organic material in waste streams (35).

The limits of the success of these processes also mark the point at which the need for research and development of improved techniques begins. Allowable limits for the discharge of many species, such as arsenic and dioxins, are already at or below the limit of detection. New methods of analysis, analytical separations, and process-scale separations are needed. It is not difficult to imagine the difficulty in devising a separation process that can efficiently remove very small amounts of dissolved or suspended material from very large volumes of aqueous effluents, especially since the chemical and physical behavior of species in very dilute solution is so poorly understood and reliable data is very scarce.

The successful application of biotechnology to waste problems has been

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

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

The reduction in the emissions of the oxides of sulfur from the burning of coal can been cited as an example of an area needing more work and also as an example of progress in waste separation technology. Although sulfur dioxide emissions have been cut dramatically, they are still much too high and the efforts to reduce the emissions of the oxides of nitrogen and other pollutants have been much less successful. An integrated, systems approach will be needed to achieve a completely satisfactory solution to the problem of emissions that occur during the burning of fossil fuels. This observation can be generalized to include many processes that produce hazardous and

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

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

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