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Separation Science and Technology

Barbara F. Smith*, Nan Sauer, Rebecca M. Chamberlin, Shimshon Gottesfeld,
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Abstract

This is the final report of a two-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The focus of this project is the demonstration and advancement of membrane-based separation and destruction technologies. We are exploring development of membrane systems for gas separations, selective metal ion recovery, and for separation or destruction of hazardous organics. We evaluated existing polymers and polymer formulations for recovery of toxic oxyanionic metals such as chromate and arsenate from selected waste streams and developed second-generation water-soluble polymeric systems for highly selective oxyanion removal and recovery. We optimized the simultaneous removal of radioactive strontium and cesium from aqueous solutions using our new nonhazardous separations agents, and developed recyclable, redox-active extractants that permitted recovery of the radioactive ions into a minimal waste volume. We produced hollow fibers and fabricated prototype hollow-fiber membrane modules for applications to gas separations and the liquid-liquid extraction and recovery of actinides and nuclear materials from process streams. We developed and fabricated cyclodextrin-based microporous materials that selectively absorb organic compounds in an aqueous environment; the resultant products gave pure water with organics at less than 0.05 parts per billion. We developed new, more efficient, membrane-based electrochemical reactors for use in organic destruction in process waste treatment. We addressed the need for advanced oxidation technologies based on molecular-level materials designs that selectively remove or destroy target species. We prepared and characterized surface-modified TiO_2 thin films using different linking approaches to attach ruthenium photosensitizers, and we started the measurement of the photo-degradation products generated using surface modified TiO_2 films in reaction with chlorophenol.

Introduction

This project was organized into six tasks: (1) Water-Soluble Chelating Polymers; (2) Fission Product Separations using Cobalt Dicarbolide for Solvent Extraction, Ion Exchange, and Membrane Technologies; (3) Advanced Electrochemical Reactors for Improved Separations and Waste Treatment; (4) Advanced Materials Fabricated as Hollow Fiber Membranes for Separation Processes; (5) Host for Removal of Organics from Water; and (6) Selective Waste Remediation Using In-Situ Photocatalytic Reactors. Full reports on each of these tasks are included in this document.

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Task 1. Water-Soluble Chelating Polymers

(Nan Sauer, e-mail: nsauer@lanl.gov)

Background and Research Objectives

Host complexes that specifically coordinate charged organic and inorganic species have been used as models to facilitate understanding of biological processes such as membrane channeling and substrate recognition. More recently, research has been motivated by the need to remove valuable and/or toxic inorganic ions from industrial waste streams and contaminated soils. Although competent cation hosts have been found, anion binding, crucial for complexation of toxic metalloxyanions, has had little success. In general, macrocyclic crown ether or aza-crown ether ligands have been shown to bind molecules such as selenate and phosphate, but affinities are low and these ligands are difficult to synthesize [1].

Previous research in our group has focused on utilizing water soluble polymers as chelating systems for the removal of metal cations from contaminated water and soils. Simple organic linking reactions have been used to attach ligands to polymer backbones for selective targeting of heavy metals such as lead and cadmium. Our goal was to design and synthesize analogous systems to target metalloxyanions such as chromate, arsenate, and pertechnetate.

Importance to LANL's Science and Technology Base and National R&D Needs

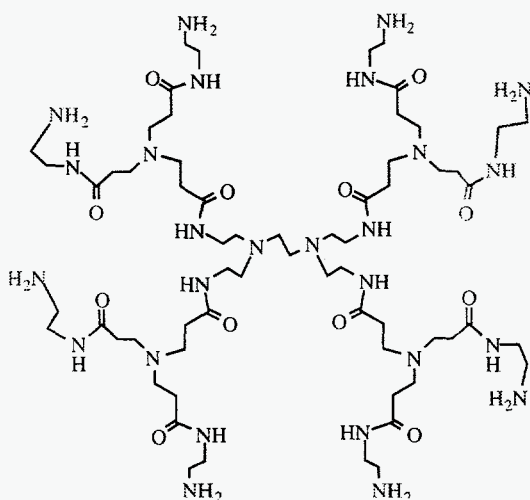
Chemical waste treatment/pollution prevention are critical needs in nuclear materials control, recovery and purification. Separations processes will constitute a key element in any Advanced Design and Production Technology (ADAPT) for nuclear materials. The high cost associated with the long-term storage of radioactive wastes mandates separations of the radioactive components from the non-radioactive components in a process waste stream, prior to packaging and storage of the waste. Separations will also be an integral part of managing the plutonium legacy; the costs and energy required to remediate old chemical processing sites are staggering. When these advanced separations technologies are adapted or co-developed to industrial needs, energy savings will result from the reduction in loss of raw material, metals processing, transportation, metal sludge processing, and sludge disposal. Toxic and valuable metal-bearing process and waste

streams are common to DOE, DoD and industry, and advanced metal separations from dilute aqueous waste streams are needed.

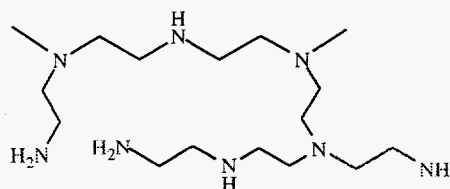
Scientific Approach and Accomplishments

Both electrostatic and hydrogen bonding interactions are known to be important for selective binding of anions [2]. Many functional groups have hydrogen bond donors capable of bonding to the oxygen atoms of toxic metalloxyanions such as chromate, arsenate, selenate, and pertechnetate. Our approach was to design binding sites for negatively charged anions by combining the electrostatic attraction from a positively charged polymer backbone with hydrogen bonding interactions from attached ligands. This combination of forces was intended to generate selectivity for oxyanions, which are capable of forming hydrogen bonds, over halides or other anions. As with previous cation binding experiments with various water-soluble polymers, binding should be reversible at extreme pH, allowing recovery of the polymer and isolation of the metal substrates.

Several modified polymer and dendrimer complexes have been investigated for their



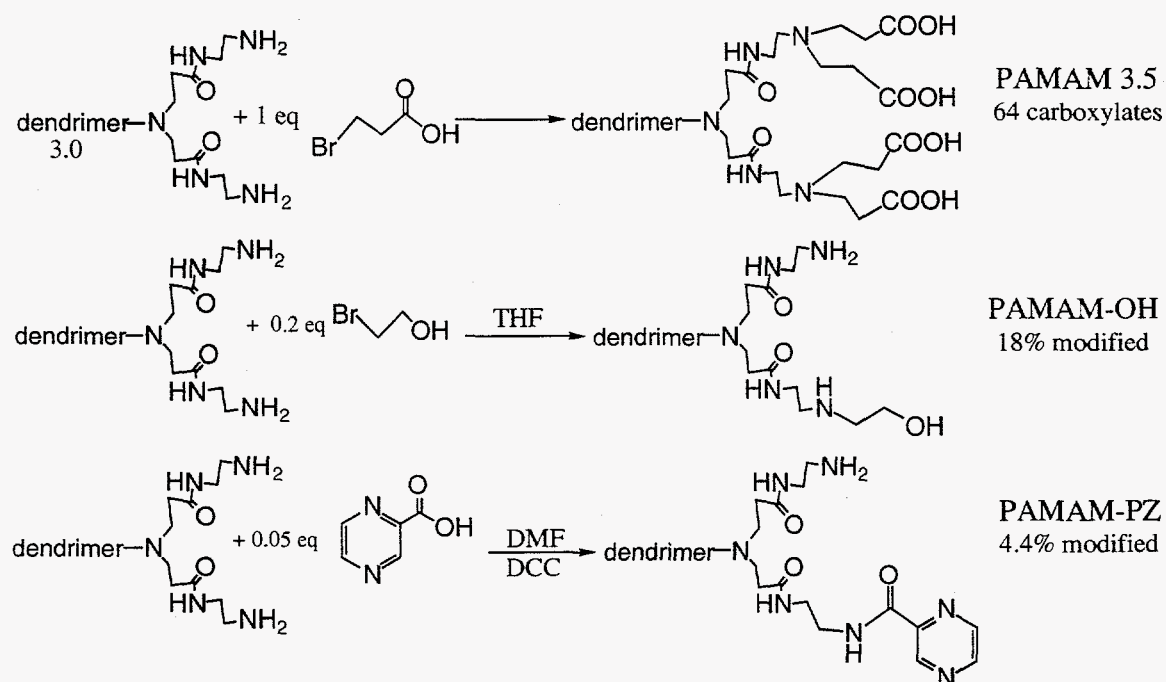
**Starburst Panam dendrimer
generation 1**



Polyethyleneimine

ability to bind oxyanions. Polyethyleneimine (PEI) was chosen as a polymer backbone because it has been well studied in our group, has a net positive charge in neutral pH water, and is easily modified. Starburst PAMAM dendrimers were also investigated. These complexes are more rigid than PEI, but share a similar polyamine structure (see above); our hope was that these would serve as tractable model complexes for the amorphous polymers. Hydrogen bond donating sites from carboxylate, hydroxy, and pyrazine groups have been used to create anion binding sites on the polymer. The reactions for the

dendrimer are shown below; analogous reactions with PEI would generate PEIC, PEI-OH, and PEI-PZ, respectively.



The PAMAM and PEI complexes have been fully characterized by NMR spectroscopy.

In solution, these complexes bind sodium salts of chromate, arsenate, and phosphate with high capacity (see below). The polymers have higher capacity than the analogous dendrimer complexes; the negative carboxylate groups on PAMAM 3.5 have no affinity for oxyanions.

Capacity ^a (mmol/ g polymer)	HCrO_4^-	HAsO_4^{2-}	HPO_4^{2-}
PEI	4.13	4.91	6.25
PEI-OH	2.53	3.04	3.93
PEI-PZ	1.79	1.70	2.03
PAMAM 4.0	1.99	1.89	1.53
PAMAM-OH	2.39	1.28	2.18
PAMAM-PZ	1.17	1.08	0.40
PAMAM 3.5	0.03	0	0

^aBinding capacity from a 2000 ppm solution of anion.

Binding studies from a mixture of anions show a selectivity for chromate over phosphate or arsenate. The polymers have less capacity at higher ionic strength, which may be due to a disruption of electrostatic effects in the presence of more ions.

We also investigated the effects of competing ions such as chloride on chromate binding. As can be seen in Figures 1 and 2, chloride does not compete well for oxyanion binding sites. Although both negatively charged species should share the electrostatic affinity for protonated sites on the polymer/dendrimer, the availability of hydrogen bond donor and acceptor ligands does seem to result in some selectivity for the oxyanions over halides. A potential hydrogen bonding site with arsenate bound is shown in Figure 3. Low concentrations of carbonate also show only minimal competition for chromium with the polymers and dendrimers.

Reference

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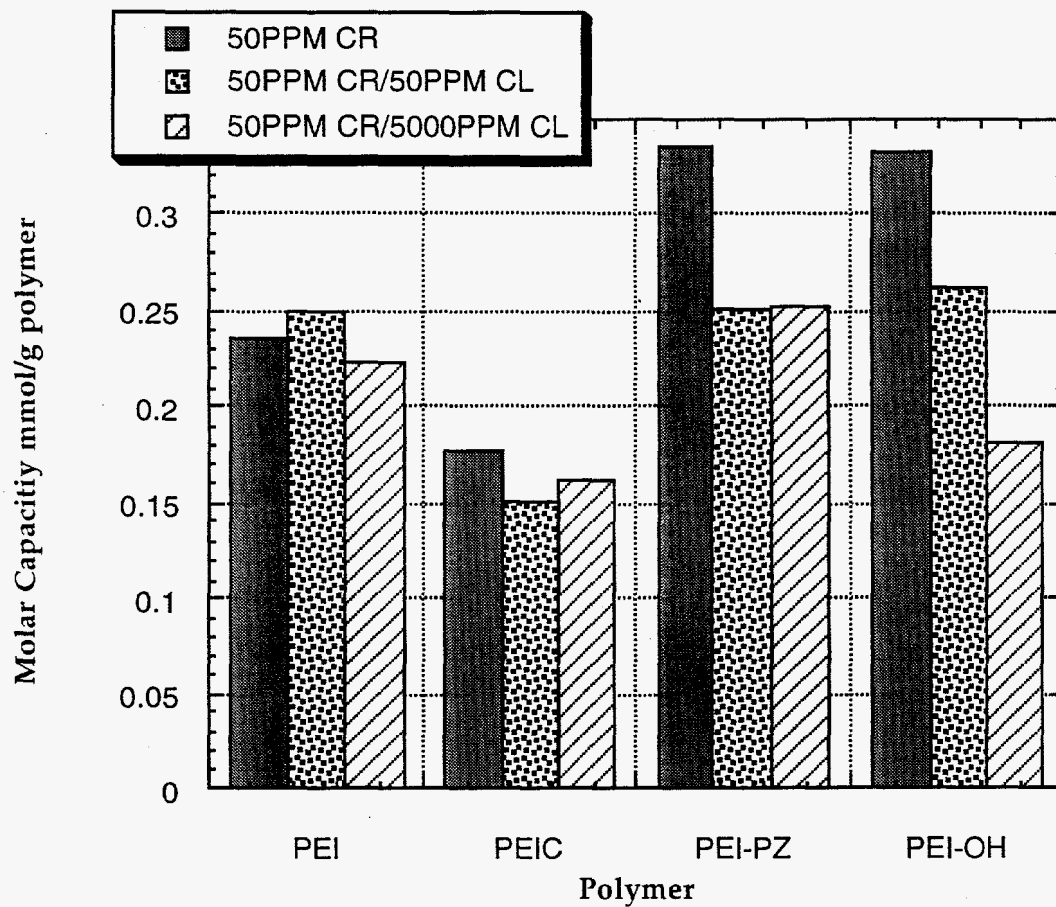


Figure 1. Chromate binding by four polymers with different competing chloride concentrations. NaCl has only a slight effect on capacity, even at 100-fold excess.

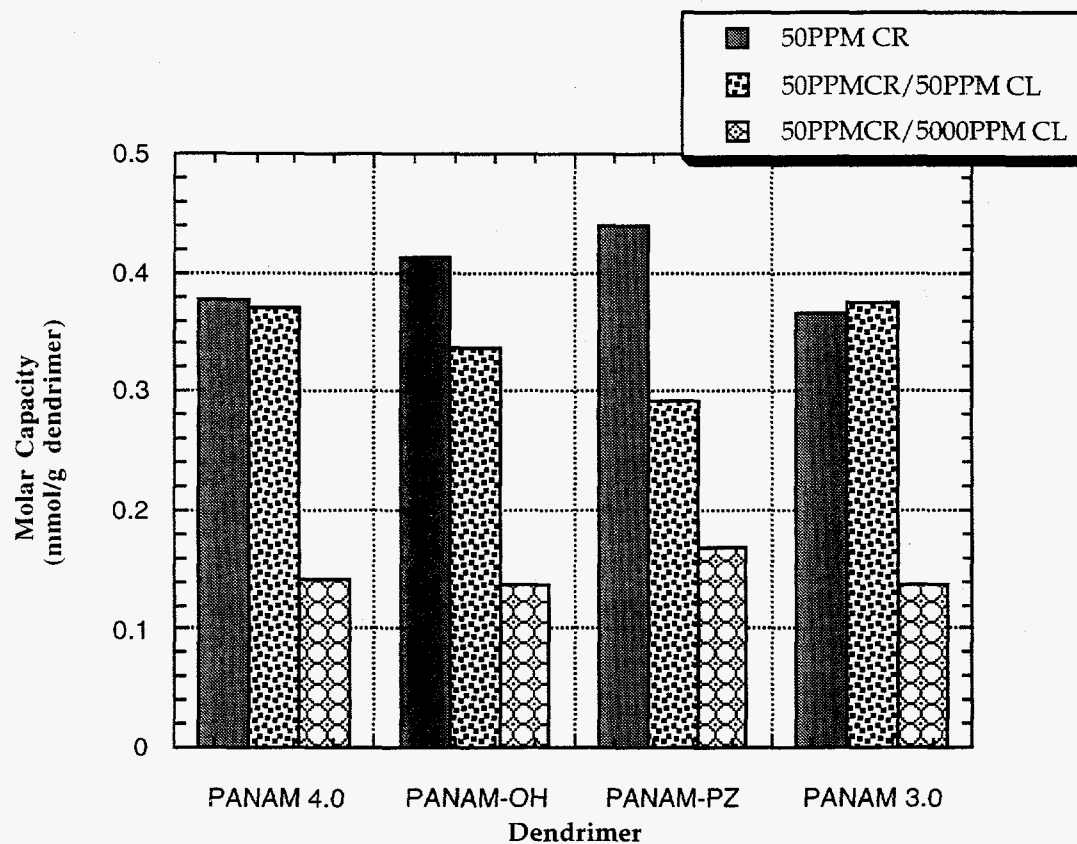


Figure 2. Chromate binding by four dendrimers with different competing chloride concentrations. A large excess (5000 ppm) of chloride does decrease binding significantly, but some capacity is still observed.

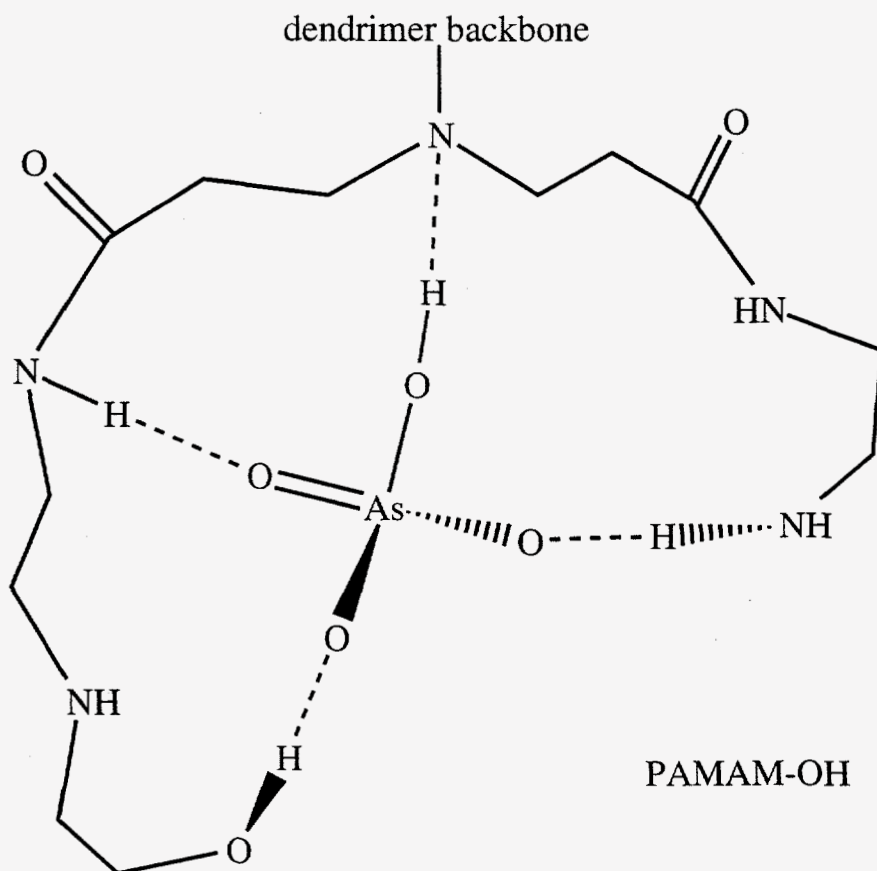


Figure 3. Potential hydrogen bonding interactions shown for PAMAM-OH with an arsenate ion.

Task 2. Fission Product Separations using Cobalt Dicarbollide for Solvent Extraction, Ion Exchange, and Membrane Technologies

(Rebecca M. Chamberlin, e-mail: rlmiller@lanl.gov)

Background and Research Objectives

The cobalt dicarbollide process for selective extractions of radioactive cesium and strontium from nuclear wastes has been known since the 1970s [1], but until recently suffered from the significant disadvantages of requiring toxic solvents and expensive liquid-liquid extraction equipment, and generating large quantities of secondary wastes during use. This research task aimed to solve the major problems associated with the use of cobalt dicarbollide and related extractants in the extraction and recovery of the highly radioactive fission products cesium-137 and strontium-90 from nuclear wastes. These problems are:

1) Previous cobalt dicarbollide separation technology required the use of liquid-liquid extraction as the engineered process. While liquid-liquid extraction has a long history of success as an approach to nuclear fuel processing (e.g., Pu production) in the DOE complex, and while it is still under consideration for certain applications, it has the disadvantage of high capital costs for start-up. This makes it impractical for treating small volumes of waste at multiple sites. Implementation of a cobalt dicarbollide-type process in an alternative engineered form would allow its broader use in the DOE complex.

2) Early work on liquid-liquid extraction using cobalt dicarbollide required the use of highly toxic nitrobenzene as the process solvent. Our work prior to this LDRD project indicated that alternative, non-hazardous hydrocarbon diluents could be used for the extraction of cesium, provided that appropriate modifications were made to the cobalt dicarbollide extractant [2]. An objective of this task was to improve and optimize the co-extraction of strontium into these new diluents.

3) Recovery of the Cs and Sr and reuse of the cobalt dicarbollide has been a long-standing problem for the solvent extraction processes. Because of the high affinity of the extractant for these radioactive ions, it was necessary to use high concentrations of nitric acid to recover them from the extractant phase. This approach results in the generation of large quantities of secondary radioactive wastes. Our final objective for this task was to develop an alternative class of extractants whose recycle could be accomplished efficiently and with minimal generation of secondary wastes.

Importance to LANL's Science and Technology Base and National R&D Needs

A significant reduction in the amount of high-level nuclear waste requiring long-term isolation is one of the highest priorities of the DOE Environmental Management programs. The primary requirement is an efficient method to segregate the short-lived fission products ^{137}Cs and ^{90}Sr from the bulk of the inert matrix materials and the extremely long-lived nuclides in the wastes. If sufficiently selective and cost-effective separations are developed, the cesium and strontium could be disposed of in a different, and substantially less costly, manner than the long-lived components, which must be safely contained for hundreds of thousands of years. Additional government and industry sector needs for efficient cesium and strontium separations include low-level waste storage, environmental decontamination, monitoring of environmental releases and safe storage of spent nuclear fuels.

The DOE has repeatedly expressed interest in modifying the Czech and Russian cobalt dicarbollide solvent extraction technology into a non-hazardous, cost-effective separation method for cesium and strontium. Our earlier efforts already produced a hydrocarbon-based solvent extraction system to replace the nitrobenzene-based solvent system. However, these incremental modifications on the existing solvent extraction technology have not yet yielded a technology that meets the strict combined criteria of selectivity, efficiency, regenerability and cost-effectiveness. The current LDRD effort addresses the three remaining problems as outlined above.

Scientific Approach and Accomplishments

Membrane Processes for Cesium and Strontium Separations. Based upon the known solvent extraction methods for separating cesium and strontium ions from aqueous solution into an organic phase containing cobalt dicarbollide, several membrane-based processes can be envisioned. The simplest is a membrane-mediated liquid-liquid extraction process (Fig. 1a) in which the organic and aqueous phases are contacted in a membrane-separated dispersionless extraction system; interphase contact occurs in the membrane pores, while diffusion of phases is prevented through control of the pressure applied on either side of the membrane. A second alternative (Fig. 1b) is a supported liquid membrane, which is absorbed into the pores of a porous membrane support. The membrane separates an aqueous source phase from an aqueous receiving phase, and acts as a sieve for the ions of interest. While these membranes are simple to prepare, they often suffer from mechanical instability as the supported liquid phase leaks from the pores. A

final alternative (Fig. 1c) is the polymer inclusion membrane, formed as a gelatinous phase by evaporation of a solution of polymer, non-volatile solvent, and ion-selective extractant. This membrane operates much like the supported liquid membrane but is an integral unit that does not rely on an inert support material.

Our research has confirmed that polymer inclusion membranes prepared using cobalt dicarbollide and non-volatile solvents such as nitrophenyloctyl ether (NPOE) in a polyvinyl chloride (PVC) support matrix are selective for cesium uptake from a variety of aqueous solutions [3]. Adding polyethylene glycol as a "synergistic" extractant enhances the uptake of strontium, as expected based on the related solvent extraction work. Moreover, the sorption is lower from an aqueous phase of high salt content, indicating that membrane transport can be accomplished using a receiving phase of high sodium or hydrogen ion concentration.

This work was extended to alternative polymer matrix systems including polystyrene, and alternative solvents such as the inexpensive nitro compound, nitrophenylnonane (NPN) or the hydrocarbon phenylnonane (PN). The objective in these studies was to determine whether the use of nitrophenyloctyl ether caused a preference for the uptake of sodium ions that would interfere with the overall efficiency of cesium separation. While the polystyrene membranes prepared with PN and NPN were brittle and tended to phase-segregate, the PVC-NPN membranes showed good stability and flexibility characteristics and should be suitable for separations. Although their cesium and strontium uptake was unchanged compared to the NPOE membranes, the NPN solvent may be a good substitute because it is significantly less expensive than NPOE.

Cesium and Strontium Separations using Non-Hazardous Diluents. In the case of the membrane-mediated liquid-liquid extraction (Fig. 1a) and the supported liquid membrane (Fig. 1b) separations, the separations behavior can be understood using an analogous classical liquid-liquid extraction experiment. Thus we investigated the extraction of cesium into aromatic hydrocarbon diluents, such as diethylbenzene, as non-hazardous replacements for the traditional solvent nitrobenzene. Previously we reported the ability to extract cesium into diethylbenzene with a selectivity of 10,000 to 1 for cesium over sodium ion [2]. This represented an improvement of a factor of 10 over existing cobalt dicarbollide extractions and provides the ability to extract cesium efficiently from very high sodium-content wastes such as those stored at the Hanford site. A key limitation of that work was the lack of demonstrated extraction of strontium.

The current studies have focused on the use of polyethylene glycol (PEG) synergists and their compatibility with the aromatic hydrocarbon diluents. An unexpected benefit of the use of PEG is an improvement in the physical characteristics of the extraction

media; the aqueous and organic phases separate more cleanly and rapidly in the presence of PEG. While this advantage may be limited in a membrane system, it is still applicable to potential solvent extraction processes. This effect is observed even at very low PEG-400 concentrations of 0.002 M in diethylbenzene with 0.05-M cobalt dicarbollide.

More importantly, PEG enhances the extraction of Sr from nitric acid by a factor of 100, as its concentration is increased from 0.002 M to 0.2 M. At the same time, the cesium extraction efficiency is only diminished by a factor of 3 at the highest PEG concentrations. This provides the opportunity to "tune" the extraction system for uptake of cesium, or strontium, or both ions simultaneously. A similar effect is observed in sodium hydroxide solution, with an overall enhancement of the Sr extraction of 100 at 0.2 M PEG concentration.

The synergistic extraction effect provided by the PEG arises because the PEG can self-organize to wrap around the strontium ion in the manner of chemically similar, but more expensive, crown ether molecules. When bound to the strontium ion, the PEG provides an organic exterior that allows the strontium to pass into the organic phase more readily. Experiments with different concentrations of acid, base or salt show that strontium is extracted as a doubly charged PEG complex, except from highly alkaline solutions where it is extracted as a neutral PEG complex of $\text{Sr}(\text{OH})_2$. Another important observation from these experiments is that potassium ion, which is present in sub-molar quantities in several DOE wastes, interferes with strontium extraction more significantly than does sodium. The apparent reason for this is the closer fit of the potassium into the PEG. While good extraction efficiencies were still attained in the presence of 1-M potassium nitrate, significantly higher potassium concentrations may be problematic for the cobalt dicarbollide extractants.

Development of Redox-Recyclable Extractants for Cesium and Strontium. A final concern for this system was the inefficiency of the extractant recycle and radionuclide recovery steps. Because the extraction is driven by the greater tendency of cesium to partition into organic solvents versus water, it is difficult to force the cesium back out of the organic solvent so that that cobalt dicarbollide can be reused—a necessity given the significant production cost of the cobalt dicarbollide.

An efficient solution to this difficulty is provided by the concept of redox-recycling. As shown in Fig. 2, a neutral molecule is activated for extraction by a one-electron reduction to produce an anionic extractant. After the metal ion is extracted into the organic phase to form an ion pair, the extractant is oxidized back to its neutral form. Lacking the charge balance previously provided by the anionic extractant, the metal ion is now

transferred back into an aqueous "stripping" phase. The final step in the cycle is a reduction to reactivate the extractant for its next cycle of use.

While this system has been demonstrated in principle for the extraction of anions (using a cationic extractant [4]), there remained the significant challenge of designing and synthesizing an anionic extractant that is insoluble in water, highly soluble in hydrocarbons, and chemically stable in both its anionic and neutral forms. Ultimately the ideal choice proved to be the iron complex shown in Fig. 3 containing dicarbollide and cyclopentadienyl ligands. Fortuitously, this compound eliminates the use of cobalt, a regulated metal in some states, from the separation process. Synthesis of two related complexes was achieved. The first (Fig. 3a) was found to have a reduction potential of -0.2 V and tended to be oxidized by air. While problematic from a laboratory standpoint, this may be an advantage if a process can be designed that excludes air until the recycle step. The use of oxygen as the recycle chemical is attractive from a cost and environmental standpoint. The second extractant (Fig. 3b) adds two bromine atoms to the structure to adjust the reduction potential to approximately 0 V. In this region it is possible to handle the extractant in air without incidental oxidation, which could lower the extraction efficiency.

The extractions with both reagents were similar. From a simple waste simulant of 1.0-M sodium hydroxide and 1.5-M sodium nitrate, 95% of the cesium was extracted in one contact. After three contacts, we expect over 99.9% of the cesium to be removed from the aqueous phase. More significantly, oxidation of the extractant to its neutral form using a water-soluble oxidizing agent recovered 99.9% of the cesium in a single-phase contact step. This crucial recovery step demonstrates that the concept of redox-recycling can be applied to cesium and strontium extraction to eliminate a key secondary waste problem that has severely limited its implementation in the past.

Publications

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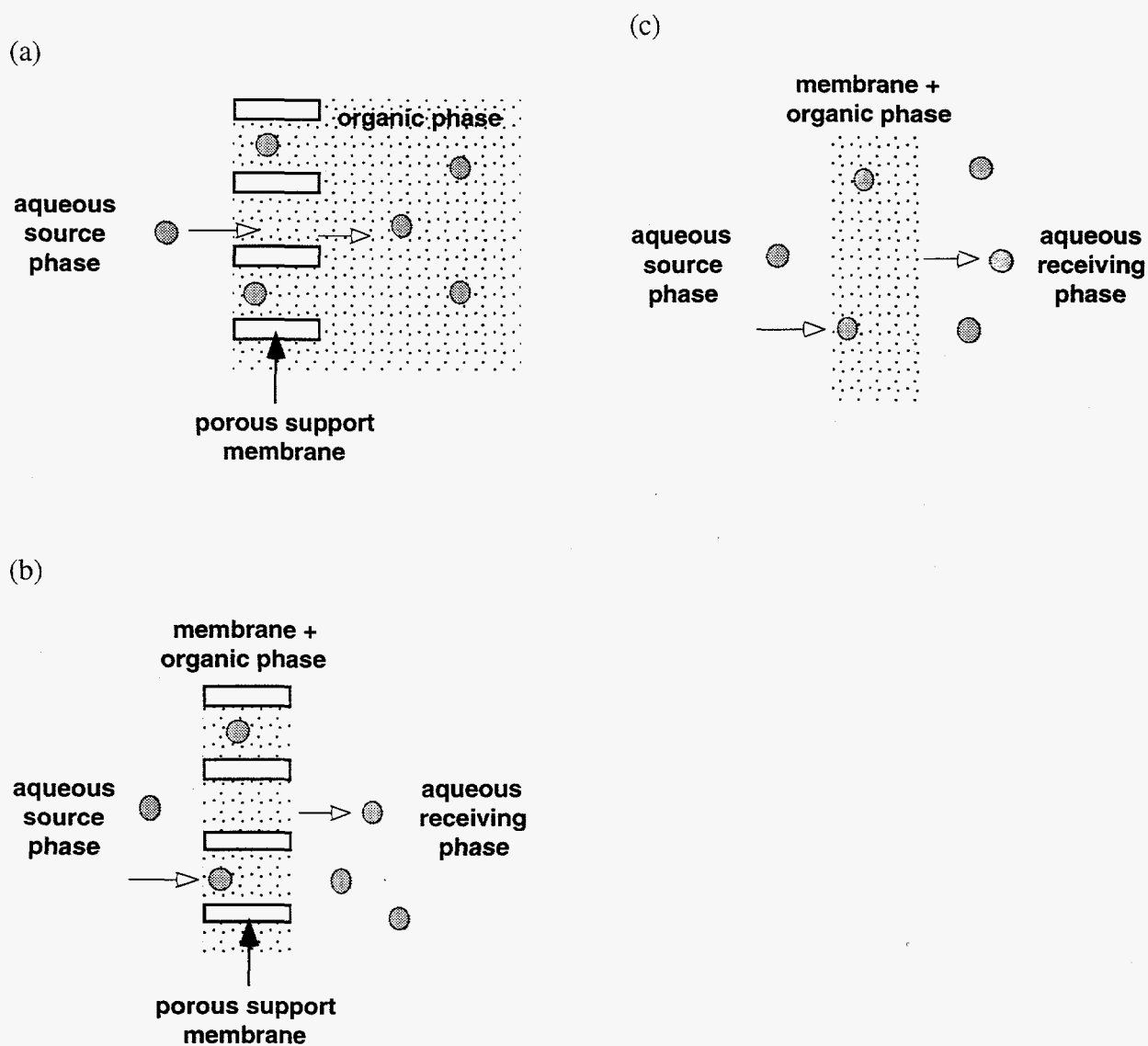


Fig. 1. Schematic of cobalt-dicarbollide-process cesium separations using (a) membrane-mediated liquid-liquid extraction, (b) supported liquid membranes and (c) polymer inclusion membranes.

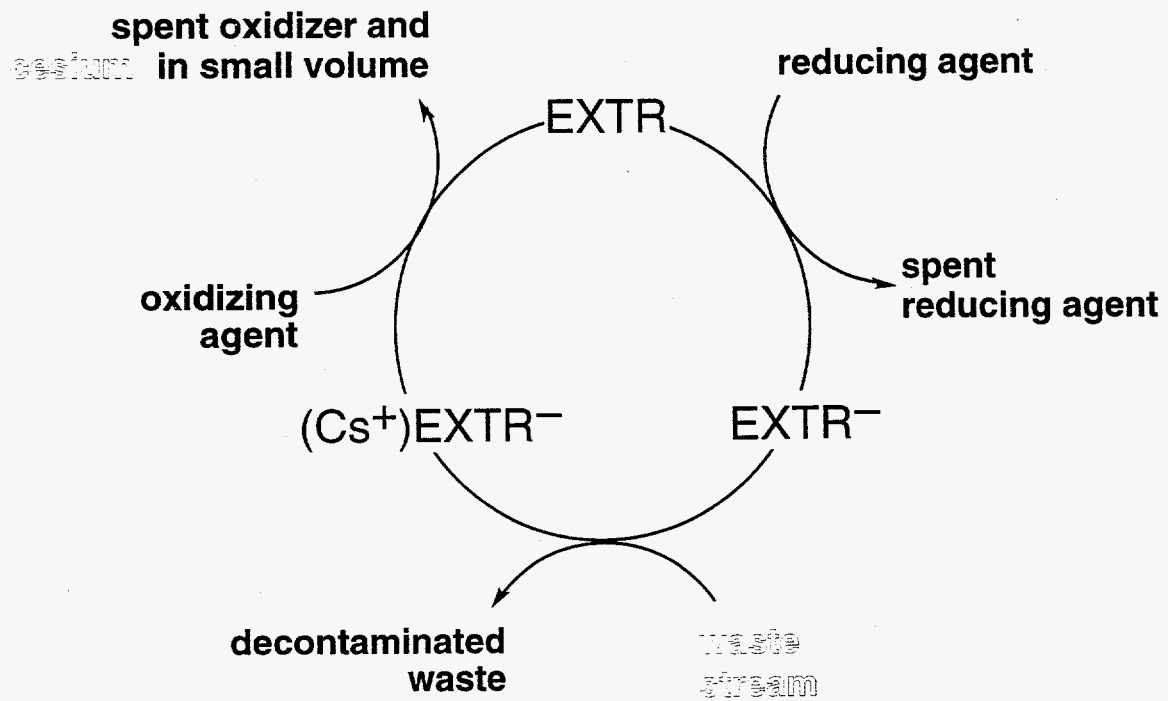


Fig. 2. A generic redox-recycling extraction scheme.

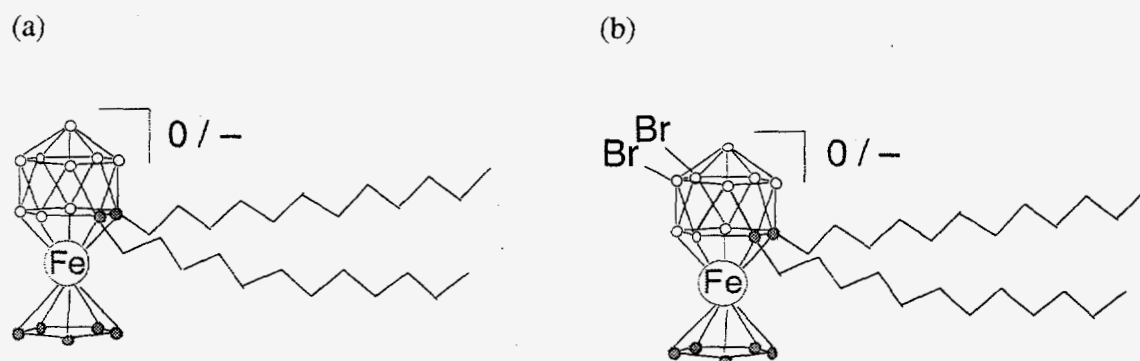


Fig. 3. Iron-based redox-recyclable extractants for cesium and strontium.

Task 3. Advanced Electrochemical Reactors (ECR) for Improved Separations and Waste Treatment

(Shimshon Gottesfeld, e-mail: gottesfeld@lanl.gov)

Background and Objective

The objective of this task was to develop energy-efficient and environmentally benign electrochemical reactors based on the use of solid polymer electrolytes (SPE) and gas-diffusion electrodes. Electrode catalysts are bonded directly to an SPE to provide a near "zero-gap" electrode configuration that minimizes cell voltage and energy consumption. Gas-diffusion cathodes that consume oxygen to produce water replace conventional hydrogen-evolving cathodes and lower cell voltage as well. We applied this technology to the electro-oxidation of a "trace" organic species in water.

NafionTM -105 membranes were coated with Ru-based anode catalysts to determine their effect on the oxidation of low concentrations of isopropanol in water. Isopropanol was chosen as a benign, yet difficult to oxidize, representative of common organic contaminants. While both Pt-Ru and RuO₂ catalysts provided equally high oxidation rates, the Pt-Ru based cells rapidly degraded. Figure 1 demonstrates the best performance obtained with the oxidation of a 0.1-M solution of isopropanol in water using a membrane coated with the RuO₂ catalyst. In general, about 60% of the isopropanol was oxidized to acetone within the experimental time frame. Though the current efficiency of this process is not particularly high, the use of an electrochemical reactor of this configuration allows dilute organics in water to be oxidized without introducing new chemical entities into the flow-stream.

Work continued with O₂ cathode/SPE-based chlor-alkali electrolyzers as well. The process has been demonstrated in 58 cm² industrial configuration cells with similar performance to the 5 cm² laboratory cells.

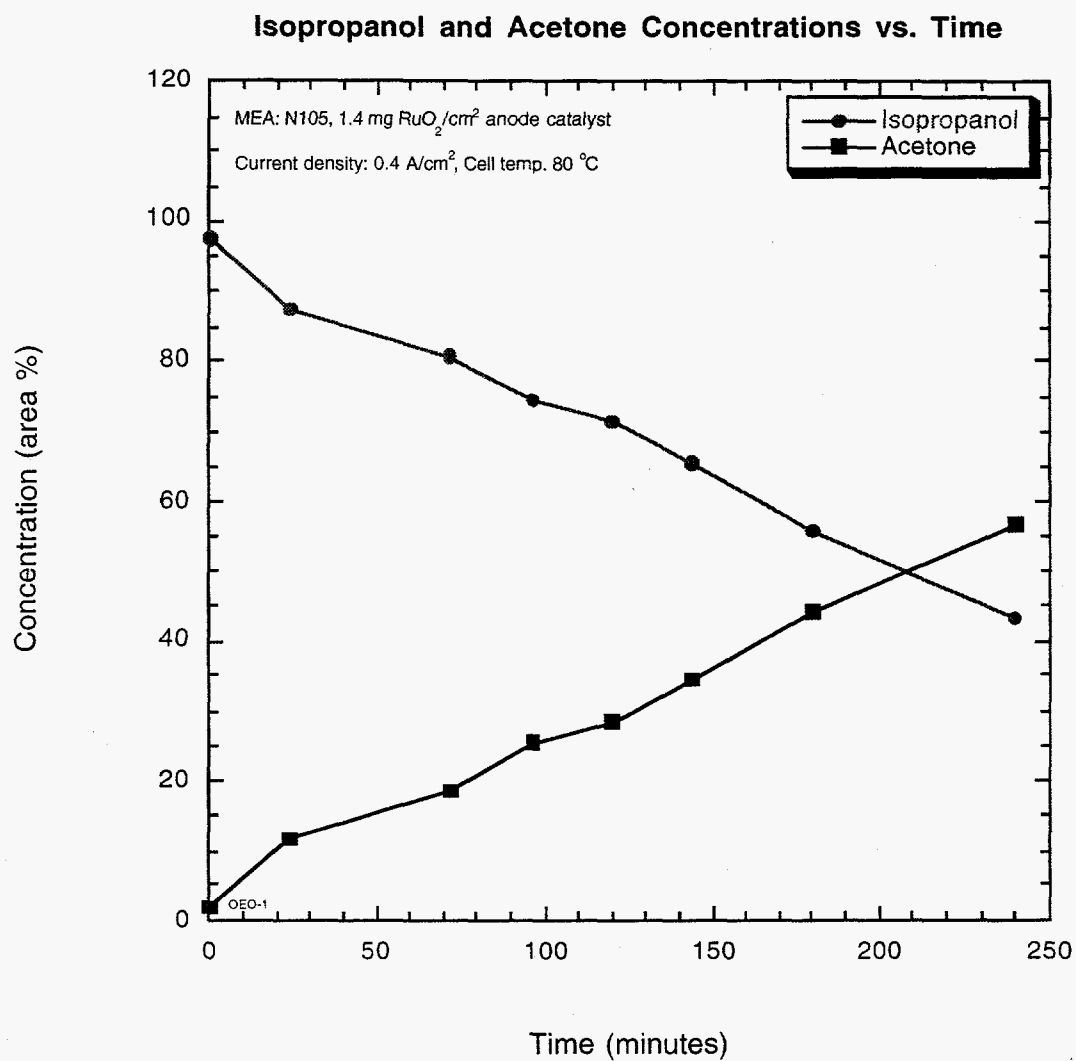


Figure 1. The oxidation of isopropanol by a RuO₂ catalyst. Isopropanol and acetone concentrations were determined by GC-MS.

Task 4. Advanced Materials Fabricated as Hollow Fiber Membranes for Separation Processes

(Benjamin R. Mattes, e-mail: mattes@lanl.gov)

Background and Objective

Our research objective is to produce hollow fibers and to fabricate prototype hollow-fiber membrane modules (HFMM) for applications to gas separations and the liquid-liquid extraction and recovery of actinides and nuclear materials from process streams. Our specific HFMM's are not commercially available; they were prepared at LANL and subsequently field tested by our Laboratory collaborators and by our industrial partners. To accomplish this objective, we continued the basic science necessary to improve the performance of our targeted polymers and simultaneously, we developed HFMMs based on the advanced polymer materials.

We have continued our work with PTMSP for commercial separation of gas mixtures. This work has led to the preparation of five manuscripts and one publication in a refereed journal. We submitted a joint proposal, together with two Russian institutes and our industrial partner, through the United States Industrial Coalition. This effort has led to a significant new program at LANL with funding at the \$600K level. Additionally, Pittsburg Plate Glass (PPG) has funded a small exploratory R&D effort at LANL in the area of measuring gas transmission rates through some of their proprietary barrier materials.

We have demonstrated the feasibility of producing ultraporous and microporous polyetheretherketone (PEEK) flat sheet membranes. These membranes are produced by dissolution of the polymer in concentrated sulfuric acid together with N-methylpyrrolidinone (NMP) as the non-solvent. PEEK is soluble only in 98% sulfuric acid, and hence it is an attractive membrane material for operation in extremely low (or high) pH.

Scientific Approach and Accomplishments

Our experimental work was performed primarily in the area of conjugated-polymer hollow-fiber membrane and module formation, processing, characterization, and application to gas separations [e.g., polyaniline and poly-(1-trimethylsilyl-propyne)]. However, we began new investigations into novel polyimides for gas separation. This work leads us now to a new patent disclosure and filing. In terms of program development, PPG is presently in the process of evaluating one aspect of the patent we filed one year ago, and we have been working informally with Spectrum Microgon on

biomedical and biotechnology separation applications for electrically conducting hollow fibers. Dialogue was established with C. Russomanno (DOE/ OIT) on integrating our experimental activities with the Chemical Industries of the Future Program.

Several significant accomplishments resulted from our efforts during the first year of this task. First, we installed complex industrial processing equipment for dry-wet spinning of fiber and hollow fiber in our laboratory. A number of well-known membrane materials (e.g., polysulfone) have been spun into microporous and ultraporous hollow fibers, and evaluated for separation properties. Second, the electrically conducting polymer polyaniline (PANI) was prepared, for the first time, as an integrally skinned asymmetric (ISAM) flat sheet membrane. These PANI membranes show substantially increased gas flux. The non-porous skin thickness can now be reproducibly prepared in the range from 0.5 to 0.8 mm with selectivities for $H_2/N_2 > 1,000$ and $O_2/N_2 > 15$.

These same solution-processing advances have led us to develop the first generation of electrically conductive, polyaniline, hollow-fiber prototype modules that have commercial value. Several major companies are interested in this technology for gas separations. These PANI hollow fibers have the same gas separation properties (high flux and selectivity) as do the flat-sheet PANI ISAM membranes. Moreover, preliminary experiments show that the base nitrogen atoms in the polyaniline repeat unit have a very high selective affinity for metals in solution (e.g., Ag, Au, Cr, Pt), which make them attractive alternatives to commercial resin systems for cleaning up electroplating waste streams. A variation of this research effort has allowed us to produce high strength, highly conductive (>50 S/cm), polyaniline solid fibers that have many commercial applications. Our work on this task has resulted in three patent disclosures. Figure 1 shows the different geometries for electrically conducting polyaniline achieved by our proprietary technology developments, i.e., dense flat sheet film, flat sheet ISAM, hollow fiber ISAM, and solid fiber.

Publications

- (1) B. R. Mattes, H.L. Wang, and J.P. Pellegrino. "Temperature and Pressure Dependant Gas Transport Through Polyaniline Membranes." *International Journal of Thermophysics*. (in press).
- (2) I. N. Shennikova, G. F. Kolbina, V. S. Khotimsky, E.G. Litinova, N. A. Platè, and B. R. Mattes. "Rigidity and Conformation of Poly-(1-trimethylsilyl-propyne) in Solutions." *Macromolecules*. (in press).
- (3) M. Espe, J. Schaefer, and B. R. Mattes. "Packing in Amorphous Regions of Hydrofluoric-Acid Doped Polyaniline Powder by ^{15}N - ^{19}F REDOR NMR." *Journal of the American Chemical Society*. (in press).

- (4) M. J. Winokur and B. R. Mattes. "Determination of the Local Molecular Structure in Amorphous Polyaniline." *Physical Review B: Rapid Communications*. **54**, 18 (1996).
- (5) M. J. Winokur and B. R. Mattes. "Polyaniline as Viewed from a Structural Perspective." *Society of Plastics Engineers, Technical Papers Volume XLIII*. pp. 1325-1333, (1997).
- (6) B. R. Mattes, H.L. Wang, and D. Yang. "Electrically Conductive Polyaniline Fibers Prepared by Dry-Wet Spinning Techniques." *Society of Plastics Engineers, Technical Papers Volume XLIII*. pp. 1463-1467, (1997).
- (7) B. R. Mattes, H. L. Wang, D. Yang, Y. T. Zhu, W. R. Blumenthal, and M. F. Hundley. "Formation of Conductive Polyaniline Fibers Derived from Highly Concentrated Emeraldine Base Solutions." *Synthetic Metals*. **84**, 1-3, pp.45-50, (1997).
- (8) M. J. Winokur and B. R. Mattes. "Differential Anomalous Scattering Studies of Amorphous HBr-Doped Polyaniline." *Synthetic Metals* **84**, 1-3, pp. 725-729, (1997).
- (9) Espe, M., Schaefer, J., and Mattes, B. R. "Conformational Dynamics of Emeraldine as Determined by Solid State NMR Spectroscopic Techniques." *Macromolecules* (accepted).

Invited Papers and University Seminars

- (1) B. R. Mattes, H. L. Wang, D. Yang, Y. T. Zhu, W. R. Blumenthal, and M. F. Hundley. "Formation of Conductive Polyaniline Fibers Derived from Highly Concentrated Emeraldine Base Solutions." International Conference of Synthetic Metals. Chair: A. G. Mac Diarmid. Snowbird, Utah.
- (2) B. R. Mattes and H. L. Wang. "Conducting Polymer Membranes for Chemical Separations." Seoul, Korea. 36th IUPAC International Symposium on Macromolecules. August 5, 1996.
- (3) B. R. Mattes and H. L. Wang. "Formation Parameters for Integrally Skinned Polyaniline Hollow Fibers." Korean Institute of Science and Technology. Seoul, Korea August 12th, 1996. Host: Dr. Yong Soo Kang.
- (4) B. R. Mattes and H. L. Wang. "Gas Separations with Integrally Skinned Asymmetric Polyaniline Membranes." Samsung Corporation. August 13, 1996. Host: Dr. Shinee Kang
- (5) B. R. Mattes and H. L. Wang. "Some Recent Advances in Solution Processing of Polyaniline." SoGang University, Seoul, Korea. August 15th, 1996. Hosts: Profs. Li and Rhee.
- (6) B. R. Mattes, H. L. Wang, and D. Yang. "The Development of High Strength Electrically Conducting Fibers with High Conductivity." International Symposium on the Technology of Inherently Conducting Polymers. San Diego, CA. Chair: M. Aldissi. March 3-5, 1997.
- (7) B. R. Mattes, H. L. Wang, and D. Yang. "Electrically Conductive Polyaniline Fibers Prepared by Dry-Wet Spinning Techniques." Antech '97: Society of Plastics Engineers. April 27-May 1, 1997. Chair: A. J. Mac Diarmid. Toronto, Canada.

(8) B. R. Mattes, H. L. Wang, and J. P. Pelligrino. "Temperature and Pressure Dependant Gas Transport Through Polyaniline Membranes." 13th International Symposium on Thermophysical Properties. June 16-19, 1997. Boulder, Colorado.

(9) B. R. Mattes. "New Solution Processing Routes to Thin Films of Conducting Polymers and Their Applications." Gordon Conference on Thin Films and Coatings. July 14-17, 1997. Chair: D. Boyd. New Hampshire.

Patents

1. Mattes, B. R. and H.S. Wang, "Stable concentrated solutions of high molecular weight polyaniline and articles therefrom," Filed May, 1996.

2. Mattes, B. R. and H.S. Wang, "Engineered porous polyaniline articles," Disclosed June 1996.

3. Mattes, B. R. and Michael Courmoyer, "Selective Metal Removal from Aqueous Streams with Polyaniline Films, Powders, and Hollow Fibers," Disclosed June, 1996.

4. Y. Yampolskii, N. Platè, J. Henis, and B. R. Mattes, "Process of Membrane Separation of Gas Mixtures," Disclosed June, 1997.

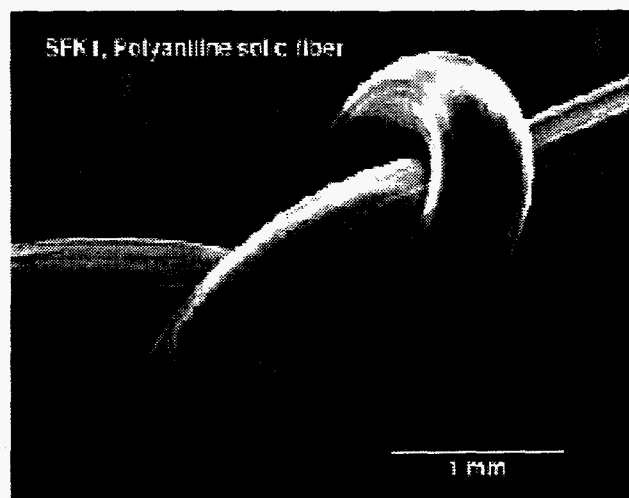
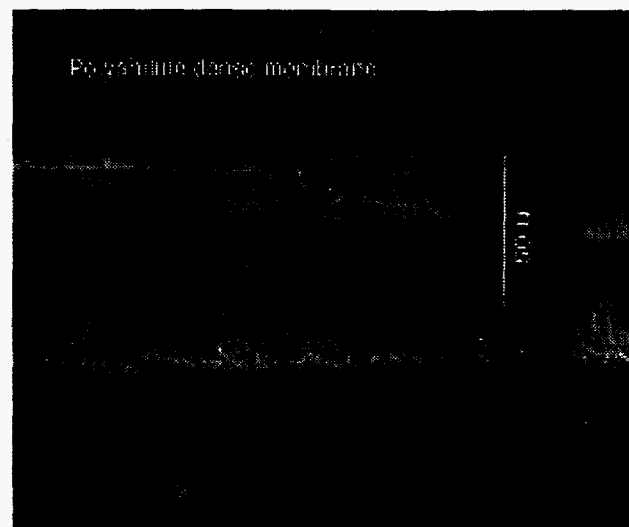
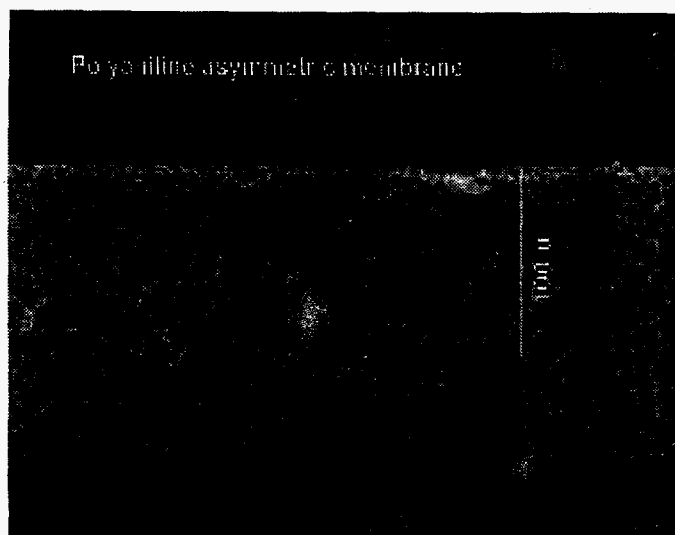


Figure 1. Four patented geometries of the electrically conducting polymer polyaniline were developed: (a) engineered porous flat sheet membranes, (b) barrier coatings, (c) engineered porous and integrally skinned asymmetric hollow fibers, and (d) electrically conductive solid fibers (clockwise from top left to bottom right.)

Task 5. Host for Removal of Organics from Water

(DeQuan Li, e-mail: dequan@lanl.gov)

Background and Research Objectives

Cleaning municipal and industrial water supplies has become an increasingly important issue. In many cities, contaminants in water have threatened the health and safety of both humans and the environment. Both government and industry face stringent environmental regulations and environmental cleanup standards. Ultra-pure water is becoming more and more critical for all of us. The water treatment market continues to seek new technologies that can economically ensure a high-quality water supply. This task presents a novel innovation to address this critical problem.

Importance to LANL's Science and Technology Base and National R&D Needs

This task supports several LANL tactical goals including (1) Safety First!, (2) Reducing the Threat of Nuclear, Biological, and Chemical (NBC) Proliferation and Terrorism, (3) Integrated Environmental Science, and (4) Science-Based Stockpile Stewardship and Management. For example, our nanoporous polymers have the ability to provide safer and cleaner air and water, which are critical in many areas such as NBC and environmental clean-up. The success of this task will directly contribute to the following Laboratory core competencies and enhance LANL's capabilities: Complex Experimentation and Measurement, Earth and Environmental Systems, and Nuclear and Advanced Materials.

Scientific Approach and Accomplishments

This work on nanoporous polymers has been very successful; major accomplishments are the following: (1) a new class of organic porous materials was invented and an invention disclosure was made, (2) the nanoporous polymers show great promise in water purification, and (3) an external program was initiated. These significant results were achieved in two years; further evaluation is required including the kinetics of molecular inclusion of organic species and molecular transport properties inside nanoporous polymers.

Fabrication Flexibility. Nanoporous polymers can be fabricated as granular solids, powders, and membranes. Consequently, they can be adapted to many types of existing water treatment components and facilities. For example, a polymer designed and fabricated

as a membrane could be placed on a household water faucet. This membrane would purify water much like conventional filters soften it. The only difference is that water softeners introduce soft ions (Na^+) in exchange of hard ions (Ca^{++}), whereas nanoporous polymers "catch" toxic organic materials and introduce nothing into the water.

Comparison of Nanoporous Polymers to Industrial Standards. We have compared our molecularly engineered nanoporous polymers with current industrial standards such as activated carbon and zeolites. The results of our preliminary studies of p-nitrophenol and nanoporous polymers are shown in Table 1. Although we are comparing nanoporous polymers with absorbing materials (such as activated carbon), we have planned to replace the latter with nanoporous polymers for certain applications. Nanoporous polymers are superior to these absorbents because they can be fabricated into thin-film membranes and the polymers can be used to treat organics *in situ* because their high stability constants prevent leaching organics in water.

As shown in Table 1, zeolites have no affinity to organic molecules in water. Moreover, activated carbon, which industry presently uses, has shown moderate binding affinity but it is not strong enough to achieve the present target level (~5 ppb for most organics). In addition, activated carbon will not hold organic compounds in its porosity and the organic leaches out very fast. It is also very difficult to use activated carbon because it non-selectively absorbs water in air and quickly loses its effectiveness.

The nanoporous polymers possess a stability constant more than 5 orders of magnitude larger than the industrial standard (activated carbon, which is presently used in "pump and treat") and can reduce the concentration of many organics below ppb level—even to 3 parts per trillion (pptr) for p-nitrophenol. Unlike activated carbon, nanoporous polymers do not absorb water in air and possess the desired film formation properties that can be readily fabricated into membranes. We have also obtained similar favorable results on chlorinated hydrocarbon (e.g., TCE) and aromatic hydrocarbon (e.g., toluene) as well as many organic dyes.

Table 1. Comparison Matrix (of p-nitrophenol) for CD Polymers to Other Absorbents

<i>p</i> -Nitrophenol	Nanoporous	Activated Carbon	Zeolites
Stability constant K	6.0 X 10 ⁴	1.4 X 10 ⁴	~0.0 M ⁻¹
Loading Level	22 mg per gram	58 mg per gram	~0.0
Analyte Equilibrium Concentration	3.0 pptr	1.3 ppm	—
Leaching Target Organics in H ₂ O	No	Yes	Yes
Film Fabrication	Yes	No	No
Nonselectively Absorbing Water in Air	No	19.6 mg/hr·g	Yes

Task 6. Selective Waste Remediation Using In-Situ Photocatalytic Reactors

(Basil Swanson, e-mail: basil@lanl.gov)

Background and Research objectives

The removal of toxic organic compounds from industrial process and waste streams is important as the nation moves towards sustainable technology and economy. Even small concentrations (~ 1 ppm) of toxic organics can be deleterious to waste stream processing, as is the case for chlorophenol, which destroys the active bacteria in bioremediation plants. The objective of this task is to develop a species selective photo-oxidation process capable of removing selected organics that are present at low concentrations. The approach is unique in that the target is oxidation to a non-toxic form rather than "mineralization," which is the target of other photoremediation processes based on semiconductors.

Importance to LANL Science and Technology Base

This work integrates self-assembly techniques, molecular synthesis, and inorganic photophysics to address an important problem in environmental management and industrial ecology. The work builds on the emerging areas of self-assembling materials and molecular recognition and will strengthen the capability area of soft condensed matter.

Scientific Approach and Accomplishments.

Effort. The developed technology addresses the need for species-selective, advanced oxidation technologies based on molecular-level materials design (smart-materials), which selectively remove or destroy target species in a waste stream. In particular, the technology targets treatment of low-level (ppm) contamination in process streams that are problematic for recycling, raw material minimization, or for conventional remediation technologies. The species-selective technology utilizes a photo-oxidant (sensitizer) that is bound to the surface of a semiconductor-modified nanoporous membrane. The semiconductor acts as a molecular support and electron shuttle.

The studies focus on molecular-level engineering of nanometer-scale porous aluminum oxide:titanium membranes to develop a photoremediation reactor targeting low-level contamination in process streams. In particular, we probed treatment of low-level (ppm) phenolic contamination in aqueous process streams. The photo-selective reactor operates passively under visible-light photolysis conditions. Photo-initiated destruction

and ultrafiltration occur at surface-derivatized nanoporous Al_2O_3 :titania membranes allowing a modular approach to process stream control. We have demonstrated selective oxidation of the chlorinated phenols by conversion to benzoquinones at molecularly engineered oxide membranes. A patent titled "Species Selective Photo-Oxidation of Environmental Toxins in Industrial Process Streams and Effluents" has been filed and is pending.

Research Approach. This technology is an outgrowth of our research efforts into visible-light sensitization of TiO_2 and the development of molecular "anchors" in our sensor technologies effort. Figure 1 illustrates selective binding of organic molecules on an engineered TiO_2 oxide layer. The membrane support is a 0.02 mm nanoporous alumina membrane in which the TiO_2 is deposited via sol gel techniques. The solvated organics compete for the hydrophobic cavity of the membrane nanopore.

The high selectivity of the modified surfaces will allow membrane reactor technologies to be applied for transitioning the basic research into applications. One advantage of the membrane technology is the adaptability to existing technologies and the modularity of the approach.

The assembly of several different membranes can be envisioned to address different low-level toxins in the process stream. It represents a visible-light-driven, active-destruction technique that is passively operated, requiring no operational shutdowns for secondary remediation steps, filter removal, or mechanical replacement. The nanoporous membrane improves mass transport via increased surface area and turbulent flow, modularity of the system, and structural rigidity.

Molecular-Level Modification of Membranes. The molecular membrane is based on molecular-level modification of nanoporous alumina membranes that are coated by TiO_2 , as illustrated in Figure 2. By varying controlled deposition, the inner porosity of the TiO_2 tubule can be modified from 0.02 mm to 6 nm. The titania deposition is carried out by acid-catalyzed sol-gel deposition of TiO_2 into the pores of a preformed porous Al_2O_3 membrane (20-nm pores). SEM and AFM images of the pore structures following titania modification indicate pores ranging from 5-15 nm.

Species selective oxidation at the membrane is achieved through selection of an appropriate transition metal photo-sensitizer. For instance, ruthenium-based sensitizers are chosen because of the ease of tuning of their excited state oxidation potentials via ligand synthesis or changing the central metal ion. These transition metal polypyridyl complexes can be excited by visible light, producing a strong oxidant ($E_{\text{OX}} \sim 1.1 \text{ V}$) and a strong reductant ($E_{\text{red}} \sim -0.9 \text{ V}$). Surface derivatization of the ceramic membrane with the photosensitizer is carried out by application of standard self-assembly techniques.

Derivatization of the titania surface occurs through conversion of the hydroxyl groups on the titania surface to ether linkages. Treatment of the ceramic membrane with a ruthenium based photo-sensitizer results in surface coverage of the titania layer with the dye molecule. Optical absorption and Raman scattering experiments indicate surface coverage without changes in the structure of the dye (see Figure 3). AFM and SEM images following coating indicate no changes in the pore structure of the ceramic membrane.

Photoremediation of 4-Chlorophenol. It has been recently demonstrated that exposure of the membrane to low-intensity, visible light in a nanomolar solution of 4-chlorophenol results in efficient degradation of the phenol to 1,4-benzoquinone and 1,4-hydroquinone (Figure 4). Verification of the products by HPLC and optical absorption indicate high conversion efficiencies (Figure 5). A proposed mechanism for degradation involves visible light excitation of the sensitizer followed by injection of an electron into the TiO_2 membrane. This results in formation of an oxidation site at the sensitizer. Under visible light illumination, the photo-generated hole centered on the transition metal photosensitizer directly oxidizes the organic-producing benzoquinone and HCl. It is postulated that the electron further reduces the initial benzoquinone product to the hydroquinone. The semiconductor is not *photo-excited*, its primary functions are structural support and trapping the injected electron (electron shuttle).

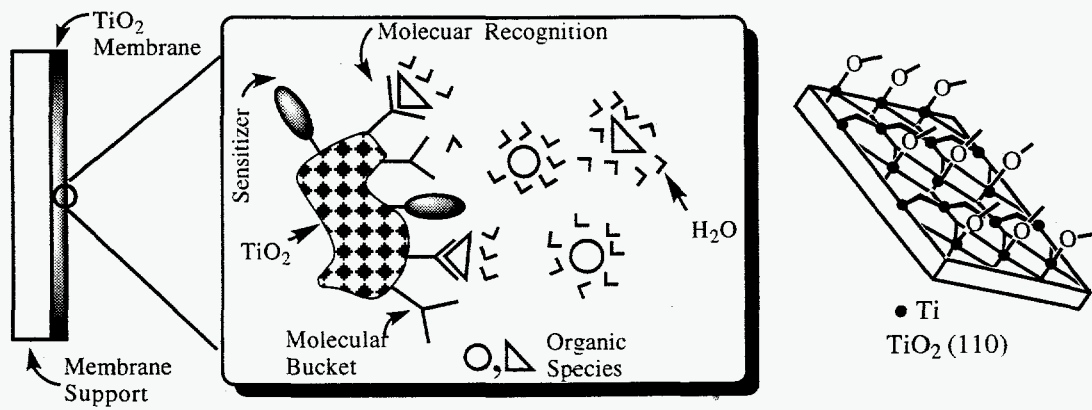


Figure 1. Selective binding of organic molecules on an engineered TiO_2 oxide layer.

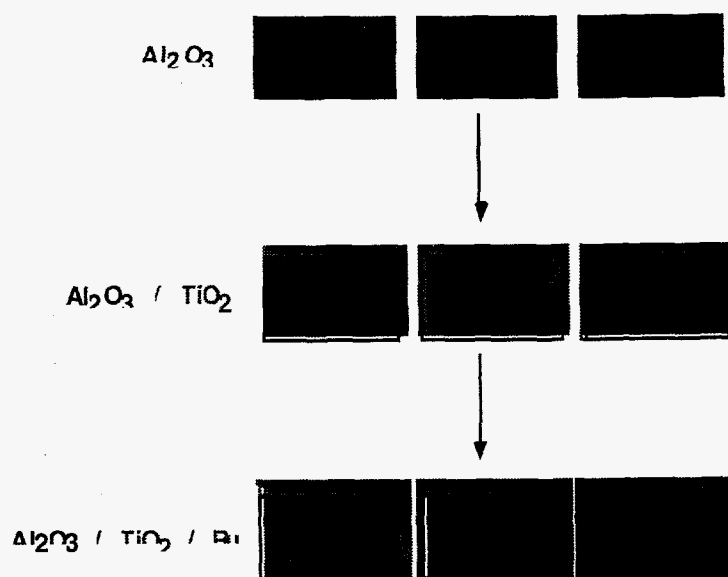
Figure 2. Self-assembly on nanoporous Al_2O_3 membrane.

Figure 3. Optical absorption and Raman scattering experiments indicate surface coverage of the titania layer with the dye molecule without changes in the structure of the dye.

Assembly of Dye Molecule at TiO₂ Surface

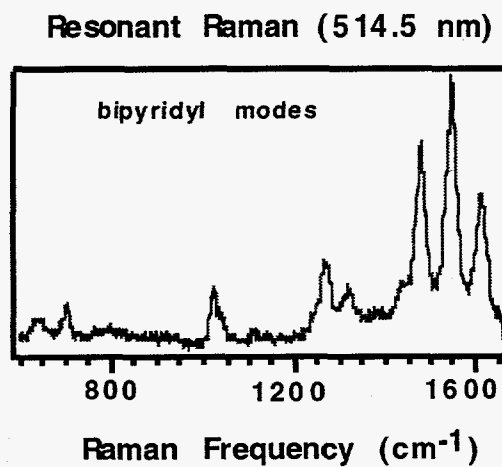
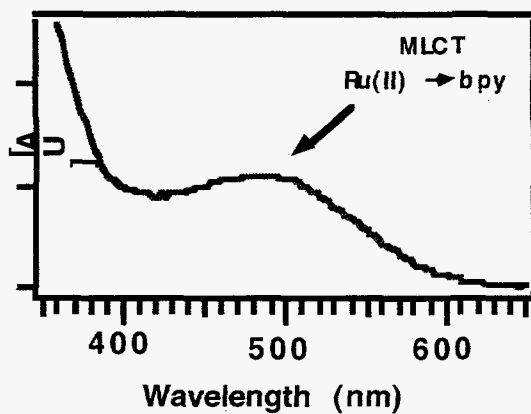


Figure 4. Degradation of 4-chlorophenol.

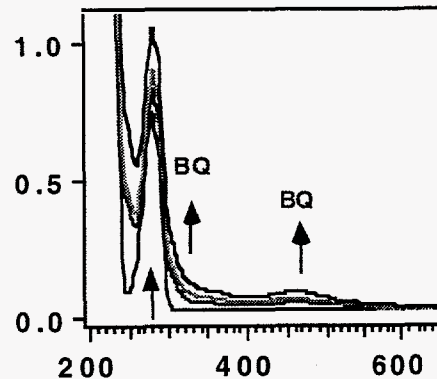
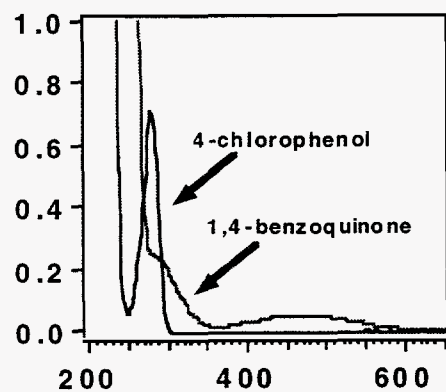
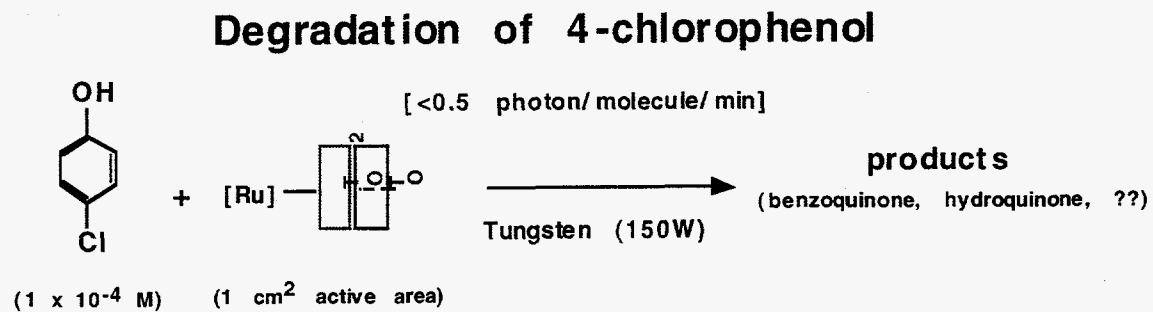


Figure 5. Verification of the products by HPLC and optical absorption indicate high conversion efficiencies

HPLC Analysis of Photo-degradation Products of 4-Clphenol (1×10^{-4} M)

