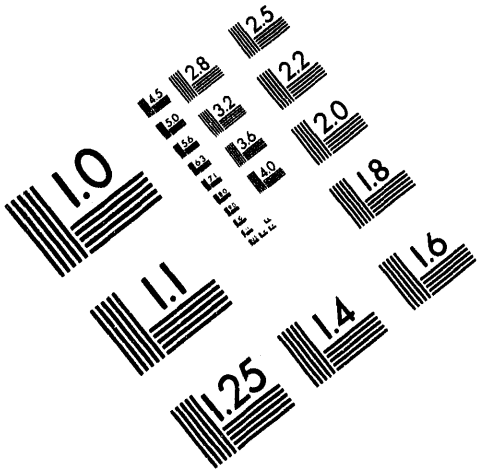

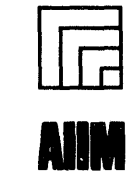

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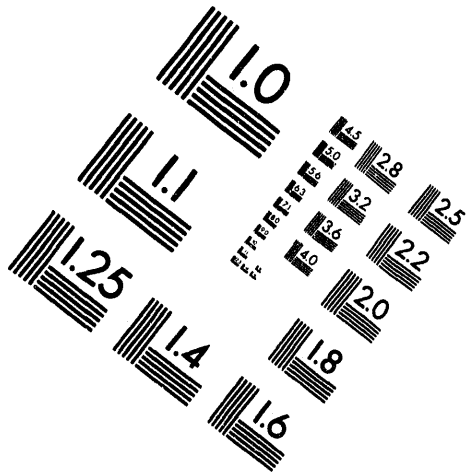

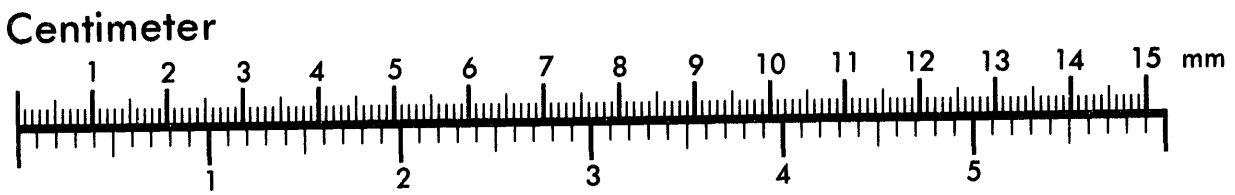


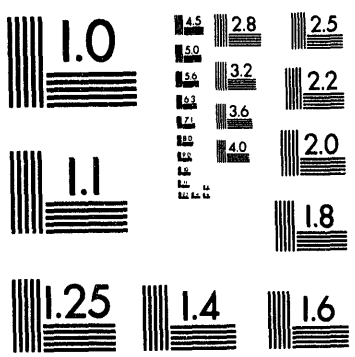

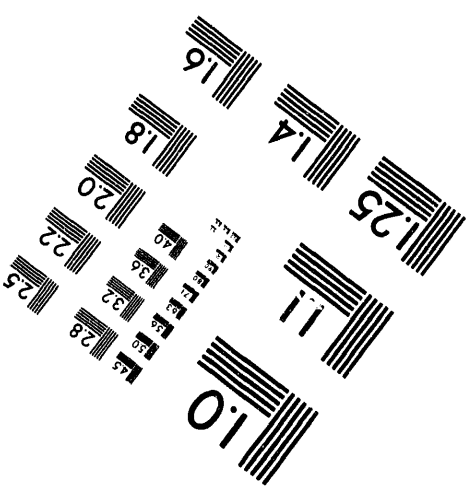

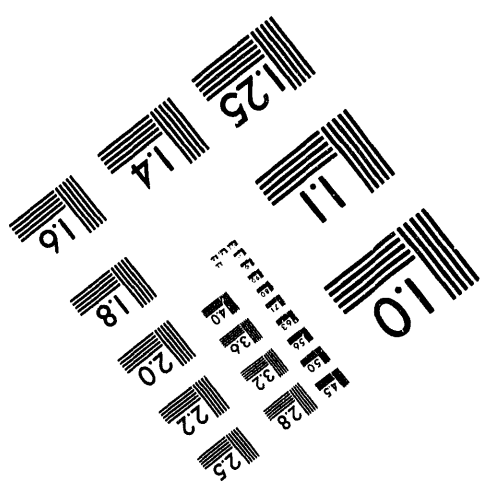

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# Selective Separation of $Eu^{3+}$ Using Polymer-Enhanced Ultrafiltration

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## Abstract

The U.S. Department of Energy is actively pursuing new and improved separation techniques to concentrate high-level liquid radioactive waste, particularly at the Hanford Site, in order to minimize the waste volume requiring vitrification. A process to selectively remove $^{241}Am$ from liquid radioactive waste was investigated as an actinide separation method that could be applicable to Hanford and other waste sites.

The experimental procedures involved removal of Eu, a nonradioactive surrogate for $^{241}Am$, from aqueous solutions at pH 5 using organic polymers in conjunction with ultrafiltration. Commercially available polyacrylic acid (60,000 MW) and Pacific Northwest Laboratory's[1] (PNL) synthesized E3 copolymer (~10,000 MW) were tested. Test solutions containing 10 μg/mL of Eu were dosed with each polymer at various concentrations in order to bind Eu (i.e., by complexation and/or cation exchange) for subsequent rejection by an ultrafiltration coupon. Test solutions were filtered with and without polymer to determine if enhanced Eu separation could be achieved from polymer treatment. Both polymers significantly increased Eu removal. The optimum concentrations were 20 μg/mL of polyacrylic acid and 100 μg/mL of E3 for 100% Eu rejection by the Amicon PM10 membrane at 55 psi. In addition to enhancement of removal, the polymers selectively bound Eu over Na, suggesting that selective separation of Eu was possible.

The results of this study suggest that polymer-enhanced ultrafiltration is a potential process for separation of $^{241}Am$ from Hanford tank waste. Thus, further investigation of binding agents and membranes effective under conditions similar to the tank waste (e.g., very alkaline and high ionic strength) is warranted. This process also has potential applications for selective separation of metals from industrial


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[1] Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

process streams and the use of the polymers evaluated in this study and other high molecular weight binding agents that exhibit an affinity for regulated toxic metals should be further examined.

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# 1.0 Introduction

Management of radioactive liquid waste is an ongoing challenge for both the commercial nuclear power industry and the U.S. Department of Energy (DOE). This challenge is driven by two major criteria: 1) regulatory requirements for the protection of human health and the environment and 2) the cost for handling and disposal. The commercial nuclear power industry manages liquid radioactive wastes by implementing separation techniques to isolate and concentrate high-energy radioactive species from the bulk liquid. The concentrated, reduced volume of waste requires less high-energy shielding material for interim storage and conditioning for final disposal. Vitrification is the standard treatment technique used to condition the high-energy fraction into a very inert waste form for ultimate disposal in a proposed geologic repository. It is an energy-intensive, expensive, immobilization/stabilization process. The less radioactive bulk liquid does not require the expensive shielding requirements and conditioning process for final disposal. It is typically grouted/cemented to immobilize the low-energy species for shallow land burial.

The strategy being pursued by DOE for managing its radioactive liquid wastes is similar to the commercial approach. At the Hanford Site, radioactive liquid wastes generated from past manufacturing and reprocessing of plutonium weapons-grade fuel have been stored in single-shell and double-shell underground tanks. The total estimated tank waste volume is 245,000 $m^3$ (64.7 million gallons). The fraction containing high-energy species will be vitrified, and the remaining low-level waste fraction will be grouted. Because vitrification is such an expensive process, DOE is actively pursuing new and improved separation techniques to minimize the volume of high-level waste to be vitrified.

Among the many types of ionic radioactive species found in liquid radioactive wastes, actinides are important owing to their high radiotoxicity and long half-lives (Ali and Ache 1984). The objective of the research described here is to evaluate a potential actinide separation process for aqueous radioactive waste streams that could be applied to Hanford, other DOE sites, and commercial nuclear facilities. The specific

actinide of interest was americium-241 ($^{241}$Am) because it is present in the supernate of many of the Hanford waste tanks and, consequently, the supernate is considered a high-level waste. Selective separation of $^{241}$Am from the bulk supernate may reduce the volume of high-level supernate requiring vitirfication.

Metal ion separation techniques using inorganic ion exchangers or water- soluble complexing polymers in conjunction with ultrafiltration have been explored. The low-energy requirements and potential cost savings associated with ultrafiltration and the selective binding capacity of the absorbing and polymeric materials make this a promising separation process to meet DOE needs. Pacific Northwest Laboratory (PNL) has synthesized a copolymer with functionalities known to have a binding affinity for lanthanides. The specific objectives of this research were to characterize the copolymer and develop a protocol to evaluate its binding capacity and selectivity for trivalent europium, a nonradioactive lanthanide selected as a surrogate for $^{241}Am^{3+}$. A comparison was made with commercial polyacrylic acid. Ultrafiltration was used for macromolecular separation of the europium-polymer complexes from simple aqueous solutions. The experimental methods and test results are given here along with a literature review conducted to provide a background for the research.

# 2.0 Background

This section provides an overview of techniques found in the literature for actinide separations applicable to liquid radioactive wastes. Both advantages and disadvantages of these techniques are compared to provide the basis of motivation for pursuing the specific objectives of this research. The areas reviewed are conventional treatment, treatment involving separation by ultrafiltration, and potential binding agents for actinide separation.

## 2.1 Overview of Liquid Radioactive Waste Treatment Methods

Chemical and physical separation techniques utilized in water and wastewater treatment have been implemented by the commercial nuclear industry to treat liquid radioactive waste streams (Carley-Macauly 1984). These processes include chemical precipitation, evaporation, ion exchange, solvent extraction, and filtration. These techniques are often combined based on the specific waste stream characteristics and discharge/disposal requirements. The process performance is typically evaluated by the decontamination factor (DF) achieved. The decontamination factor is defined as (Hooper 1991):

DF = radioactivity in feed stream/radioactivity in treated effluent.

### 2.1.1 Precipitation

Chemical precipitation is a proven, easy to implement, low cost process technology that has been used successfully for separation of radionuclides from aqueous streams. If effective settling occurs (i.e., good solid/liquid separation of the radioactive precipitates from the bulk solution), good DFs can be achieved (Cecille et al. 1985). Cecille (1985) indicated that a DF of about 20 for alpha emitters is required for effective partitioning of low- and medium-level liquid radioactive waste. A typical alpha DF using chemical precipitation was about 30. If higher DFs are required, the treated bulk solution (i.e., supernatant) can be filtered to remove colloidal, radioactive precipitates. Direct ultrafiltration (pH ~ 9 - 10) achieved an alpha DF range of 330 to 3300. Cross-flow ultrafiltration has proven to be an effective

polishing technique for meeting high DF requirements (Carley-Macauly 1984). Some of the disadvantages of chemical precipitation are facility requirements for gravitational settling, chemical requirements for pH adjustment and flocculation, slow settling velocities, and low sludge solids content. Sludge dewatering steps are typically required to minimize the volume of radioactive solids and achieve a suitable solids content for immobilization processes.

### 2.1.2 Evaporation

Evaporation is a well-demonstrated and proven technology for radionuclide separation of liquid radioactive wastes. With the exception of volatile contaminants, extremely efficient separation of radioactive species from the bulk liquid is achieved (Carley-Macauly 1984). However, the process is usually not cost competitive compared with alternative treatments because of its high energy requirements. Also, the process is nonselective for removal/separation of target radionuclides from solution (i.e., it is a "catchall" process).

### 2.1.3 Fixed-Bed Ion Exchange

Fixed-bed ion exchange columns can process large throughputs of dilute radioactive streams and achieve high DFs. Once-through operations are employed to avoid flush, regeneration, and washing steps and thus ensure minimal handling of the high-energy radionuclides. The once-through constraint requires a high-capacity exchange resin with sufficient selectivity for the soluble radionuclides, particularly when high concentrations of competing ions are present. These constraints limit the use of fixed-bed ion exchangers for liquid radioactive waste treatment, especially for commonly found high-sodium streams. An ion exchange system designed to concentrate soluble plutonium, in the form of $[Pu(NO_3)_6]^{2-}$, achieved distribution coefficients (q) ranging from $10^2$ to $10^4$ using a resin containing quarternary amine groups. The sample matrix contained 1.0 M $NaNO_3$ (Ali and Ache 1984).

### 2.1.4 Solvent Extraction

Solvent extraction, or liquid-liquid extraction, has been utilized for effective separation of dissolved radioactive species from aqueous streams. The process uses an organic solvent with a high selectivity for target soluble radionuclides that extracts these high-energy species from the aqueous bulk solution. One solvent extraction process, Transuranium Extraction (TRUEX), has been developed by DOE for the removal of actinides from specific Hanford tank wastes (Lumetta and Swanson 1993). The TRUEX solvent consists of 0.2 M octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) plus 1.4 M tributylphosphate (TPB) in a normal paraffin hydrocarbon (NPH) diluent. An important advantage of this technology is its selectivity for target ions, such as actinides, from a solution containing numerous radioactive and nonradioactive cations. The TRUEX process has achieved distribution ratio values, D, (D = organic phase concentration/aqueous phase concentration) >100, >1000, and 7, for U(VI), Pu(IV), and Am(III), respectively, for an acid high-level waste. The waste also contained Na, Al, Cr, Fe, and Ni, and their D values were all less than 0.01 (Horwitz and Schulz 1985).

## 2.2 Treatment Involving Separation by Ultrafiltration

In the past, ultrafiltration has been used as a supernatant polishing step for removing colloidal precipitates following chemical precipitation treatment of liquid radioactive waste. Ultrafiltration is a pressure-driven, physical separation process capable of retaining submicron particles. The reported ultrafiltration particle size range is approximately 0.003 to 1 μm (AWWA 1990). In comparison with reverse osmosis, which is used for liquid phase ion separation, ultrafiltration operates under lower filtration pressures and effectively retains colloids. The ultrafiltration pressure ranges are typically 10 to 100 psi, while reverse osmosis systems are operated between 200 psi and 1500 psi (AWWA 1990). The energy and cost savings coupled with effective separation of colloids render ultrafiltration a viable technology for liquid phase macromolecular separation applications. A recent Sandia National Laboratory report

evaluating DOE's waste management needs suggests considering inorganic ultrafiltration membranes in waste separations applications (Pohl 1993). Because ultrafiltration is susceptible to fouling and is limited to treatment of dilute suspensions, the report stresses the need for future research and development of membranes that would be more resistant to fouling.

### 2.2.1 Precipitation FOllowed by Ultrafiltration

Research on actinide decontamination of liquid radioactive wastes from commercial nuclear reactors has been conducted by the United Kingdom Atomic Energy Authority (UKAEA) since the early 1980s. The original work (Knibbs 1984) investigated the combination of coprecipitation with ferric hydroxide in conjunction with ultrafiltration for removal of plutonium from wastewater. The results of that study indicate that an increase in iron dose corresponds to an increase in DF for ultrafiltered samples. The plutonium surrogates evaluated were Ce(III), Th(IV), and U(VI) for the Pu (III, IV, and VI) oxidation states, respectively. Because ultrafiltration is based on particle retention, precipitation of ferric iron as $Fe(OH)_3$ is necessary to provide a medium available for sorption of the soluble target radionuclides. Without a precipitate, which can be retained by the ultrafiltration membrane, the soluble species easily pass through the membrane pores. The coprecipitation step requires a pH adjustment of the bulk solution to the pH required for minimum Fe(III) solubility. However, the pH can also be adjusted to achieve suitable conditions for direct precipitation of a target radionuclide. Knibbs (1984) investigated the pH region for achieving coprecipitation of $Fe(OH)_3$ and the surrogate plutonium species. The surrogate with the minimum solubility at the pH selected for optimum Fe(III) precipitation coprecipitated with the Fe(III) to create particulates for sorption of the remaining soluble target species.

Knibbs (1984) also investigated membrane fouling and cleaning. An increase in iron feed concentration resulted in a decrease in membrane flux. In situ acid rinsing of the membranes proved effective for removing the floc build-up on the membrane surface and for flux recovery. Thus, tradeoffs

between Fe(III) feed concentrations and fouling, as well as an effective cleaning technique, must be considered for this application. Also, the chemical stability (i.e., usable pH range) of the membrane material is important because the membrane will be subjected to extreme pH variations between filtration of the alkaline bulk solution and the acid rinse.

The coprecipitation/ultrafiltration process relies on good precipitate formation and sorption kinetics to achieve high DFs. Without these mechanisms, effective ultrafiltration retention of the target soluble radionuclides is not possible. However, excess precipitate formation can cause rapid fouling of the membrane. Thus, as with feed concentration, tradeoffs between precipitate concentration and membrane fouling must be considered. If numerous ionic species are present in the waste matrix (e.g., $Na^+$), selective separation of target radionuclides (e.g., actinides) may be difficult because sorption of the remaining soluble species present is likely. Furthermore, depending on their solubility characteristics, these nontarget species can also coprecipitate with iron and remain in the concentrated stream. Knibbs' experiments were conducted with simple feed solutions [i.e., only the plutonium surrogate tracers, base, and Fe(III) present]. In the 1984 report, Knibbs points out the significant impacts of the presence of complexing agents in the waste matrix. When 0.25 M $Na_2CO_3$ was added to the feed, significant decreases in the DFs resulted. Carbonate complexes [of the Ce(III), Th(IV), and U(VI) plutonium surrogates] inhibited the sorption interaction between the tracers and the inorganic adsorbers, thus preventing effective ultrafiltration retention. Organic complexing agents are also expected to affect the solubility of target radionuclides and adversely impact this process.

### 2.2.2 Ion Exchange Followed by Ultrafiltration

Because of the problems associated with chemical precipitation, the UKAEA continued investigating ultrafiltration, without precipitation, as an actinide decontamination technique. A process combining ultrafiltration and ion exchange, called seeded ultrafiltration, was evaluated and proved to be

effective for actinide decontamination (Hooper 1991). The seed material was finely divided inorganic ion exchange materials that were added to the bulk solution in small concentrations to adsorb the soluble target actinides (americium and plutonium) prior to ultrafiltration. Hooper (1991) indicates several advantages to seeded ultrafiltration over conventional fixed-bed ion exchange: 1) ultrafiltration is an effective solid/liquid separation process for removal of colloidal material; 2) smaller volumes of secondary wastes are generated because smaller quantities of floc/ion exchange materials are used; 3) the process can be tailored to the specific removal of target radionuclides (e.g., using hexacyanoferrate for cesium removal); 4) using ion exchangers as additives versus packed-bed configurations results in a wider range of available adsorbers that are easier and cheaper to make. Also, the additional available adsorber surface area acquired from not using a fixed-bed configuration and using finely divided materials improves the sorption kinetics. An important advantage of seeded ultrafiltration over precipitation/ultrafiltration is the control over the concentration of colloidal precipitates added to the bulk solution to minimize membrane fouling.

Hooper selected seed materials known to have ion exchange selectivity for radionuclides. The precipitate/solid seeds were pre-made as stock slurry solutions to be added to the bulk solution and were large enough to be completely rejected by an ultrafiltration membrane. Sodium nickel hexacyanoferrate (II), manganese dioxide, hydrous titanium oxide, ferric hydroxide, and polyantimonic acid were investigated. The highest DF achieved for americium decontamination was 4120 using 0.5 mL hydrous titanium oxide (100 ppm titanium) and 25 ppm Fe(III) at pH 10. Using 0.5 mL polyantimonic acid (initial concentration of 2426 ppm) at pH 10 yielded a maximum plutonium DF of 2080. On the other hand, using only 25 ppm Fe(III) at pH 10 yielded an americium DF=39 and a plutonium DF=72, demonstrating the enhanced DFs achieved using the inorganic adsorbers. Interestingly, a control sample at pH 10 (without seed material present) resulted in an americium DF=266 and a plutonium DF=13.7. It is possible that soluble americium and plutonium species adsorbed to the membrane and/or americium and plutonium precipitates formed at pH 10 and were retained by the membrane.

### 2.2.3 Complexation with Polymers Followed by Ultrafiltration

A process combining water-soluble polymers and ultrafiltration has been investigated for separation of both hazardous and radioactive inorganic ions (specifically metals) from aqueous streams (Kichik et al. 1985). This process is similar to seeded ultrafiltration in that it uses water-soluble polymers as seed materials to chemically bind the target soluble species. However, the primary binding mechanism is complexation instead of ion exchange. The molecular weight of the polymers is sufficient for effective separation of the metal-polymer macromolecule via ultrafiltration. The noncomplexed ions easily pass through the ultrafiltration membrane, providing selective ion separation capability for this technique. Thus, selective separation of target ions (specifically metal cations) can be achieved from a matrix containing many ionic species of like charge. This is a valuable feature of this technique because most hazardous and radioactive liquid wastes contain many dissolved cationic species.

Polymer-enhanced ultrafiltration was applied to a liquid radioactive waste for separating radionuclides from bulk solution with a salt concentration of 500 mg/L by Kichik et al. (1985), who point out some important polymer characteristics necessary for effective separation of the target ionic species: 1) high binding capacity and selectivity for the target species; 2) sufficient molecular weight for complete retention with an ultrafiltration coupon (>10,000); 3) sharp molecular weight distribution to ensure retention of all of the polymeric species; and 4) good water solubility, low cost, and availability. The polymers selected were 40,000 molecular weight (MW) polyethylenimine (PEI) and 100,000 MW polyacrylic acid (PAA). The target species included $^{137}Cs$, $^{134}Cs$, $^{60}Co$, $^{54}Mn$, $^{51}Cr$, and $^{131}I$. Because cesium and iodine are weak complexers, copper hexacyanoferrate and starch were used to bind the $^{137/134}Cs$ and $^{131}I$, respectively.

Hollow fiber membranes were used for cross-flow ultrafiltration of the polymer-treated solutions. The reported treatment results are based on a purification factor $K_{pur}$, which is the same as the

aforementioned DF. The results indicate $K_{pur}$ values >360 for $^{137}Cs$ and >30 for $^{60}Co$. Although these values are not nearly as high as the DFs reported for seeded ultrafiltration, they are significant for selective separation in a multiple cation matrix, which is not addressed in the seeded ultrafiltration literature cited above. The treated liquid radioactive waste stream contained approximately 500 mg/L salt (primarily $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$).

The effects of pH and polymer concentration were reported for separation of $^{60}Co$; $K_{pur}$ values increased with increasing pH (from 4 to 10) and increasing polymer concentration. However, polymer concentrations > 10 mg/L did not increase the $K_{pur}$ values, indicating that 10 mg/L of polymer (PEI or PAA) is the optimum concentration for separation of $^{60}Co$ under the test conditions evaluated. Kichik et al. (1985) indicated a need for future research on the interaction of the binding agents with the membrane material, each other, and surface-active substances. Also, because this work yielded such promising results, Kichik et al. (1985) recommended the search for, and synthesis of, new and more effective binding agents.

A similar technique for selective removal of metal ions from aqueous solutions containing other ions of the same charge is ligand-modified, micellar-enhanced ultrafiltration [LM-MEUF] (HazTECH 1989). This technique complexes the target metal ions with the ligand, which is then solubilized in the micelles. The micelles then aggregate to form macromolecules for separation by ultrafiltration. The results of an experiment with wastewater containing both copper and calcium treated with *N*-n-dodecyl-iminodiacetic acid and a cationic surfactant were 99.2% removal of the copper and no removal of the calcium. Thus, the *N*-n-dodecyl-iminodiacetic acid ligand selectively complexed the divalent copper in the presence of divalent calcium. The soluble noncomplexed calcium passed through the ultrafiltration membrane, and the desired separation was achieved.

The use of polymeric complexing agents for the separation of actinides has been evaluated to alleviate matrix interferences for trace actinide analysis using atomic absorption spectrometry and inductively coupled plasma/atomic emission spectrometry (Geckeler et al. 1986). The process is called liquid-phase polymer-based retention and utilizes water-soluble, non-crosslinked polymers and ultrafiltration to selectively complex and separate (preconcentrate) soluble actinide species from aqueous solutions. A significant advantage of this process is that it is homogeneous, unlike solvent extraction, precipitation, and sorption techniques, which are heterogeneous (two-phase) . The heterogeneous techniques tend to have slower reaction rates that are controlled by the diffusion mechanisms required for phase transfer. Furthermore, for both waste treatment and analytical purposes, if aqueous solutions of the concentrated ions are preferred, heterogeneous processes require additional procedures such as back extraction, desorption, and dissolution of solid concentrates. Samples treated with PEI (molecular mass range of 30,000 to 40,000 g/mole) at pH 6 and ultrafiltered through a 10,000 molecular weight cut-off (MWCO) membrane resulted in retention values >90% for the following divalent metals: Cu, Zn, Cd, Hg, Mn, Co, and Ni; 100% retention of Mn was achieved at pH 8.

## 2.3 Complexation of Actinides

The comparison of conventional separation processes for treatment of hazardous and radioactive liquid streams warranted an investigation of a homogeneous (aqueous) process for selective separation of target soluble metal ions using ultrafiltration. In light of DOE's challenging liquid radioactive waste separation needs, the study discussed here was focused on the selective separation of actinides. The specific actinide of interest was $^{241}Am^{3+}$. Trivalent europium (Eu), a member of the lanthanide series, was selected (see Section 3.1.2) as the nonradioactive surrogate for $^{241}Am^{3+}$.

### 2.3.1 Lanthanide Coordination Chemistry

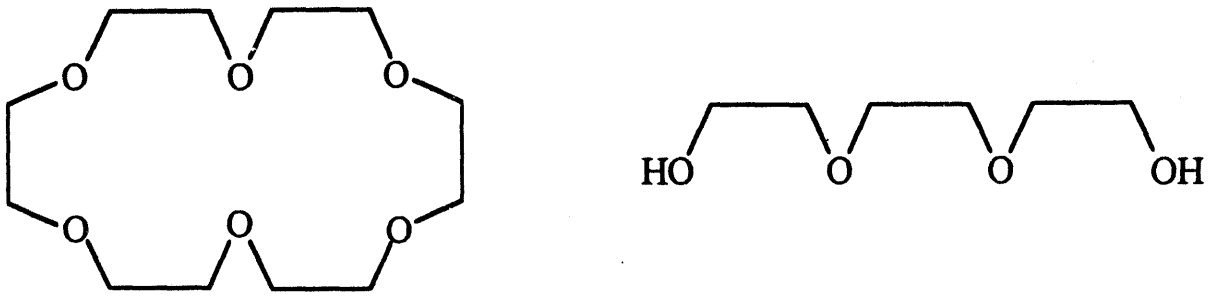
Lanthanide trivalent metal cations can have the following coordination numbers: 6, 7, 8, 9, 10, and 12 (Cotton and Wilkinson 1972). The most common ligands used to complex lanthanides are those possessing oxygen donor atoms (i.e., electron pair donors). These complexes are typically formed with lanthanides having coordination numbers of 7, 8, and 9. An example of a trivalent lanthanide ($Ln^{3+}$) nine-coordinate complex is $[Ln(H_2O)_9]^{3+}$. Its structural geometry is tricapped trigonal prismatic. Each water molecule serves as a monodentate ligand that donates an unshared pair of electrons from the oxygen atom (i.e., is a Lewis base) to form a coordinate-covalent bond.

### 2.3.2 Crown Ethers and Open-Chained Ligands

When crown ethers were first discovered in the late 1960s, they were found to exhibit the unique property of preferentially complexing alkali metal ions that generally would not interact with ligands used to complex transition metal ions (Pederson 1988). These synthetic organic compounds are described as macrocyclic polyethers having a ring-shaped geometry which contains multiple oxygen donor atoms that complex metal cations. This ring-shaped coordination geometry, referred to as the cavity, has a unique size that influences the stability of the metal-crown complex. Pederson (1988) indicates that optimum complex stability occurs when the ionic radius of the cation closely matches cavity size of the crown ether. Continued development of crown ethers has produced specific compounds that form trivalent lanthanide complexes (Bunzli and Pilloud 1989). However, crown ethers are not very water soluble, are expensive to synthesize, and do not satisfy the molecular weight requirements for ultrafiltration.

Bunzli and Pilloud (1989) compared the stability of $Ln^{3+}$ complexes with cyclic ligands (crown ethers) and open-chain ligands (polyethers) having the same number of donor atoms. Their experimental results indicate that open-chain ethylene glycols are suitable analogs to crown ethers for complexation of $Ln^{3+}$ metal cations. However, they form less stable $Ln^{3+}$ complexes than crown ethers with the same

number of donor atoms. Stability constants for Eu complexes with four, five, and six ethylene glycol chains (EO4, EO5, and EO6) were reported. These small-chain ethylene glycols are potential binding agents for the current study because they are commercially available (can be purchased from Aldrich Chemical Company, Inc.), inexpensive, and water soluble. Figure 2.1 illustrates the two-dimensional structures of a crown ether (18C6) and small-chain ethylene glycol (EO3).




**Crown Ether (18C6)** **Triethylene Glycol (EO3)**

**Figure 2.1.** Two-Dimensional Structures of Crown Ether (18C6) and Triethylene Glycol (EO3)

Structural features of small-chain ethylene glycol complexes of neodymium ($Nd^{3+}$) using three, four, five, and six ethylene glycol chains (EO3 through EO6) have been investigated (Rogers et al. 1991). The open-chain glycol ligands form a helical wrap about the $Nd^{3+}$ metal cation (i.e., adopt a "crown-like" conformation). Cystallographic analysis of EO3 through EO6 $Nd^{3+}$ complexes indicated that they form a nine-coordinate tricapped trigonal prismatic structure (similar structural geometry as the $[Ln(H_2O)_9]^{3+}$ complex). The oxygen donor atoms of the glycol ligands displace the water molecules and preferentially complex the $Nd^{3+}$ cation. The number of displaced water molecules (inner sphere ligands) correspond to the number of oxygen donor atoms present in the glycol chain. Increasing the glycol chain length by one ethylene oxide unit correspondingly replaces an additional inner sphere ligand. For example, EO3 is a tetradentate ligand (chelate) that replaces four waters of hydration with five water molecules remaining in the $Nd^{3+}$ inner sphere. The complex formation reaction is written as

$$[Nd(H_2O)_9]^{3+} + EO3 \rightarrow [Nd(EO3)(H_2O)_5]^{3+} + 4H_2O$$

Figure 2.2 is a simple two-dimensional drawing of this reaction and does not illustrate the actual three-dimensional tricapped trigonal prismatic geometry. The oxygen donor atoms of both the water molecules and the EO3 ligands form coordinate-covalent bonds with the $Nd^{3+}$ metal cation.

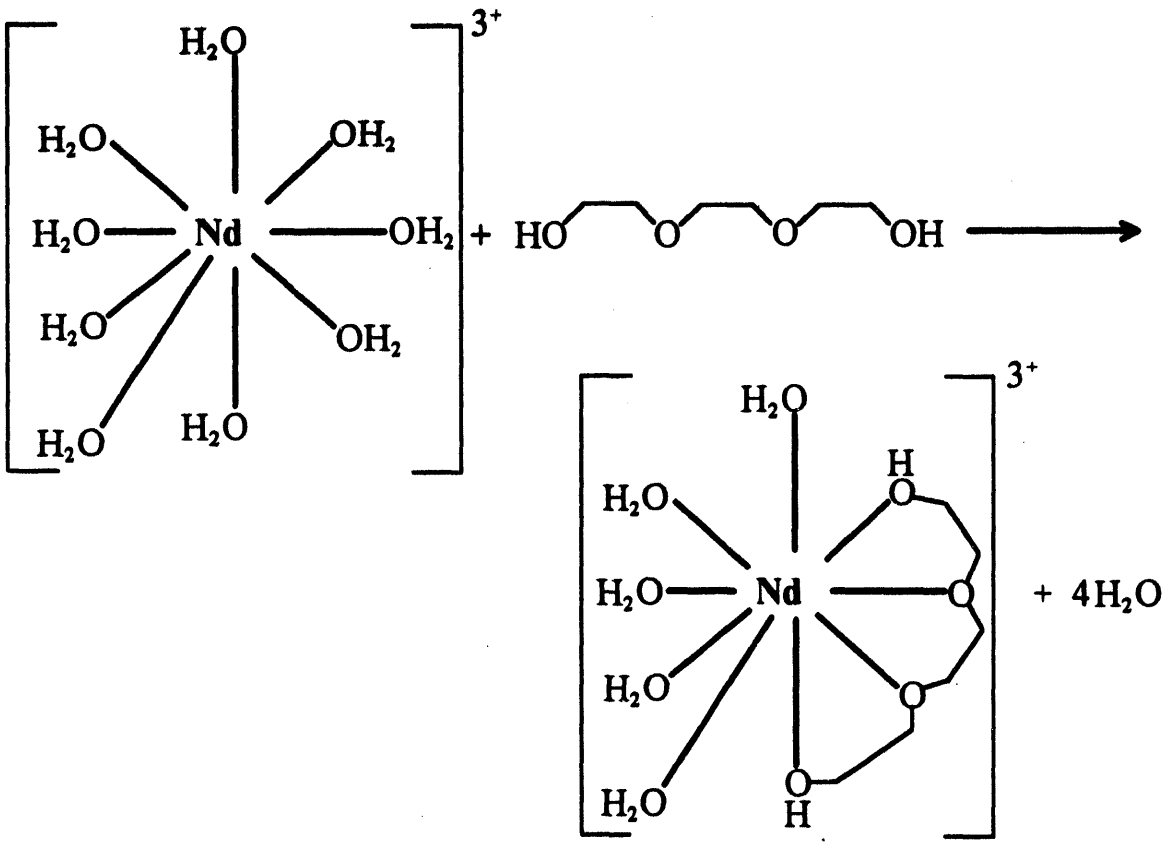



**Figure 2.2.** Two-Dimensional Structure of the $[Nd(EO3)(H_2O)_5]^{3+}$ Complex

From the results of the research cited in the literature on the use of binding agents to enhance the rejection of metals by ultrafiltration, PNL began investigating binding agents with an affinity for Eu (a nonradioactive surrogate for $^{241}Am$) for separation of Eu from aqueous solutions by ultrafiltration. The experimental methods are detailed in Section 3.0.

# 3.0 Experimental Methods

The methods used to determine the results discussed in Sections 4.0 and 5.0 are given here. Along with the overall approach, this section describes the selection of test polymers and ultrafiltration membranes, the modules used for ultrafiltration testing, the experimental design, and the analytical methods.

## 3.1 Overall Approach

The objective of this work was to evaluate PNL-synthesized copolymers for selectively binding soluble Eu in an aqueous system. Commercial polymers were evaluated for comparison. During the experiments, Eu binding was measured in solutions containing as few ionic species as possible so that potential matrix interferences (e.g., competing cations) would be minimized. The initial phase of the experimental design isolated the polymer as the only binding mechanism present in the system. Once it was established that polymers can bind Eu in a simple system, their selectivity for Eu was investigated by adding Na to the bulk solution.

### 3.1.1 Proposed Polymer-Ultrafiltration Treatment Process

The proposed treatment process includes the following two steps: polymer addition to the bulk Eu solution followed by ultrafiltration to separate the Eu-polymer complexes from solution. For this laboratory-scale study, each step was conducted separately in batch mode as shown schematically in Figure 3.1. The retentate is the fraction of the solution that does not pass through the ultrafiltration membrane and contains the Eu-polymer complexes. The filtrate is the remaining fraction of the solution that passes through the membrane and is, ideally, Eu free.

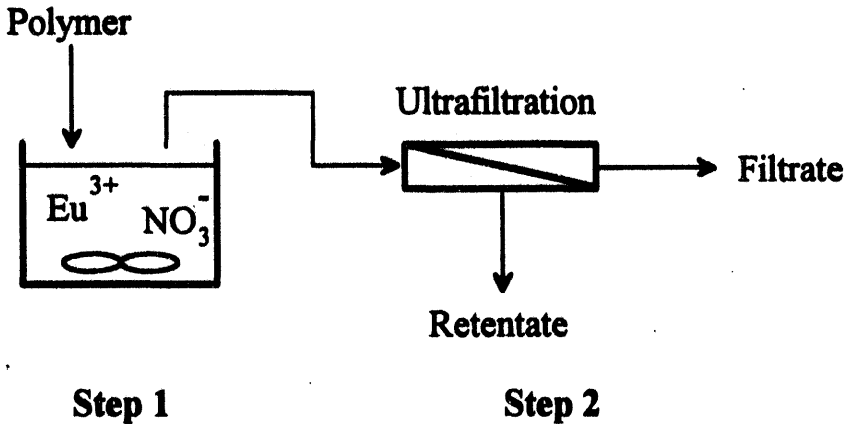



**Figure 3.1.** Conceptual Polymer-Ultrafiltration Process

### 3.1.2 Eu as Surrogate for $^{241}Am$

The laboratory facilities used for this research were not equipped for radioactive materials, which meant a nonradioactive surrogate for $^{241}Am^{3+}$ had to be selected instead. This surrogate had to be similar to $^{241}Am^{3+}$ in the following respects: oxidation state, ionic radius, and similar coordination [f-block element] chemistry (Cotton and Wilkinson 1972). Americium is a member of the actinide series, and all actinide isotopes are radioactive. In general, the most common and dominant oxidation state for actinides, including americium, is +3 and the chemistry of +3 actinides resembles that of the lanthanides (Cotton and Wilkinson 1972). Ionic radius is an important characteristic for similarities in chemical behavior among the actinides and lanthanides. The ionic radius for $^{241}Am^{3+}$ is 0.99 Å (Cotton and Wilkinson 1972). Therefore, a nonradioactive +3 lanthanide with an ionic radius close to 0.99 Å would be a desirable surrogate.

Both Nd and Eu are lanthanide elements that have nonradioactive isotopes with +3 oxidation states. Each has an atomic radius close to $^{241}Am^{3+}$ (0.995 Å for Nd and 0.950 Å for Eu). While Nd has only one oxidation state (+3) as opposed to two for Eu (+2 and +3), Eu was selected for analytical convenience (i.e., Eu has a wider linear working range than Nd for analysis by atomic absorption spectroscopy).

In addition to oxidation state and ionic radius, similarities in chemical behavior between Am and Eu is evident by comparing the stability constants of of both trivalent metals for a common ligand. The reported log $\beta_1$ values for the formation of $Am(CO_3)^+$ and $Eu(CO_3)^+$ are 5.81±0.04 and 5.93±0.05, respectively (Lundqvist 1982). The specific chemical reaction is

$$M^{3+} + CO_3^{2-} \rightarrow M(CO_3)^+$$

and was conducted in aqueous solution containing 1 M $NaClO_4$. These similar stability constant values indicate that the complex formation chemistry, with the carbonate ligand, for $Am^{3+}$ and $Eu^{3+}$, is comparable. A comparison of the solubility products, $K_s$, for $Am(OH)_{3(s)}$ and $Eu(OH)_{3(s)}$ further substantiates the similar chemistry of Eu and Am. The reported $K_s$ values are -24 and -24.5 for Am and Eu respectively (Lundqvist 1982).

### 3.1.3 Eu Speciation and pH

Trivalent lanthanides ($Ln^{3+}$) can form insoluble hydroxides, fluorides, oxalates, basic halides, and basic carbonates (Baes and Mesmer 1986). Because of the simple bulk solution matrix, insoluble Eu hydroxide was the only concern for inhibiting Eu binding to the polymers. According to Baes and Mesmer, hydroxide formation of $Ln^{3+}$ metal cations does not become appreciable until the solution pH >6. Thus, a bulk solution pH <6 was selected to minimize the formation of Eu hydroxide precipitate [$Eu(OH)_3$] and promote a predominance of soluble Eu (weakly complexed by $H_2O$) available for more stable complex formation with the test polymers.

Preventing the formation of $Eu(OH)_3$ precipitate was essential for evaluating Eu binding with the test polymers for two reasons: 1) the polymers would have to compete with a very stable, neutral Eu hydroxide complex which inhibits the ability of the polymer to bind Eu; and 2) the hydroxide precipitate could be rejected by and/or adsorbed to the ultrafiltration membrane. This mechanism of rejection could not be experimentally distinguished from rejection of the Eu-polymer complexes.

The pH was also important for cation exchange binding of Eu. Test polymers selected for this study contained functional groups with available cation exchange sites in a pH regime where the functional groups were ionized. Therefore, the cation exchange capacity was a function of pH.

## 3.2 Selection of Test Polymers

Organic polymers were selected as binding agents because they exhibit a selective affinity for Eu and/or cation exchange capabilities. In addition to binding characteristics, molecular weight and water solubility were important. The polymers should have a molecular weight high enough for effective ultrafiltration rejection. Water solubility was also important to maintain a homogeneous process that would optimize binding kinetics and alleviate the disadvantages of two-phase processes. Finally, availability and low cost of commercial polymers for direct use or synthesis were considered.

### 3.2.1 Commercial Polymers

The commercial polymers selected for this study were polyethylene glycol (PEG) having a molecular weight of 3000 and two polyacrylic acids (PAA) having molecular weights of 2000 and 60,000. Both polymers are water soluble, inexpensive, and readily available. The molecular weights of each polymer were selected based on the molecular weight cut-off (MWCO) of each ultrafiltration membrane selected for polymer separation. These polymers were also chosen because they are similar to the two monomers that comprise the major components of PNL's synthesized polymers, which are discussed in the following subsection. Inclusion of commercial polymers with similar binding capabilities for Eu provided a basis for comparison with the synthesized polymers.

PEG was chosen as the selective complexing agent, and PAA as the cation exchanger. The calculated cation exchange capacity [i.e., the amount of cation exchange sites expressed as milliequivalents of $H^+$ (meq) per gram of polymer] for PAA was 16.67 meq/g. This capacity was calculated based on the

molecular weight of one repeating unit of PAA polymer (60 g/mole) with each unit containing one equivalent of $H^+$ from the carboxyl group. The pKa of acrylic acid is 4.25 (Merck & Co. 1989). Thus, a bulk solution pH >4.25 was necessary for ionized carboxyl groups (carboxylates) to serve as cation exchange sites

### 3.2.2 PNL-Synthesized Copolymers

PNL synthesized five copolymers for evaluation of Eu binding[2], but only one was investigated in this study. These binding agents were designed and polymerized as dual functionality copolymers that exhibit both selective complexation and cation exchange binding mechanisms. The selected copolymer was polymerized using two monomers: acrylic acid (AA) and triethylene glycol, monomethyl ether (EO3Me) acrylate. The AA monomer was selected for ease of synthesis and to provide cation exchange sites for Eu. The EO3Me acrylate monomer was selected to provide an EO3 glycol chain to selectively complex Eu. Its acrylate functionality was utilized for polymerization with the AA. The polymerization step was tailored to generate a copolymer with "dangling" glycols attached to alternating (every other) AA units of a polyethylene backbone. A target molecular weight of 10,000 was selected because it fell within the retention range of ultrafiltration and was low enough to maintain good water solubility. This copolymer was named EO3Me-AA to represent both monomer constituents (abbreviated to E3 throughout the rest of the document). Figure 3.2 illustrates the proposed E3 two-dimensional structure (drawn as two repeating units) based on the assumption that the AA to EO3Me monomer ratio is 1:1.

[2] Copolymer synthesis was conducted by Dr. D.A. Nelson, Senior Research Scientist, PNL.

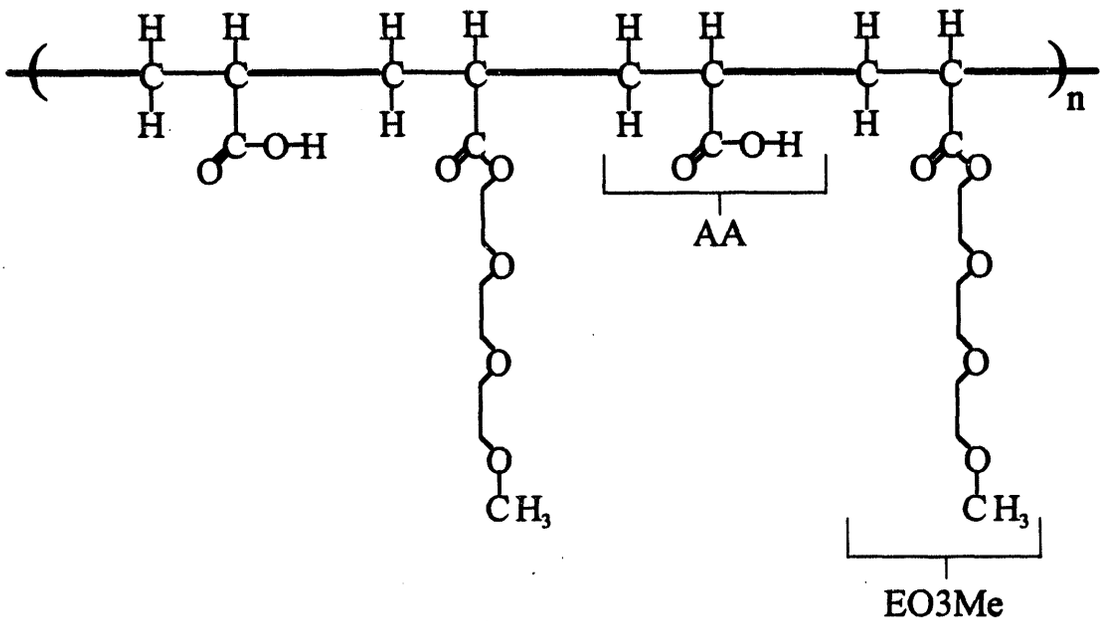



**Figure 3.2.** Proposed E3 Two-Dimensional Structure

The proposed binding interactions of one E3 copolymer unit with one Eu metal cation are shown in Figure 3.3. The five water ligands are not shown for ease of illustration (assuming a nine-coordinate Eu complex). This figure does not represent the exact binding configuration/structure of the EO3Me acrylate oxygen donor atoms which are coordinate-covalently bound to Eu. The close proximity of the Eu cation and the carboxylate group suggests a possible cation exchange interaction between the trivalent cation and the available exchange site. Charge neutralization is a possible driving force for this interaction, and its effect is indicated by the overall complex valence of +2 shown in Figure 3.3.

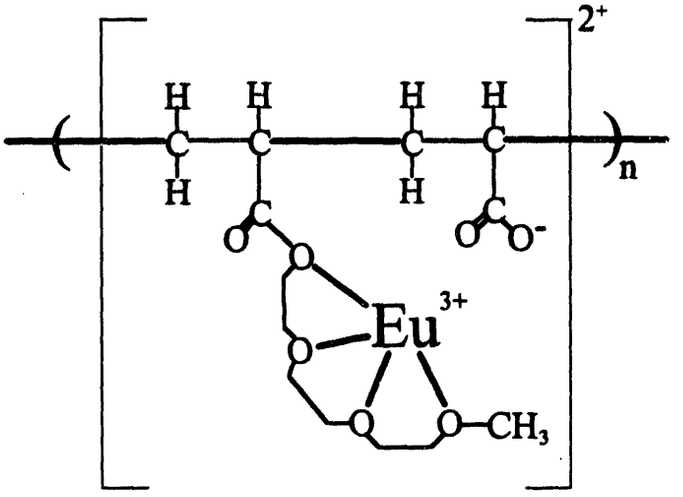



**Figure 3.3.** Possible $[Eu(E3)]^{2+}$ Complex

The cation exchange capacity of the E3 was calculated based on the 1:1 ratio of the AA to EO3Me-AA monomer for one repeating unit of the copolymer. The molecular weight of one unit is 290 g/mole and contains one equivalent of $H^+$ from the carboxyl group of the AA. Therefore, if the structure shown in Figure 3.2 represents the full length of the copolymer, the cation exchange capacity of E3 is theoretically 3.45 meq/g. This computed cation exchange capacity was calculated as follows:

$$\frac{(1 \text{ equiv. } H^+)(\text{mole AA})(\text{mole E3})(1000 \text{ meq})}{(\text{mole AA})(\text{mole E3})(290 \text{ g E3})(\text{equiv.})}$$

## 3.3 Selection of Test Ultrafiltration Membranes

Effective separation of the test polymers from a polymer-treated solution was a critical step in the proposed treatment process. The binding affinity of the test polymers for Eu was determined by comparing the Eu concentrations of the polymer-treated samples before and after ultrafiltration. This approach relied on the assumption that all of the Eu-polymer complexes were effectively rejected by the ultrafiltration membranes (i.e., were concentrated in the retentate). Therefore, any Eu found in the filtrate fraction was designated "unbound" Eu. The Eu analysis, discussed in a subsequent section, did not distinguish between

"unbound" soluble Eu and "bound" Eu. Therefore, any Eu-polymer complexes that passed through a membrane would contribute to the "unbound" soluble Eu concentration in the filtrate.

An Amicon ultrafiltration stirred cell with 25-mm-diameter ultrafiltration membrane coupons was chosen as the filtration test apparatus. The MWCO is based on the ability of the coupon to retain globular solutes of a known, well-characterized molecular weight (i.e., effective size). Because the test polymers for this study were linear and not globular, a membrane MWCO of at least half the average molecular weight of the polymers was recommended to ensure adequate polymer retention (J. Krenn, personal communication with Amicon, August 13, 1992). The Amicon membrane coupons met that criterion.

### 3.3.1 Characteristics of YM Series Membrane

The Amicon YM series membranes are made of cellulose acetate, which is a hydrophilic, polymeric membrane material. The YM1 with a MWCO of 1000 and YM10 with a MWCO of 10,000 were selected for this study. The YM1 should retain the 3000 MW PEG; the 2000 MW PAA; and more definitely, the 10,000 MW E3 copolymer, while the YM10 should retain only the E3.

### 3.3.2 Characteristics of PM Series Membrane

The PM series membranes are made of polyether sulfone, which is a hydrophobic, polymeric membrane material. Amicon manufactures PM coupons with the following MWCOs: 10,000 (PM10) and 30,000 (PM30). The PM10 coupon should retain the E3 and the PM30 coupon, the 60,000 MW PAA. Amicon does not manufacture a PM coupon with a MWCO less than 10,000. Therefore, complete retention of the E3 copolymer with PM10 coupons was not expected because the MWCO was very close to the expected molecular weight of the test polymer.

## 3.4 Laboratory Ultrafiltration Modules

This subsection describes the ultrafiltration test module setup, calculation of solute rejection and recovery, membrane flux, and the established test protocol.

### 3.4.1 Test Module

The Amicon model 8010 stirred cell was used for batch filtration as depicted in Figure 3.4. Three separate time frames are shown to illustrate the three possible stages of batch ultrafiltration: 1) pre-filtration, 2) during filtration, and 3) post-filtration. The portion of sample that passes through the membrane is the permeate (or filtrate), and the retentate is the fraction of the sample remaining in the cell. The cell is rated for a maximum filtration pressure of 75 psi and can filter up to a 10-mL sample volume. The sample is placed in the cell above the filtration coupon, and the head space is pressurized with an inert gas (i.e., nitrogen) that pushes the sample through the membrane. The cell operation mode is termed "dead-end" filtration because the direction of flow is perpendicular to the coupon surface. During filtration, the sample is stirred to minimize the formation of a layer of retained species on the membrane surface, which can greatly affect the retention characteristics of the membrane. This layering effect is called concentration polarization (Amicon 1992).

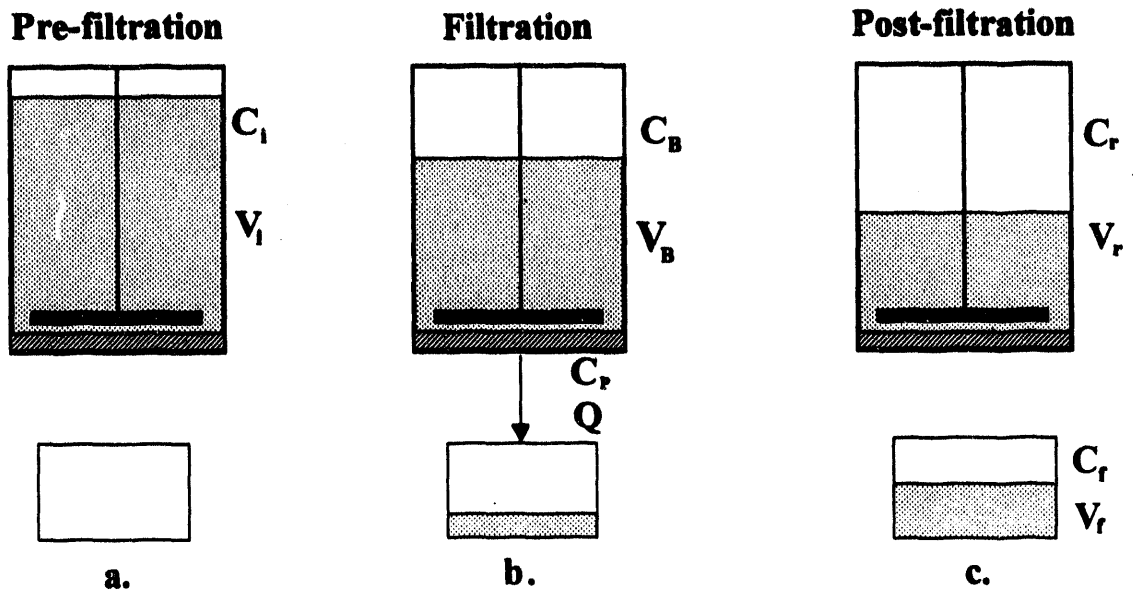



**Figure 3.4.** Batch Ultrafiltration Stirred Cell

The nomenclature of the variables shown in Figure 3.4 is as follows:

$C_i$ = the initial sample solute concentration.

$C_B$ = the measured instantaneous sample solute concentration.

$C_P$ = the measured instantaneous filtrate (permeate) solute concentration.

$C_r$ = the post-filtration retentate solute concentration.

$C_f$ = the post-filtration filtrate solute concentration.

Q = sample flow rate through the membrane.

$V_i$ = the initial sample volume.

$V_B$ = the instantaneous (bulk) sample volume in the cell.

$V_r$ = the post-filtration retentate volume.

$V_f$ = the post-filtration filtrate volume.

### 3.4.2 Calculation of Rejection

Membrane rejection was calculated using the approach provided by Amicon (J. Krenn, personal communication with Amicon, August 13, 1992). The rejection of any solute by an ultrafiltration

membrane is described using the rejection coefficient, R. At any point during ultrafiltration (i.e., Figure 3.4b) the rejection coefficient is defined as

$$R = 1 - \frac{C_P}{C_B} \qquad (1)$$

where $C_P$ is the concentration of the solute of interest in the filtrate and $C_B$ is the solute concentration in the bulk solution (e.g., above the membrane). In batch-mode filtration, both $C_P$ and $C_B$ vary with time. $C_B$ will increase over time as the solute is rejected and the solution volume in the cell decreases (compare $V_i$ and $V_r$ in Figures 3.4a and 3.4c, respectively). $C_P$ is also dependent on solute movement through the membrane over time. Given that both $C_B$ and $C_P$ can vary over time, it is necessary to define an average rejection coefficient, $\overline{R}$. This average rejection value is given by Amicon as

$$\overline{R} = \frac{Ln\left(\frac{C_r}{C_i}\right)}{Ln\left(\frac{V_i}{V_r}\right)} \qquad (2)$$

The product literature from Amicon includes a recommendation to measure the permeate rather than the retentate concentration. Thus, Eq. (2) was modified to calculate $\overline{R}$ based on $C_f$:

$$\overline{R} = \frac{Ln\left[\frac{V_i}{V_r} - \frac{C_f}{C_i}\left(\frac{V_i}{V_r} - 1\right)\right]}{Ln\left(\frac{V_i}{V_r}\right)} \qquad (3)$$

Both Eqs. (2) and (3) assume complete mixing of the retentate. Their derivations are presented in Appendix A. For the remainder of this document, R will be used to denote average membrane rejection coefficients. The calculated R values represent a fractional solute rejection (i.e., R = 1.0 indicates 100% rejection).

The solute recovery, REC, was determined to monitor the solute mass balance in the samples during ultrafiltration. Recovery was calculated by comparing the mass of the solute recovered in the filtrate and retentate to the original solute mass in the bulk solution using the following mass balance equation:

$$REC = \frac{V_f C_f + V_r C_r}{V_i C_i} \qquad (4)$$

The calculated REC values represent a fractional solute mass recovery (i.e., REC = 1.0 indicates 100% recovery).

### 3.4.3 Measurement of Flux

Membrane flux is important because it can be reduced through the concentration polarization effect. Concentration polarization creates a greater solute concentration gradient at the membrane surface, which promotes solute diffusion through the membrane that may adversely impact (i.e., decrease) the solute average rejection results. Flux is a function of pore size, membrane effective surface area, driving pressure, and the effective molecular size and concentration of the solute. The effective membrane surface area of the 25-mm-diameter Amicon membranes was 4.1 $cm^2$ (Amicon 1992). Flux is calculated by

$$\text{flux } (mL/cm^2\text{-min}) = \frac{V_f}{(t_f)(4.1)} \qquad (5)$$

where $t_f$ is the filtration time elapsed to pass volume, $V_f$, through the membrane, and 4.1 is the surface area ($cm^2$) of the membrane. The typical range of clean water fluxes for these Amicon membranes using a filtration pressure of 55 psi for 5 min is given in Table 3.1.

Table 3.1. Clean Water Flux Ranges at 55 psi (Amicon 1992)

| Membrane Type | Flux ($mL/cm^2$-min) |
|---|---|
| YM1 | 0.02 to 0.04 |
| YM10 | 0.15 to 0.20 |
| PM10 | 1.5 to 3.0 |
| PM30 | 2.0 to 6.0 |

### 3.4.4 Typical Test Protocol

The bulk solution used in all of the experimental work contained 10 μg/mL Eu [from $Eu(NO_3)\cdot 6H_2O$] dissolved in Milli-Q de-ionized water (DDI). This Eu concentration was selected because it is the mid-range value of the linear working range for atomic absorption spectroscopy, the analytical technique used to determine Eu concentrations. The bulk solution pH was adjusted to 5 using NaOH and/or $HNO_3$. This pH was selected to maintain Eu solubility [i.e., prevent the formation of $Eu(OH)_3$ precipitate] and to provide a solution pH greater than the pKa of acrylic acid (4.25), thus promoting Eu binding to the polymer by the cation exchange mechanism.

The possible formation of $Eu(OH)_3$ precipitate at pH 5 was determined by filtering an aliquot of the Eu bulk solution through a 0.2-μm microfilter, the pore size cut-off designated as the working definition of soluble species. The fraction of Eu retained by the 0.2-μm microfilter, $Eu_{Ppt}$, was calculated using the following equation:

$$Eu_{Ppt} = \left(\frac{C_i - C_{mf}}{C_i}\right) \qquad (6)$$

where $C_i$ is the initial bulk solution Eu concentration and $C_{mf}$ is the microfilter filtrate Eu concentration. The lack of a precipitate was assumed if the Eu concentration in the bulk solution was equal to that in the filtrate from the 0.2-μm filter. The presence of Eu precipitates was also determined in the polymer-treated samples. The presence of a precipitate in these samples could be due either to the formation of $Eu(OH)_3$ or

Eu-polymer precipitates (assuming precipitate retention on the microfilter). The solubility test was conducted by using 5-mL disposable syringes which contained a Gelman[3] disposable filter at the base.

Polymer addition consisted of combining the polymer with 100-mL solutions which were then stirred at a controlled, uniform speed of 300 rpm in a Phipps and Bird gang stirrer apparatus. Calibrated, adjustable pipettes were used to add aliquots of concentrated stock polymer solutions to achieve the desired polymer concentration. The stir speed was reduced to 30 rpm to remove the sample aliquots for ultrafiltration tests.

Two stirred "dead-end" filtration cells were placed on magnetic stir plates and plumbed to a nitrogen cylinder. The filtration pressure was controlled with the cylinder regulator, and the magnetic stir speeds were set to maximum throughout the filtration. The volume of sample aliquots to be ultrafiltered was 10 mL, the maximum sample capacity of the model 8010 stirred cells. The aliquots were filtered at constant pressure until approximately one-half of the starting volume, $V_i$, passed through the membrane. This filtration approach, called a half-reduction filtration (J. Krenn, personal communication with Amicon, August 13, 1992), is Amicon's standard protocol for characterizing/quality testing their ultrafiltration membrane coupon average rejection performance. Instead of filtering all of the initial sample aliquot volume, approximately half of $V_i$ is filtered to reduce the filtration time and collect a retentate fraction for calculating solute recovery. Filtering all of $V_i$ increases the chance of solute build-up (concentration polarization) at the membrane surface that can impact the solute recovery and membrane cleaning.

Each test run included a control sample (i.e., a sample of bulk solution containing Eu that was not polymer-treated) to determine if the membrane rejected "unbound" Eu in the bulk solution. Therefore, the control samples in each test run were subjected to the same test protocol and analysis, with the exception of polymer addition, as the polymer-treated samples.

[3] Gelman Sciences, Ann Arbor, Michigan.

The ultrafiltration experiments began with three aliquots (two 5-mL and one 10-mL) of each test sample that were removed with a disposable syringe from the polymer-treated samples stirring at 30 rpm in the Phipps and Bird apparatus. The first 5-mL aliquot was filtered through a disposable 0.2-μm filter to determine whether a precipitate had formed. The second 5-mL aliquot was not filtered and saved for analysis. The 10-mL aliquot was placed in a stirred cell for ultrafiltration. The filtrate and retentate fractions collected from the ultrafiltration step, the 0.2-μm filtrate aliquot, and the unfiltered aliquot were analyzed for Eu and polymer concentrations.

Membrane rejection coefficients (R) and fractional recoveries (REC) were calculated for Eu and polymer, individually, using Eqs. (3) and (4). Membrane flux was calculated using Eq. (5). The sample aliquot volumes were calculated by weight (assuming a sample density of 1 g/mL). The densities of several control and polymer-treated samples were determined to validate this assumption.

The same ultrafiltration membrane coupons were used for each test run and the membranes were cleaned between aliquot filtrations using a cleaning protocol specified by Amicon. This protocol involved the following steps:

1. Triple-rinse the cell and membrane with DDI.
2. Add several mL of 0.1 N NaOH and let stir for 5 min.
3. Triple-rinse the cell and membrane with DDI.

The membrane coupons remained in the stirred cells to minimize handling.

Some aspects of the test protocol changed during the progression of the testing because of interferences discovered from data analysis. These changes are noted in the discussion of the test results (Section 4.0).

## 3.5 Experimental Design

The laboratory experiments were designed to evaluate the following:

1. europium removal by ultrafiltration
2. enhanced Eu removal by polymer binding followed by ultrafiltration
3. selective Eu removal by polymer binding followed by ultrafiltration.

Membrane rejection of unbound and polymer-bound Eu species were the two possible mechanisms for separation of Eu from the bulk solution [assuming no formation of $Eu(OH)_3$ precipitates]. The Eu analysis technique was not able to determine the contribution of Eu removal achieved by each mechanism. Therefore, the Eu average membrane rejection coefficient values calculated for the polymer-treated samples represented the total Eu rejection achieved by both mechanisms and was designated $R_T$.

### 3.5.1 Eu Removal By Ultrafiltration

Membrane rejection of unbound Eu was determined using the control samples (without polymer) in each test run. The Eu rejection coefficients calculated for the control samples were designated $R_{UF}$.

### 3.5.2 Enhanced Eu Removal By Polymer Binding Followed By Ultrafiltration

Eu removal attributed to Eu bound to polymer and subsequently rejected by the membrane, $R_{PB}$, was determined using the polymer-treated samples. For a particular test run, the $R_{PB}$ of a polymer-treated sample was determined by calculating the $R_T$ value of the sample and then subtracting the $R_{UF}$ value of the control sample used in the test run. $R_{PB}$ represented the enhanced Eu removal caused by the polymer treatment.

The membrane rejection of test polymer in each polymer-treated sample was determined to verify the rejection of Eu-polymer complexes. The polymer average membrane rejection coefficient was designated $R_p$.

An initial test polymer concentration of 100 μg/mL was selected. The value of Eu rejection efficiency for polymer-treated samples that was considered to indicate process feasibility was 90% (i.e., $R_T$ = 0.9). Based on the $R_T$ values achieved with a polymer concentration of 100 μg/mL, additional tests with increasing or decreasing polymer concentrations were conducted to determine the concentration necessary to achieve the target 90% Eu rejection.

The commercial PAA and PEG test polymers were tested first to provide a point of comparison with PNL's E3 copolymer. Samples were treated with PEG only, PAA only, and then with a combination of PEG and PAA. For the samples treated with both PEG and PAA, PEG was added first for Eu complexation followed by PAA addition for ion exchange. After the optimum combination and concentrations of PEG and PAA were determined, E3 was evaluated to determine the concentration required to achieve 90% Eu rejection.

### 3.5.3 Selective Eu Removal By Polymer Binding Followed By Ultrafiltration

After polymer binding of Eu in a simple system was established, their selectivity for Eu was investigated by adding Na to the bulk solution. The Na was selected as a competing monovalent cation because it is present in very high concentrations (~6M) in the Hanford tank waste and was required as a matrix modifier for the Eu analysis. The bulk solution Na concentration was at least three orders of magnitude greater than the Eu concentration.

The approach described in Sections 3.5.1 and 3.5.2 to determine Eu polymer binding was also utilized for the selectivity experiment. The only difference in experimental conditions was the presence of Na in the bulk solution.

## 3.6 Analytical Methods

Several analytical methods were employed to determine Eu, Na and polymer concentrations, measure pH, and characterized the E3 copolymer. The E3 copolymer was characterized using base titration and molecular weight determination analyses. Eu was analyzed by atomic emission spectroscopy (AES), and total organic carbon (TOC) was measured to determine polymer concentrations. Na was analyzed using an ion selective electrode (ISE), and the test solution pH was monitored with a pH electrode.

### 3.6.1 Base Titration

A base titration experiment was conducted to determine the cation exchange capacity of the E3 copolymer.[4] This analysis was conducted using a Mettler Auto-Titrator. The copolymer sample was titrated with Sigma reagent-grade 0.1 N NaOH.

### 3.6.2 Molecular Weight Determinations

The molecular weight of the E3 copolymer was determined using gel permeation chromatography (GPC). A Dionex Ion Chromatography DX-300 system was used with two columns in series. Each column contained a polymer bead packing compatible with aqueous eluents within a pH range of 2 to 12. The first column packing had a size exclusion limit of 300,000 MW, and the second, a size exclusion limit of 8500 MW (with respect to PEG). Three PAA standards were purchased from Polysciences, Inc., with the following molecular weights: 2000; 8000; and 35,000. A pH 10 phosphate-buffered eluent was selected to prevent aggregation of the standards from hydrogen bonding. Standards were made at 0.25%

[4] This experiment was conducted by Dr. K.H. Pool, Staff Scientist, PNL.

(w/v) concentrations using the pH 10 eluent. The column flow rate was set at 0.5 mL/min, and an ultraviolet (UV) detector was used to monitor the elution (column retention time) of the standards. A chromatogram for each standard was generated (UV detector signal plotted against retention time).

The principle behind this size exclusion chromatography technique is that the lower molecular weight compounds are entrapped in the porous column packing, increasing their column retention time. Therefore, the higher molecular weight compounds have a shorter retention time. The retention time of each standard peak was correlated to the molecular weight of the standard, and a calibration curve was generated. Sample peak retention times were then determined and correlated to their respective molecular weights using the calibration curve.

### 3.6.3 Atomic Emission Spectroscopy

An Instrument Laboratory (IL) Model 451 flame atomic absorption/atomic emission spectrometer was used for Eu analysis. Eu was analyzed by atomic emission spectroscopy (AES) because it is a more sensitive analysis than atomic absorption spectroscopy (Bauer et al. 1978). Both the Eu AES standards and the sample aliquots contained 1200 μg/mL Na to suppress Eu ionization in the nitrous oxide flame and 0.5% $HNO_3$ to maintain Eu solubility. Thus, prior to Eu analysis, sample aliquots were spiked with Na and $HNO_3$ (using a $NaNO_3$ stock solution and reagent-grade 16 M $HNO_3$) to achieve the desired concentrations. The aliquot volumes before and after the addition of Na and acid were determined to account for the dilution effect on the aliquot Eu and polymer concentrations.

The IL 451 instrument was calibrated each time the Eu analysis was conducted. The calibration used 10 standards with Eu concentrations ranging from 0 μg/mL (blank) to 20 μg/mL, the linear working range of the instrument for Eu (Sotera and Stux 1979). The detection limit was determined by analyzing the low standard, 0.0625 μg/mL, 10 times consecutively and calculating the standard deviation. A typical

detection limit test resulted in a standard deviation of zero so 0.0625 μg/mL was designated the detection limit for Eu.

The instrument was zeroed using the blank standard, and the rest of the standards were then analyzed in order of ascending Eu concentration. A final analysis of the blank standard was then taken to ensure there was no baseline drift. A linear regression of resulting data points (standard Eu concentration, emission intensity) was calculated to determine the $r^2$ and equation of the line. An $r^2 = 0.995$ was designated as the threshold for a linear relationship between Eu concentration and emission intensity. After a linear calibration curve was generated, the corresponding equation was used to calculate the Eu concentrations of the analyzed sample aliquots. Figure 3.5 depicts a typical calibration curve generated for Eu analysis by AES.

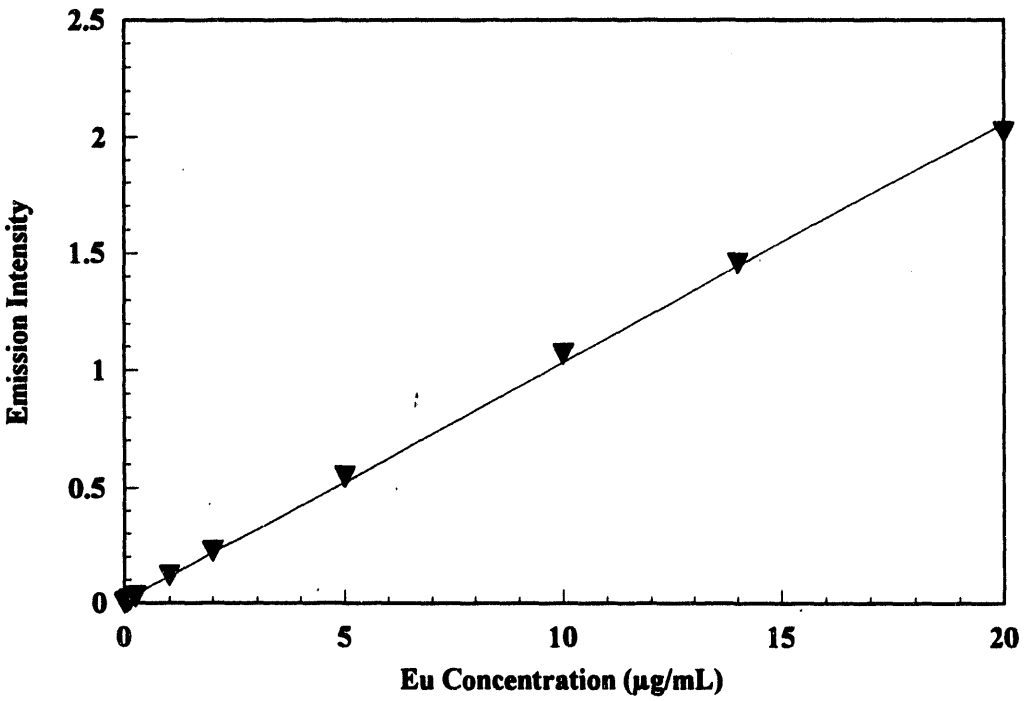



**Figure 3.5.** Typical Calibration Curve for Eu AES Analysis

### 3.6.4 Total Organic Carbon

A Dohrmann DC-80 TOC analyzer was used to determine polymer concentrations in the test solutions. These organic polymers were the only source of organic carbon in the solution matrix. The samples were acidified to pH 2 and sparged with nitrogen for 5 min before analysis to alleviate potential inorganic carbon (carbonate) interferences.

Standard solutions of organic carbon were prepared for instrument calibration at the following concentrations: 10 μg/mL, 400 μg/mL, and 2000 μg/mL. A dynamic linear working range of 0 to 4000 ppm organic carbon was established by these standards.

### 3.6.5 Sodium

Sodium concentrations were determined using an Orion model 86-11 Ross™ sodium electrode and the Orion model 720A benchtop meter. The electrode was calibrated each time the Na analysis was conducted; the Na standards were 10 μg/mL, 100 μg/mL, and 1000 μg/mL. Both the Na standards and samples were spiked with ionic strength adjuster (ISA) in accordance with the specified ratio of 1 mL ISA per 10 mL of sample.

### 3.6.6 pH

The pH of the test solutions was measured using an Orion model 720A benchtop pH/ISE meter and an Orion Triode™ pH electrode model 91-57BN. This electrode has an automatic temperature compensating feature that monitored the sample temperature and automatically adjusted the pH to correct for temperature deviations from 25°C. Calibrations were conducted daily with pH 4, 7, and 10 commercial buffers.

# 4.0 Results - Copolymer Characterization and Method Development

The experiments led to the following results on copolymer characteristics and developing a method to determine the effectiveness of polymer treatment for separating Eu.

## 4.1 Characterization of PNL's Synthesized Copolymer

The molecular weight distribution and cation exchange capacity of the E3 copolymer were determined experimentally. The copolymer molecular weight was important for selecting an ultrafiltration membrane with a MWCO adequate for effective rejection of the copolymer. The cation exchange capacity verified the AA to EO3Me monomer ratio of the E3 polymerization.

### 4.1.1 Determination of Molecular Weight Distribution

GPC analysis was used to determine the molecular weight distribution of the E3 copolymer. Three PAA standards (2000, 8000 and 35,000 MW) were used to generate the calibration curve shown in Figure 4.1. This figure illustrates the linear relationship between the column retention time for each PAA standard and its corresponding molecular weight.

The E3 copolymer chromatogram generated from the Dionex DX-300 system is shown in Figure 4.2. The E3 chromatogram shows four distinct peaks, indicating the E3 sample was composed of four different molecular weight fractions. Figure 4.1 indicates that the retention time for Peak 1 (26.60 min) corresponds to a log (molecular weight) of 4.2 (~16,000 MW). Peaks 2, 3, and 4 have retention times that fall outside of the range of the PAA standard calibration curve and represent molecular weights below 2000. Such low molecular weights were not expected because the polymerization was designed to generate a 10,000 MW copolymer. Peaks 2 to 4 may represent residual AA and/or EO3Me acrylate that were not copolymerized. If this was the case, Peak 1 represents the copolymer fraction of the E3 sample and verifies

that the polymerization exceeded the target copolymer molecular weight goal of 10,000. Detailed data of the GPC analysis are given in Table B.1 of Appendix B.

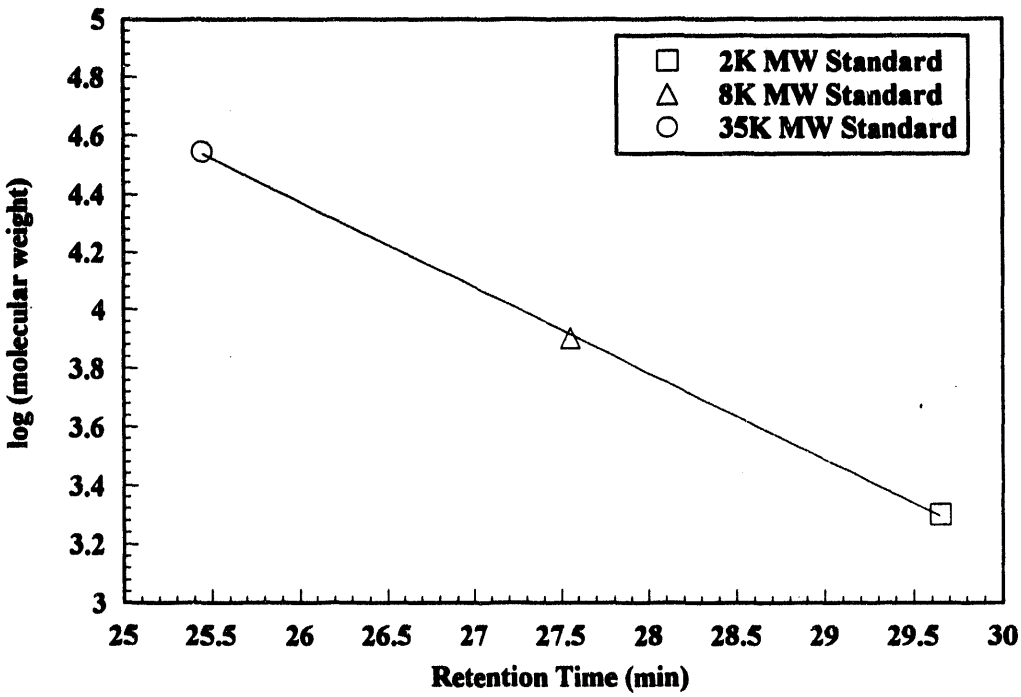



**Figure 4.1.** Molecular Weight Determination Calibration Curve - PAA Standards

The individual peaks may also represent distinct mass fractions of the E3 copolymer instead of lower molecular weight monomers (i.e., the E3 sample is 100% copolymer). If the total mass of the copolymer corresponds to the summation of the four peak areas, the mass fraction represented by Peak 1 can be estimated by calculating its fraction of the total peak area. Table B.1 tabulates the four individual peak areas and the total peak area for the E3 analysis. The fraction of the total peak area represented by Peak 1 is 0.25, indicating that only 25% of the E3 has a molecular weight of 16,000.

Regardless of the origin of Peaks 2 through 4, the GPC analysis verifies that the E3 copolymer contains a mass fraction that is greater than 10,000 MW, and this fraction should be separated effectively by ultrafiltration (i.e., $R_p = 0.25$ for E3 is expected). Effective membrane rejection was verified with the polymer average membrane rejection coefficient, $R_p$, values calculated for E3.

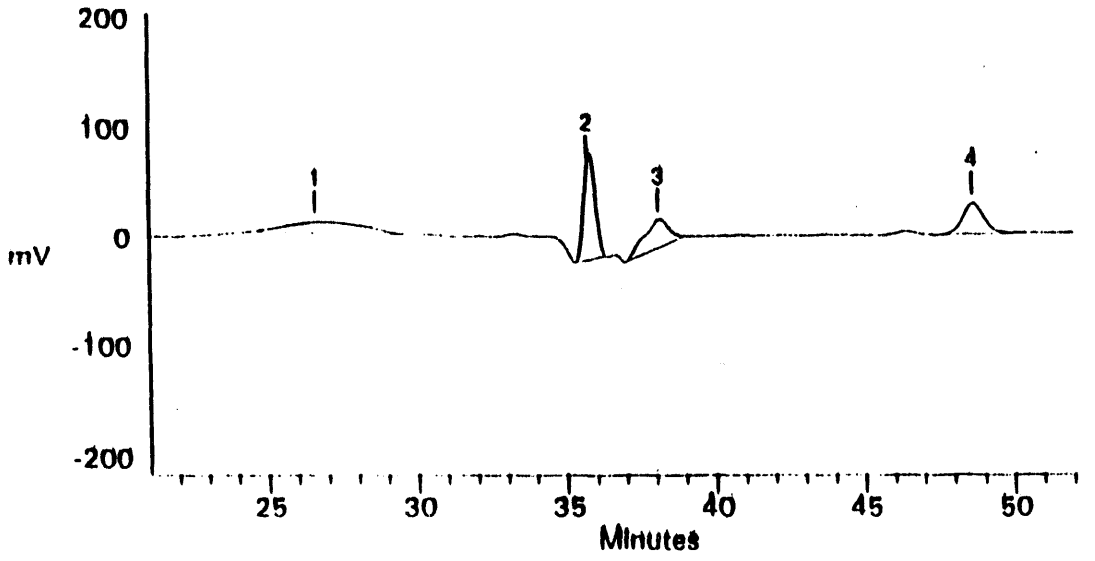



**Figure 4.2.** E3 Copolymer Chromatogram

### 4.1.2 Determination of Cation Exchange Capacity

The theoretical cation exchange capacity of 3.45 meq/g, calculated for the E3 copolymer (see section 3.2.2), was verified by conducting a base titration. A 0.1152-g sample of E3 was dissolved in a solution of 10 mL MeOH and 5 mL DDI. Because the E3 sample had a methanol content of 17.1%, the actual mass of E3 was 0.0955 g. The solution was then titrated with 0.1 N NaOH. The titration results are shown in Figure 4.3.

The titration curve indicates that the endpoint for E3 occurs at about 5.6 mL of 0.1 N NaOH (i.e., the point of inflection at the steepest portion of the curve). Therefore, the E3 was able to neutralize 5.6 mL of 0.1 N NaOH, and the neutralization capacity is

$$\frac{(5.6\ \text{mL})(0.1\ \text{mole/L})(1\ \text{equiv./mole})(1000\ \text{meq/equiv.})(1\ \text{L}/1000\ \text{mL})}{0.0955\ \text{g}} = 5.86\ \text{meq/g}.$$

This neutralization capacity is equivalent to cation exchange capacity. It represents the number of carboxylate groups available to provide cation ion exchange sites for the Eu. Comparing the measured cation exchange capacity (5.86 meq/g) to the computed cation exchange capacity (3.45 meq/g) indicates that more acrylic acids are present than would be expected for a 1:1 AA to EO3Me ratio. The computed acrylic acid to EO3Me acrylate ratio is 2.21, which can be expressed as the following average molecular formula: $(\text{EO3Me acrylate})_1(\text{AA})_{2.21}$.

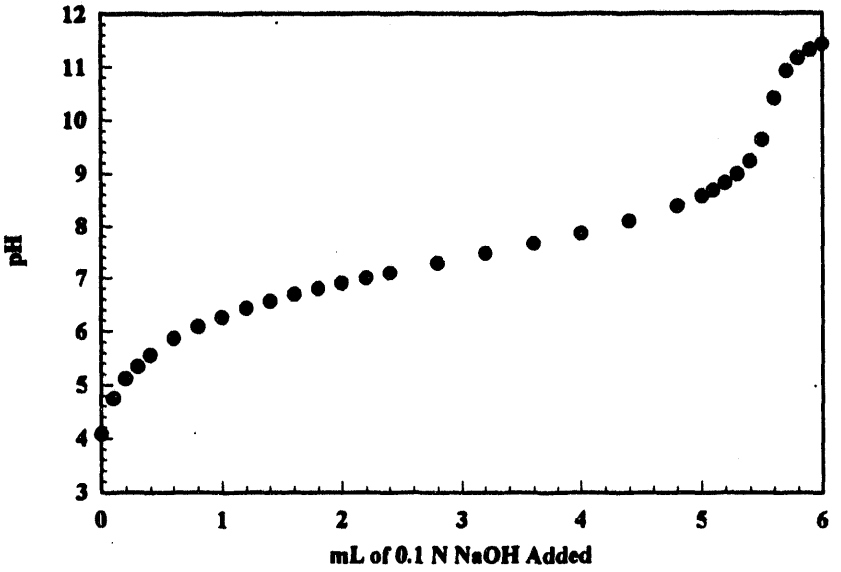



**Figure 4.3.** E3 Base Titration Curve

## 4.2 Rejection of Eu by YM Series Membranes

The intent of the experiments with YM series membranes was to evaluate the binding of Eu by commercial polymers (3000 MW PEG and 2000 MW PAA) and then to measure the rejection of these Eu-polymer complexes. However, as will be shown, Eu was rejected without being bound by the polymers.

The polymer concentration for the first test run was 100 μg/mL. This test was conducted at pH 5 and included four samples that were designated according to the polymer(s) added to the Eu bulk solutions, i.e., Control (Eu without polymer), PEG, PAA, and PEG/PAA. The filtration pressure was 30 psi. This pressure was selected based on pretesting results of rejection of the PEG and PAA test polymers (samples with 100-μg/mL polymer concentrations in neutral pH phosphate buffer) by YM1 membranes at various pressures. The rejection data for the YM1 membranes are shown in Appendix C, Table C.1. The filtrations conducted at 30 psi yielded polymer average membrane rejection coefficient ($R_p$) values for PAA, PEG and PEG/PAA samples of 0.64, 0.81, and 0.83, respectively. The $R_p$ value for PAA was probably low because its molecular weight is not much greater than the membrane MWCO.

The test results are tabulated in Table 4.1. The YM1 membrane rejected 100% of the Eu in the control sample (without polymer) [i.e., $R_{uf} = 1.0$], indicating that polymer treatment was not required to achieve complete separation of Eu from the bulk solution. This result was not expected because the effective size of soluble Eu (ionic radius of 0.950 Å) should have easily passed through the YM1 membrane pores. The fraction of Eu retained by the 0.2-μm microfilter, $Eu_{Ppt}$, was 0.09 for the control sample, which meant approximately 90% of the Eu was soluble. The Eu fractional recovery, REC, for the control sample was 0.57; i.e., only 57% of the Eu mass in the bulk solution was recovered in the filtrate and retentate fractions. Thus, about 40% of the mass was retained on the YM1 membrane.

**Table 4.1.** Eu Rejection with 100 μg/mL Commercial Polymers and YM1 Membrane

| Sample | Results |
|---|---|
| Eu without polymer (Control) | $R_{UF} = 1.00$<br>Fraction Eu Recovery = 0.57<br>$Eu_{Ppt} = 0.09$ |
| Eu with 100 μg/mL PEG | $R_T = 1.00$<br>$R_{PB} = 0.00$<br>Fraction Eu Recovery = 0.49<br>$Eu_{Ppt} = 0.08$ |
| Eu with 100 μg/mL PAA | $R_T = 1.00$<br>$R_{PB} = 0.00$<br>Fraction Eu Recovery = 1.06<br>$Eu_{Ppt} = 0.22$ |
| Eu with 100 μg/mL PEG & 100 μg/mL PAA | $R_T = 1.00$<br>$R_{PB} = 0.00$<br>Fraction Eu Recovery = 0.99<br>$Eu_{Ppt} = 0.10$ |

It was assumed that the measured membrane Eu rejection for the control sample (without polymer), $R_{UF} = 1.0$, represented the contribution of Eu rejection ($R_T$) by the membrane when filtering

polymer-treated samples. Therefore, the rejection of Eu attributed to Eu bound to polymer ($R_{PB}$) was zero for the polymer-treated samples. Hence, test conditions resulting in an $R_{UF} = 1.0$ did not allow the experiment to determine a polymer binding effect for Eu.

### 4.2.1 The Effect of pH on Eu Membrane Rejection (without polymer)

The effect of pH on Eu solubility could explain rejection of Eu in the absence of polymer and, thus, a high $R_{UF}$ value. It was reasoned that a lower pH could possibly increase Eu solubility and, thus, give a lower $R_{UF}$ value. If $R_{UF}$ could be reduced, then the polymer binding effect for Eu could be determined.

Control samples (without polymer) adjusted to pH 2.5 and 5 were filtered through YM1 and YM10 membranes, and the resulting membrane rejection coefficients, $R_{UF}$, were calculated. These results are shown in Figure 4.4. The $R_{UF}$ values for both membranes at pH 5 was 1.0. The $R_{UF}$ values for the YM1 and the YM10 membrane were much lower (0.21 and 0.04, respectively) at pH 2.5. The fractional Eu recovery for each sample is shown in parentheses above each bar. The recovery values for both membranes were much higher at pH 2.5 than those at pH 5. In other words, little or no rejection of Eu yielded high recoveries, while 100% Eu rejection resulted in low recoveries. These low REC values indicate fouling of the membranes (e.g., concentration polarization and/or adsorption) by Eu.

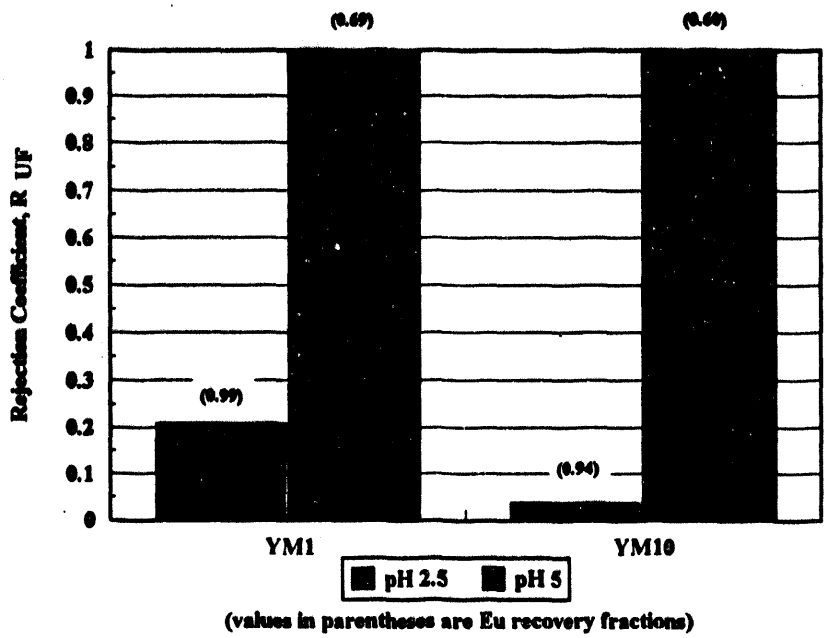



**Figure 4.4.** Effect of pH on Eu Rejection by YM Series Membranes

Aliquots of the same two control samples were filtered through a 0.2-μm microfilter to monitor Eu solubility. The resulting $Eu_{Ppt}$ values were 0.04 and 0.09 for the pH 2.5 and pH 5 samples, respectively. These low $Eu_{Ppt}$ values mean that very little Eu was insoluble based on the operational definition chosen.

A wider range of pH (2 - 10) was selected for further investigation of Eu rejection by the YM1 membrane. The objective was to determine the lowest pH at which Eu rejection by the membrane, $R_{UF}$, was minimized. Control samples (without polymer) were adjusted to six different pH values, and aliquots were ultrafiltered at 30 psi. Eu solubility for each sample was monitored using 0.2-μm microfilters.

The test results indicate that pH has an effect on both Eu rejection by the YM1 membrane and Eu solubility. The calculated $R_{UF}$, REC, and $Eu_{Ppt}$ values for each sample are shown in Figure 4.5. The lowest $R_{UF}$ achieved was 0.28 for the pH 2 sample. The $R_{UF}$ = 1.0 for the remaining samples indicated that decreasing sample pH did not reduce $R_{UF}$ until the sample pH <3. The pH sensitivity of the membrane is apparent by noting that the $R_{UF}$ fraction decreased from 1.0 to 0.28 when the pH was decreased from 3 to

2. The $Eu_{Ppt}$ values show that less than 10% of the Eu was insoluble for the samples with pH ≤6. Thus, the YM1 membrane achieved 100% rejection of Eu for the pH 3 to 6 samples even though their Eu solubility was >90%. The $Eu_{Ppt}$ values were much greater (0.96 and 1.00, respectively) for the pH 8 and pH 10 samples, suggesting that the formation of Eu hydroxide precipitates, $Eu(OH)_3$, does not become appreciable until the solution pH >6. The Eu recovery fractions are shown in parentheses above the rejection coefficient results in Figure 4.5. The REC values decrease from 0.95 to 0.31 as the pH increases from 2 to 4. However, as the pH increases from 4 to 10, the REC values increase from 0.31 to 1.14, an indication that the formation of insoluble Eu precipitates for pH > 6 did not reduce Eu recovery [i.e., cause membrane fouling by $Eu(OH)_3$].

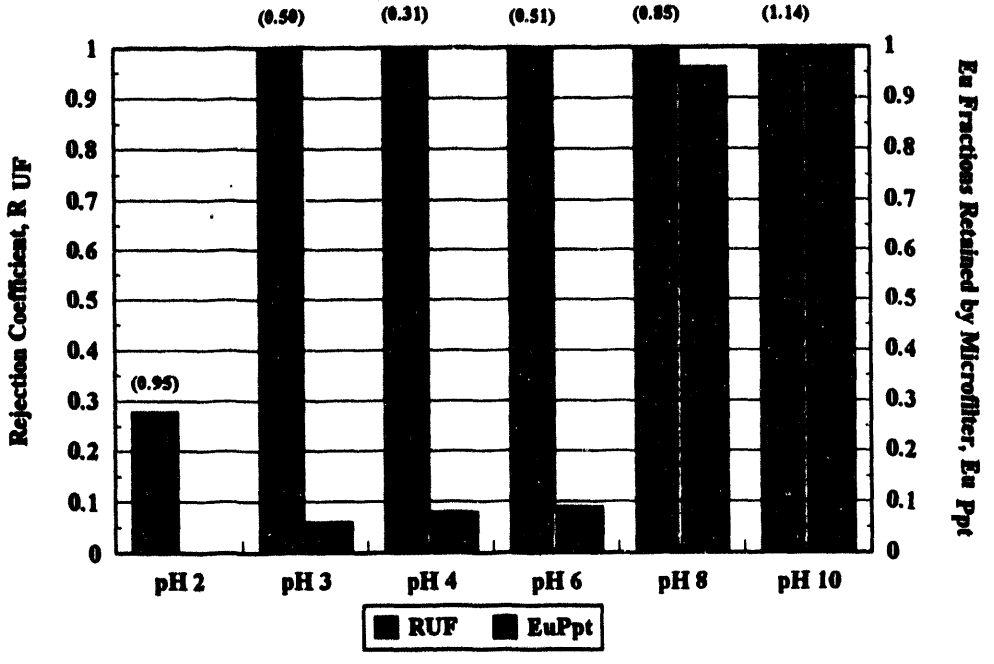



**Figure 4.5.** Effect of pH on Eu Rejection by YM1 Membrane and Eu Solubility

### 4.2.2 Possible Mechanisms to Explain pH Effect on Eu Membrane Rejection

The reason(s) for the high rejection of Eu between pH 3 and 6 for the YM1 coupon is not well understood. If insoluble Eu hydroxides, $Eu(OH)_3$, had formed in this pH range, rejection by the YM1 membranes would have been expected. However, the low $Eu_{Ppt}$ values given in Figure 4.5 showed that Eu

hydroxide formation did not occur until the pH >6. Thus, hydroxide formation does not explain the high Eu rejection for the control samples (without polymer) in the pH range between 3 and 6. One possible explanation is the formation of polynuclear Eu species with molecular weights greater than 1000 within the pH 3 to 6 range. Although the formation of polynuclear Eu species was not reported, $Nd_3(OH)_5^{4+}$ is a cationic polynuclear species that forms in small quantities as Nd hydrolyzes before forming an insoluble hydroxide precipitate (Baes and Mesmer 1986). If Eu were to form the same polynuclear species, the molecular weight would be approximately 500 g/mole (i.e., not large enough for effective retention through the 1000 MWCO membrane). Another possible explanation is membrane surface interaction (i.e., electrostatic) with the trivalent Eu. The polarity of the cellulose acetate, YM series membrane material increases the possibility of electrostatic interaction with charged species in the filtered solutions.

### 4.2.4 Rejection of Eu at pH 2 with Polymer Treatment Using YM1 Membranes

The data reported in the previous section showed that experiments would have to be conducted at pH 2 in order to minimize $R_{UF}$ and to determine the effect of Eu binding to polymers and subsequent membrane rejection by YM1 membranes. The commercial polymers and E3 copolymer were evaluated at two concentrations (100 and 1000 μg/mL). Two test runs using 100 μg/mL and three test runs using 1000 μg/mL were conducted with the commercial polymers. Two tests runs for each concentration were conducted with the E3 copolymer.

Eu solubility ($Eu_{Pu}$), Eu and polymer recovery fractions (REC), and membrane rejection of polymer-bound Eu ($R_{PB}$) and polymer ($R_P$) were calculated for each test. The average $R_{PB}$, $R_P$, and REC values of the 100-μg/mL test runs are presented in Figure 4.6. The highest Eu rejection ($R_{PB}$ = 0.24) was obtained by the PEG polymer treatment. The remainder of the polymers rejected <10% of the Eu. The Eu rejection results for the control samples (without polymer), $R_{UF}$, included in each test run, ranged between 0.13 and 0.36. This variation in $R_{UF}$ indicates the Eu rejection of control aliquots through the same YM1

membrane coupon is not reproducible and can affect the $R_{PB}$ results. Recall that $R_{PB} = R_T - R_{UF}$, where $R_T$ is the total average membrane rejection coefficient (i.e., Eu rejection of both unbound and polymer-bound Eu species) and $R_{UF}$ represents membrane rejection of unbound Eu species. The Eu and polymer fractional recoveries are shown in parentheses above the $R_{PB}$ and $R_P$ results, respectively, in Figure 4.6. All of the Eu and polymer recoveries were greater than 90% for each polymer treatment, which indicates minimal loss of solute mass on the membrane (i.e., minimal membrane fouling by Eu and polymer). Formation of Eu precipitates in the test solutions at pH 2 was not expected. This was verified by the low $Eu_{ppt}$ values (<5%) calculated for each polymer-treated solution. The results presented in Figure 4.6 are tabulated in Table C.2 of Appendix C along with the $Eu_{ppt}$ values.

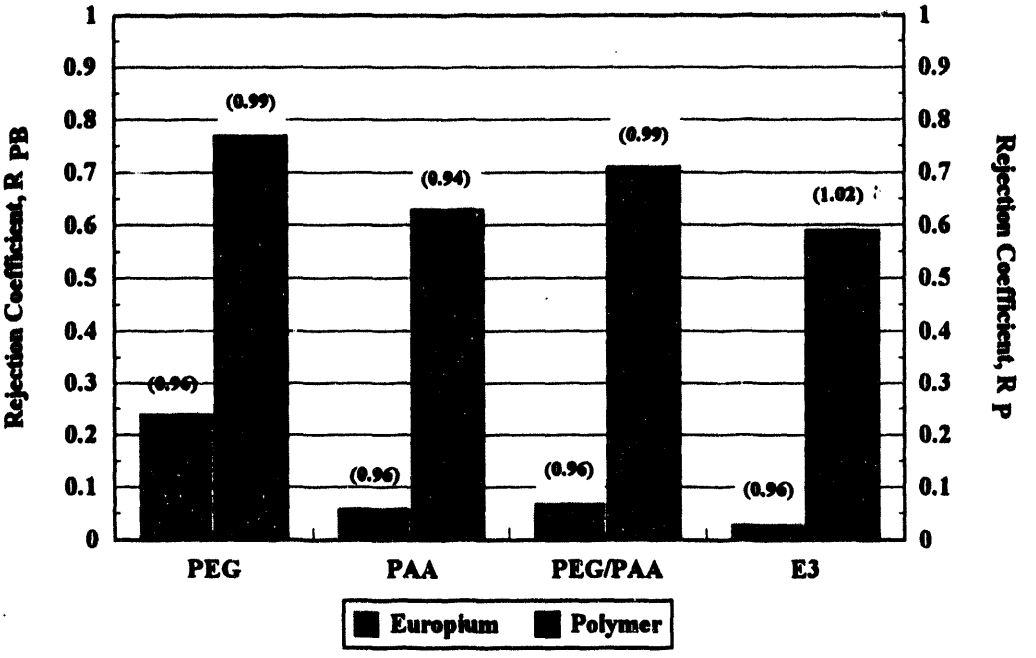



**Figure 4.6.** Eu and Polymer Rejection by YM1 Membrane at pH 2 with 100-μg/mL Polymer Concentrations

A second set of experiments was conducted at a polymer dose of 1000 μg/mL instead of 100 μg/mL in order to determine if Eu rejection could be improved. The average $R_{PB}$, $R_P$, and REC values

of these experiments are presented in Figure 4.7. As indicated in Figure 4.7, increasing the polymer concentration by an order of magnitude had no positive impact on the rejection of Eu by YM1 membranes. The enhancement of Eu rejection for all of the polymers tested was less than 10% (i.e., $Eu_{PB}$ <0.10), which indicates that this process was ineffective at pH 2. In fact, a negative impact was seen for the PEG-treated sample where the $R_{PB}$ decreased from 0.24 to zero. Similar to the 100-μg/mL tests, both the Eu and polymer fractional recoveries were greater than 90%, and the $Eu_{Ppt}$ values were less than 5% for all of the 1000-μg/mL polymer-treated samples. The results presented in Figure 4.7 and the $Eu_{Ppt}$ values are tabulated in Table C.3 of Appendix C.

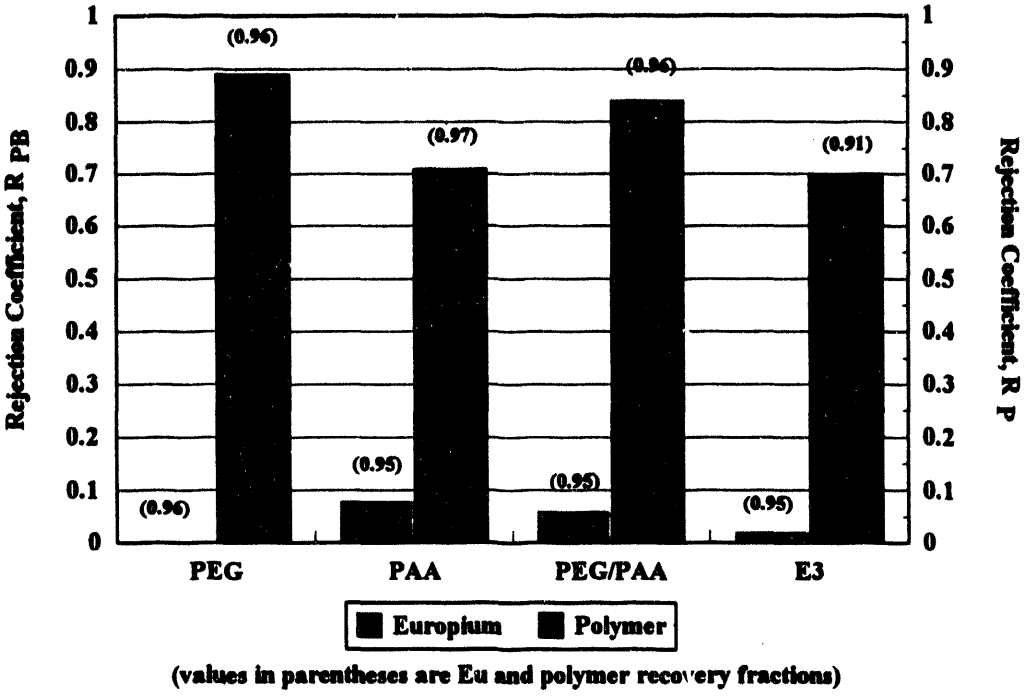



**Figure 4.7.** Eu and Polymer Rejection by YM1 Membrane at pH 2 with 1000-μg/mL Polymer Concentrations

Both Figures 4.6 and 4.7 show a much higher rejection of polymer than Eu. It can be concluded that the polymers are not binding Eu at pH 2. The lack of binding was not surprising for the PAA. The equilibrium concentration of carboxylate groups (i.e., available cation exchange sites) in PAA at pH 2 is

less than 1% of the total carboxyl group concentration for 2000 MW PAA (based on pKa = 4.25 for acrylic acid). Therefore, no exchange sites are available to bind Eu at pH 2. A possible explanation for the lack of binding for PEG and E3 is that the high concentration of $H^+$ at pH 2 may inhibit the complexation of Eu by the PEG and EO3Me component of the E3 copolymer.

### 4.2.5 Selection of YM Membrane MWCO to Minimize $R_{UF}$

The tests reported so far led to the following conclusions about test conditions to establish Eu binding by polymers: 1) the bulk solution pH should be greater than 4 to exceed the pKa of AA (4.25) but also less than 6 to prevent $Eu(OH)_3$ precipitate formation, and 2) the contributing membrane rejection of Eu (without polymer) should be less than 10%; i.e., $R_{UF} < 0.10$. A series of YM membranes were tested to determine if these two constraints could be met and Eu-polymer complexes could be rejected. The first step in the membrane rejection selection process was to determine the effect of pH on $R_{UF}$ for the following MWCOs: 3000 (YM3); 10,000 (YM1); 30,000 (YM30); and 100,000 (YM100). Six control samples were adjusted to pH 2, 3, 4, 6, 8, and 10; and aliquots were ultrafiltered at 30 psi through each membrane coupon. One coupon for each MWCO was tested, and the aliquots were filtered in descending order with respect to pH (i.e., pH 10 first and pH 2 last). Because the YM membranes can be damaged by acid burning for sample pH <3 (B. Yankopoulos, personal communication with Amicon, May 5, 1993), the acidic aliquots were filtered last. That way, potential membrane damage from the pH 2 sample filtrations would not affect subsequent filtrations with samples at higher pH.

The effect of pH on $R_{UF}$ for each MWCO in the YM series is shown in Figure 4.8 (see Table C.4 of Appendix C for data). The results indicate that Eu is 100% rejected by all four membranes at pH 10, 8, and 6. Some of the $R_{UF}$ values are less than 1.0 for pH 4 and become negative at pH 2 and 3. These negative membrane rejection coefficients were calculated using Eq. (3) and were less than zero because the filtrate Eu concentration, $C_f$, exceeded the initial aliquot Eu concentration, $C_i$. To further explain, a

negative rejection coefficient is only possible according to Eq. (3) if $C_f$ is greater than $C_i$. It is possible for $C_f$ to be greater than $C_i$ if Eu fouled on the membrane from filtration of one aliquot but then passed through the membrane in a subsequent filtration.

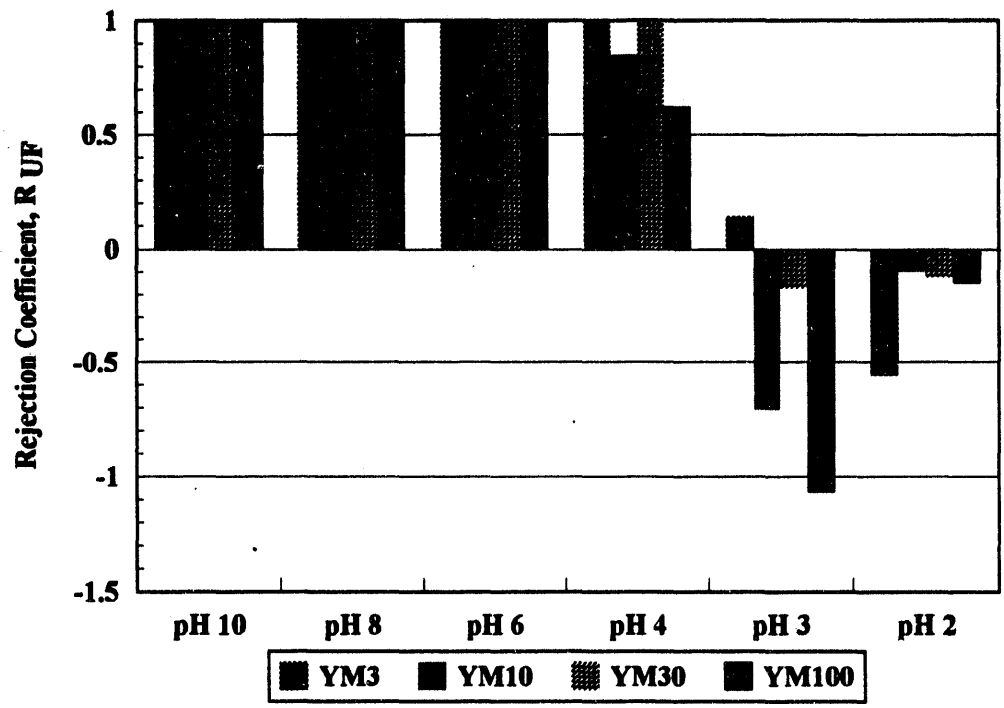



**Figure 4.8.** Effect of pH on $R_{UF}$ for YM Series Membranes

Evidence for a Eu "carry over" effect is presented in Figure 4.9 (data are found in Table C.4 of Appendix C). Eu fractional recoveries were much less than 1.0 for pH >3. Low recoveries mean a loss of Eu, probably by fouling of the membranes with $Eu(OH)_3$. Because of the filtration sequence (pH 10 first and pH 2 last), the fouling was able to "carry over" to subsequent aliquot filtrations. The Eu that accumulated at high pH filtrations was probably released at pH 3 and below as a result of $Eu(OH)_3$ dissolution. The release of accumulated Eu at pH 2 and 3 would account for the Eu recovery values being greater than 1.0 for all of the membranes. Fouling of the YM100 membrane during the pH 10, 8, 6, and 4 aliquot filtrations must have been particularly extreme because the Eu recovery value at pH 3 was 1.45. It is interesting to note that Eu recovery of the YM100 membrane after the pH 3 aliquot filtration (i.e.,

filtration at pH 2) decreased to 1.02; this is a reasonable recovery to expect for an ultrafiltered sample without the "carry over" interference. The possibility that membrane fouling occurred by accumulation of $Eu(OH)_3$ has implications for the membrane cleaning protocol suggested by Amicon. This protocol, which works well for protein separations, consists of the following steps:

1. Triple-rinse the cell and membrane with DDI.
2. Add several mL of 0.1 N NaOH and let stir for 5 min.
3. Triple-rinse the cell and membrane with DDI.

The use of a NaOH rinse in Step 2 was of concern because, as shown by the pH studies, raising the pH during membrane cleaning could lead to the formation of insoluble Eu hydroxide. Therefore, an alternative protocol was adopted in which an acid rather than a caustic rinse was used. The acid rinse should inhibit the formation of $Eu(OH)_3$ and remove any build-up on the membrane between filtrations.

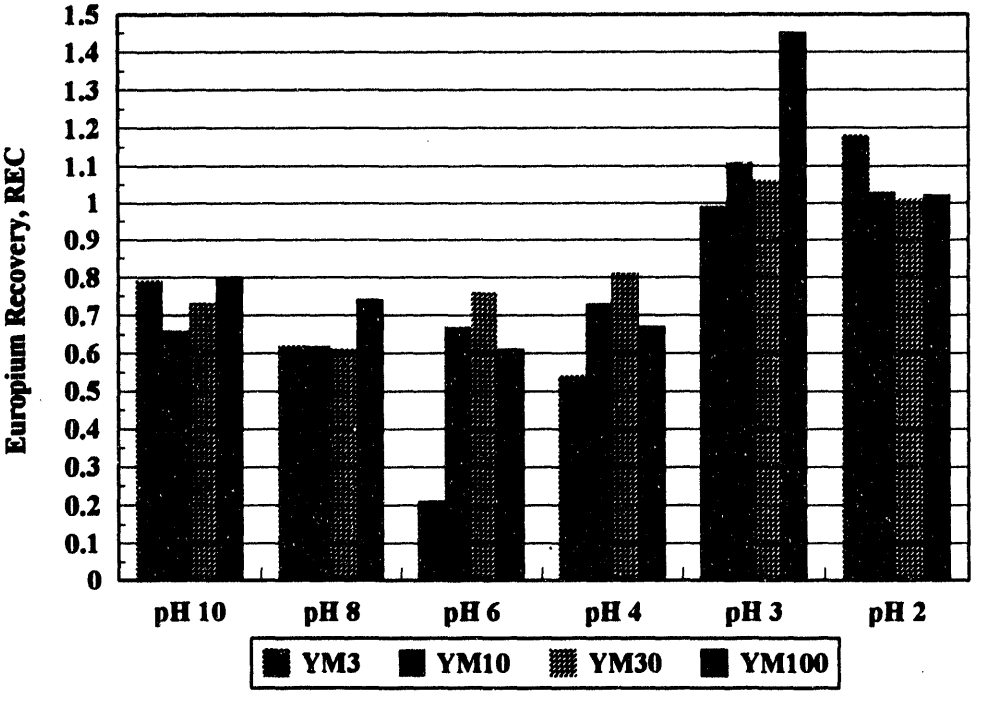



**Figure 4.9.** Effect of pH on Europium Recovery for YM Series Membranes

A 0.5% $HNO_3$ solution (equivalent to 0.08 N $HNO_3$) was selected to use as the acid rinse used in the cleaning protocol. The YM series membranes are not compatible with such a nitric acid rinse because short exposures can cause permanent damage but, the PM series membranes are not affected (Amicon 1992). Hence, the remaining experimental work was conducted using the PM series membranes, and the 0.5% $HNO_3$ acid rinse was used for membrane cleaning.

## 4.3 Rejection of Eu by PM Series Membranes

The only MWCOs available in the PM series membranes are 10,000 (PM10) and 30,000 (PM30). These MWCOs are much larger than the molecular weight of the PAA polymer (2000 MW) that had been used in previous experiments. Consequently, it was necessary to switch to PAA with a larger molecular weight (60,000) to ensure effective retention by the PM membranes. PEG was no longer included in this study because the results at pH 2 with the YM1 membranes indicated that it was not an effective Eu binder. Because PEG is nonionic, evaluating it at pH 5 was not expected to improve its binding affinity for Eu. Therefore, the E3 copolymer and 60,000 MW PAA were the only binding agents evaluated in the remainder of the experimental work. Eu solubility ($Eu_{Ppt}$) was measured with Gelman 0.45-μm filters instead of 0.2-μm filters because the supply of Gelman disposable 0.2-μm filters was depleted.

### 4.3.1 Effect of pH on Rejection of Eu (without polymer) by PM Series Membranes

These experiments were designed similar to the testing described in Section 4.2.5 using YM series membranes. The objective was to evaluate the effect of pH on $R_{UF}$ for a PM10 and PM30 membrane in order to determine if the $R_{UF} < 0.10$ criterion was feasible for either MWCO within the pH range of 4 to 6. The pH values investigated were 10, 8, 6, 4, and 2; this was the filtration sequence as well.

The effects of pH on membrane rejection ($R_{UF}$) and recovery (REC) of Eu (without polymer) for a PM10 and PM30 membrane are shown in Figure 4.10 (data are found in Table D.1 of Appendix D). No

negative values for $R_{UF}$ were obtained as was true for the YM series (Figure 4.8). Thus, the Eu "carry over" effect was diminished. Europium fractional recoveries (shown in parentheses above each bar) ranged between 0.76 and 0.96 and indicated that membrane fouling by $Eu(OH)_3$ was minimal. The results showed that the acid rinse was very effective for cleaning the membrane used in subsequent experiments.

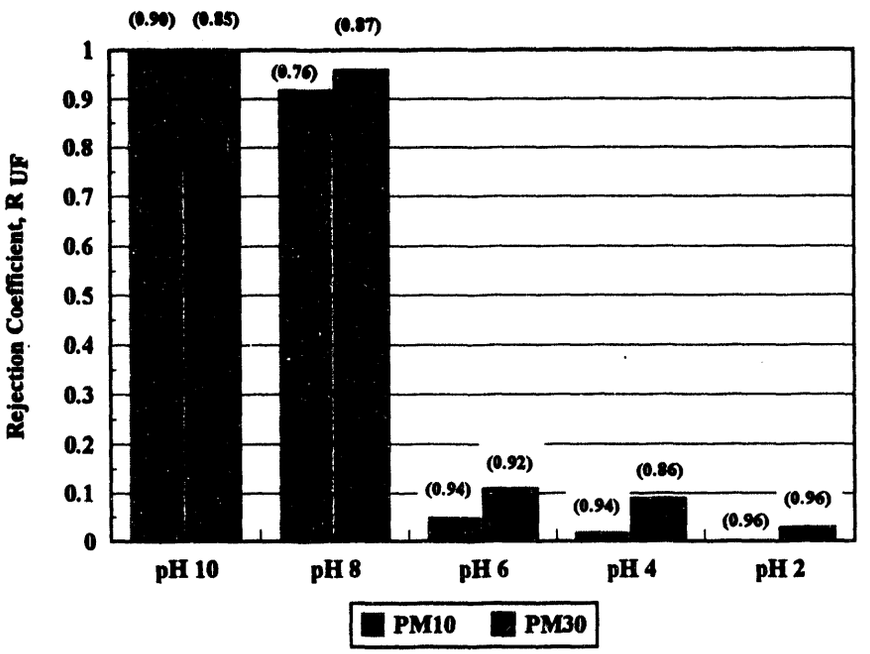



**Figure 4.10.** Effect of pH on $R_{UF}$ for PM Membranes

Figure 4.11 shows the effect of pH on Eu solubility using the 0.45-μm disposable microfilters. The results are very similar to earlier solubility tests conducted with 0.2-μm microfilters (See Figure 4.5), and they verify that the formation of $Eu(OH)_3$ is not significant below a pH of 6.

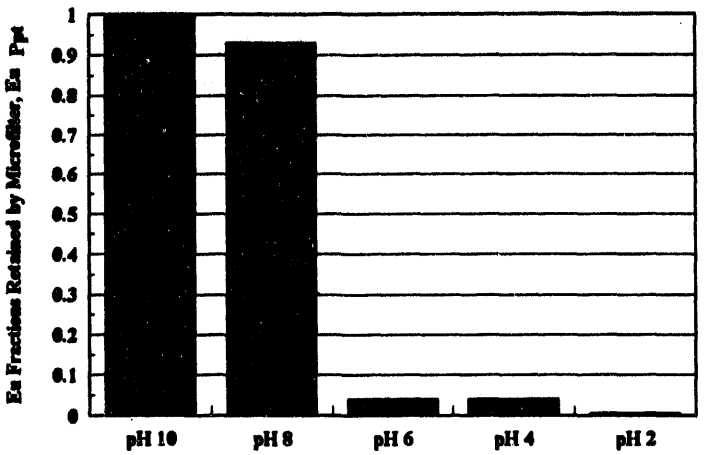



**Figure 4.11.** pH Effect on Eu Solubility (0.45-μm Microfilter)

### 4.3.2 Selection of pH

The results in Figure 4.10 were encouraging because they suggested that either PM membrane rejected less than 10% of the Eu in the pH range of 4 to 6. Thus, it was possible to study Eu binding to polymers and subsequent membrane rejection. A series of experiments were conducted to confirm that the PM membrane was suitable. New PM membrane coupons were evaluated using three new control samples (without polymer) adjusted to pH 4, 5 and 6. Tests 1 and 2 were run under identical conditions in order to verify the reproducibility of the $R_{UF}$ values for each pH using the same PM membrane. The filtration sequence was pH 4, 5, and 6. The two tests were conducted a day apart, and the membranes were kept in the stirred cells overnight.

The results shown in Figure 4.12 (data are found in Table D.2 of Appendix D) indicate that the rejection coefficients were not reproducible at pH 4 and 5 for the PM10 coupon. At pH 4, $R_{UF}$ increased from 0.10 in Test 1 to 0.62 in Test 2. The latter result could have been due to the presence a fouling layer of $Eu(OH)_3$ that had accumulated in Test 1. Europium recovery fractions (shown in parentheses above each corresponding bar) support this hypothesis. The fractional recovery value at pH 4 in Test 2, the first sample filtered after Test 1, was only 0.64 as compared with 0.94 for the last aliquot filtered in Test 1

(pH 6). A lower fractional recovery would be consistent with the presence of a leftover fouling layer. The loss of Eu mass was partially recovered in the filtrate of the pH 5 aliquot for Test 2. As a result, the Eu concentration in the filtrate was greater than the initial Eu concentration (i.e., $R_{UF}$ = -0.07).

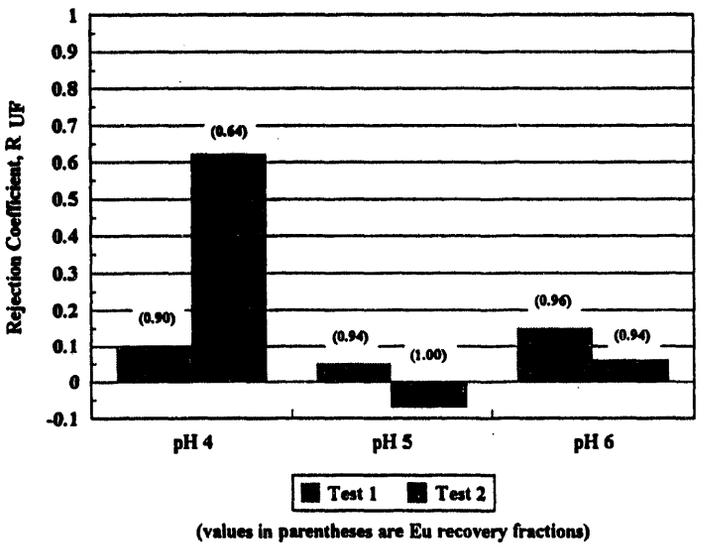



**Figure 4.12.** $R_{UF}$ Reproducibility for a PM10 Membrane at pH 4 to 6

The rejection coefficients for the PM30 membrane are shown in Figure 4.13 (data are found in Table D.2 of Appendix D). With the exception of the experiments at pH 4 and pH 5 in Test 1, all of the $R_{UF}$ values were less than 0.10. The $R_{UF}$ values were somewhat higher than 0.10 for the experiments at pH 4 and pH 5 (0.17 and 0.11, respectively) for Test 1, but even these results were close to the criterion that $R_{UF}$ not exceed 0.10. The fractional Eu recoveries (shown in parentheses above each corresponding bar) ranged between 0.88 and 0.96. These results confirm that Eu recovery was reproducible and high enough to proceed with further evaluation of Eu binding to polymers and rejection on the PM30 membrane.

Figure 4.12 and 4.13 indicate that both PM series membranes reject less than 10% of the Eu bulk solution concentration at pH 5. However, before initiating tests with the polymers and PM membranes at pH 5, the membrane cleaning protocol was further investigated and modified (See Section 4.4) in order to

prevent the inconsistent results achieved by the PM10 membrane (i.e., the difference in pH 4 $R_{UF}$ values shown in Figure 4.12).

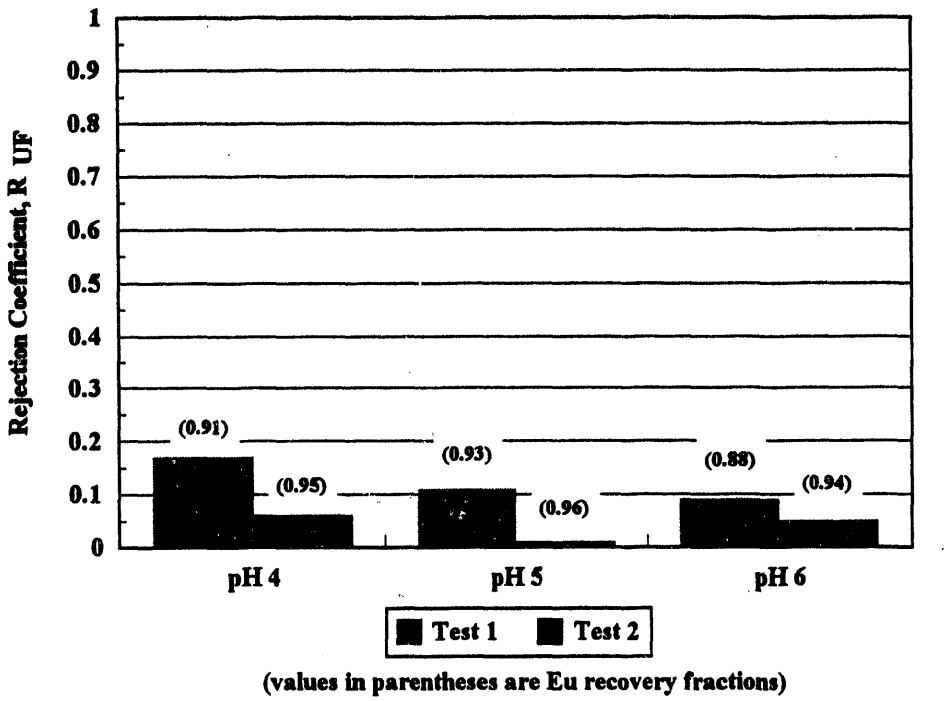



**Figure 4.13.** $R_{UF}$ Reproducibility for a PM30 Membrane at pH 4 to 6

## 4.4 Modified Membrane Cleaning Protocol

Good membrane flux recovery is important for reusing ultrafiltration membranes to achieve consistent rejection performance. Many laboratories that use Amicon membranes can get 10 or more filtrations out of a single coupon with adequate flux recovery when using an effective cleaning technique (E. Surette, personal communication with Amicon, May 20, 1993). For the specific filtration requirements of this study, the cleaning protocol was modified at the suggestion of Surette. The acid rinse contact time was increased to 15 min, and an aliquot of DDI was filtered after the acid rinse to remove residual acid and soluble Eu. The new membrane cleaning protocol consisted of the following five steps:

1. Remove sample retentate.
2. Triple-rinse stirred cell and membrane surface with DDI.

3. Add 5 mL of 0.5% $HNO_3$ rinse solution and stir for 15 min.

4. Triple-rinse stirred cell and membrane surface with DDI.

5. Filter 10 mL of DDI at 55 psi.

The filtration pressure in Step 5 was increased from 30 to 55 psi to allow comparison of fluxes with DDI water with new and used membranes to the clean water flux values stated by Amicon [1.5 to 3.0 ($mL/cm^2$-min) for the PM10 and 2.0 to 6.0 ($mL/cm^2$-min) for the PM30 membranes, respectively].

An experiment to determine the effectiveness of the modified membrane cleaning protocol was conducted by measuring the recovery of clean water flux after filtering control (without polymer) and polymer-treated samples through new PM10 and PM30 membranes. Two aliquots from a control sample and four aliquots from an E3-treated sample (35 μg/mL of E3) were filtered through each membrane. Flux values were calculated for the DDI samples filtered in Step 5 of the modified cleaning procedure in order to determine clean water flux recovery. The membrane filtration sequence is shown in Table 4.2. Eu solubility in each sample was measured with 0.45-μm filters.

The pH of the aliquots was 5 before ultrafiltration. The pH of the filtrate and retentate fractions was measured to verify that the membrane cleaning protocol did not affect the pH of the aliquots when placed in the stirred cell (i.e., this was a concern because the samples were not pH-buffered to maintain a simple aqueous system).

**Table 4.2. Filtration Sequence for Modified Membrane Cleaning Protocol Evaluation**

| Filtration Number | Aliquot |
|---|---|
| 1 | DDI |
| 2 | $Eu_I$ |
| 3 | DDI |
| 4 | E3 |
| 5 | DDI |
| 6 | E3 |
| 7 | DDI |
| 8 | E3 |
| 9 | DDI |
| 10 | E3 |
| 11 | DDI |
| 12 | $Eu_F$ |
| 13 | DDI |

The E3-treated samples were included to determine the rejection of polymer , $R_p$, and the effect of E3 treatment on the rejection of Eu, $R_{PB}$. As discussed in earlier experiments, the effect of polymer treatment on Eu rejection can only be ascertained if the rejection of Eu (without polymer addition) is known. Europium rejection ($R_{UF}$) was measured for the two control sample aliquots (without polymer), which were introduced to the PM series membranes before (aliquot $Eu_I$) and after (aliquot $Eu_F$) introducing the E3-treated sample aliquots. The average of the two $R_{UF}$ values was taken as the contribution of Eu rejection by the membrane when filtering the polymer-treated samples. Therefore, the Eu rejection attributed to the polymer, $R_{PB}$, was calculated by subtracting the mean $R_{UF}$ value from the total Eu rejection value, $R_T$, calculated for each polymer-treated sample; $R_{PB} = R_T - R_{UF}$ (avg.).

### 4.4.2 Cleaning Protocol Effectiveness for and Rejection of Eu-Polymer Complexes and E3 Copolymer by the PM10 Membrane

The flux values measured for the PM10 membrane are tabulated in Table 4.3. The clean water flux for the new PM10 membrane (1.72 mL/cm$^2$-min), determined by the first DDI aliquot filtered (DDI-1),

fell within the clean water flux range specified by Amicon (1.5 to 3.0 mL/cm$^2$-min). The membrane flux recovery was determined by comparing the flux values of the first DDI aliquot (DDI-1) and the last DDI aliquot (DDI-7) filtered; 1.72 and 0.92 mL/min/cm$^2$, respectively. Hence, the flux recovery for this PM10 membrane was 54%. The low recovery was attributed to the E3 aliquot filtrations and indicated that the membrane cleaning protocol was not completely removing polymer build-up on the membrane (compare the flux values of the DDI aliquots filtered after each E3 aliquot to the flux value of DDI-1).

**Table 4.3.** PM10 Membrane Flux Values

| Filtration Number | Aliquot | Flux (mL/cm$^2$-min) |
|---|---|---|
| 1 | DDI-1 | 1.72 |
| 2 | $Eu_i$ | 1.81 |
| 3 | DDI-2 | 1.71 |
| 4 | E3-1 | 0.32 |
| 5 | DDI-3 | 1.27 |
| 6 | E3-2 | 0.23 |
| 7 | DDI-4 | 1.21 |
| 8 | E3-3 | 0.24 |
| 9 | DDI-5 | 0.92 |
| 10 | E3-4 | 0.19 |
| 11 | DDI-6 | 0.92 |
| 12 | $Eu_p$ | 0.72 |
| 13 | DDI-7 | 0.92 |

DDI aliquots DDI-2 to DDI-7 were analyzed for Eu and E3 (as measured by TOC) to determine if there was "carry over" from previous filtrations (see Table D.3 of Appendix D). Only trace amounts of Eu and TOC were detected which meant that "carry over" was minimal. Also, the pH remained nearly constant (5±0.2) in the filtrate and retentate fractions which meant that the modified cleaning protocol did not impact the pH of the filtered aliquots.

Polymer treatment using 35 μg/mL of E3 had a positive effect on Eu rejection, as indicated by the results tabulated in Table 4.4. The mean $R_{PB}$ for the four E3 aliquots was 0.53, suggesting that 53% of the Eu removed from the E3-treated sample can be attributed to the rejection of Eu-E3 complexes (i.e., Eu bound to E3). The average $R_{UF}$ value for $Eu_I$ and $Eu_F$ was 0.09, which satisfied the $R_{UF}$ <0.10 criterion for evaluating a polymer binding effect. The mean Eu fractional recovery value was 0.94 for the control aliquots (without polymer) and 0.88 for the E3 treated aliquots. The mean E3 fractional recovery (as measured by TOC) was also 0.88. These high recovery values indicate minimal fouling of the membrane by $Eu(OH)_3$. The formation of $Eu(OH)_3$ precipitates was minimal, as indicated by the low $Eu_{Ppt}$ values (0.04 and 0.13 for the Control and E3-treated samples, respectively).

The mean polymer rejection, $R_p$, value of the four E3-treated aliquots was 0.72. An $R_p$ <1.0 is not surprising given that the GPC results (See Figure 4.3) showed that 75% of the E3 copolymer was smaller than 10,000 MW. If the membrane rejection efficiency coincided with the GPC results, the $R_p$ value would have been 0.25. The additional membrane rejection of the E3 copolymer could be due to aggregation of the copolymer from hydrogen bonding. Recall that the GPC analysis, discussed in Section 3.6.2, was conducted at pH 10 to prevent aggregation of the PAA molecular weight standards and E3 sample through hydrogen bonding. The pH of the test solutions is 5, which could promote the hydrogen bonding effect and enhance membrane rejection.

**Table 4.4.** Eu and E3 Copolymer Rejection by PM10 Membrane

| Sample | Number of Replicates | Results (a) |
|---|---|---|
| Eu without polymer (Control) | 2 | $R_{UF}$ = 0.09±0.05 |
| | | Fractional Eu Recovery = 0.94±0.03 |
| | 1 | $Eu_{Ppt}$ = 0.04 |
| Eu with E3 polymer | 4 | $R_T$ = 0.61±0.02 |
| | | $R_{PB}$ = 0.53±0.02 |
| | | Fractional Eu Recovery = 0.88±0.02 |
| | | $R_P$ = 0.72±0.01 |
| | | Fractional TOC Recovery = 0.88±0.01 |
| | 1 | $Eu_{Ppt}$ = 0.13 |

(a) Individual aliquot data are presented in Table D.4 of Appendix D.

The membrane flux is plotted against $R_{PB}$ and $R_P$ in Figure 4.14 for each of the four E3-treated samples. The results suggest that membrane flux did not affect rejection of either Eu bound to E3 or E3 copolymer. Thus, the repeated use of a PM10 membrane with cleaning between filtrations did not appear to influence the results.

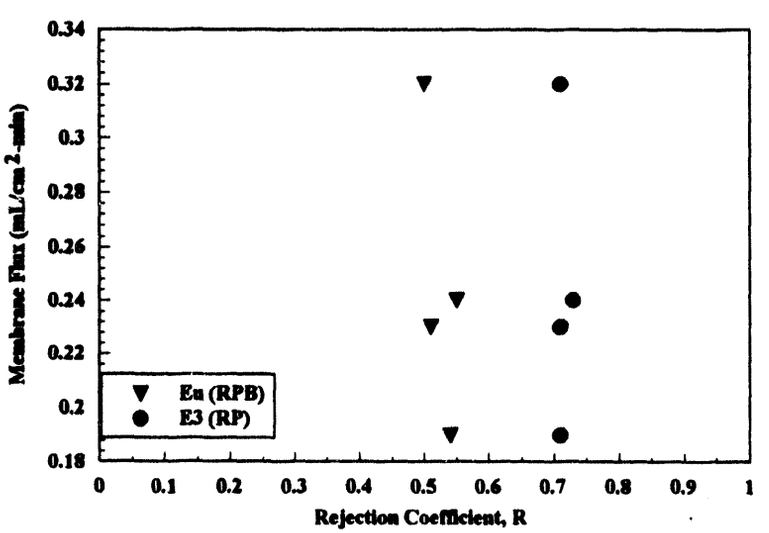



**Figure 4.14.** Effect of Membrane Flux on $R_{PB}$ and $R_P$ for the PM10 Membrane

### 4.4.3 Cleaning Protocol Effectiveness for and Rejection of Eu-Polymer Complexes and E3 Copolymer by the PM30 Membrane

The flux values measured for the PM30 membrane are tabulated in Table 4.5. The clean water flux for this new membrane (4.43 mL/cm$^2$-min for DDI-1) fell within the clean water flux range specified by Amicon (2.0 to 6.0 mL/cm$^2$-min). The flux recovery for this PM30 membrane, determined from the DDI-1 and DDI-7 flux values (4.43 mL/cm$^2$-min and 1.91 mL/cm$^2$-min, respectively) was 43%. The low recovery was attributed to the E3 aliquot filtrations (compare the flux values of the DDI aliquots filtered after each E3 aliquot to the flux value of DDI-1 in Table 4.5) and suggests that the membrane cleaning protocol was not completely removing polymer build-up on the membrane. The results are similar to those for the PM10 membrane (see Table 4.3).

**Table 4.5.** PM30 Flux Values

| Filtration Number | Aliquot | Flux (mL/cm$^2$-min) |
|---|---|---|
| 1 | DDI-1 | 4.43 |
| 2 | $Eu_I$ | 4.27 |
| 3 | DDI-2 | 4.12 |
| 4 | E3-1 | 0.56 |
| 5 | DDI-3 | 2.5 |
| 6 | E3-2 | 0.4 |
| 7 | DDI-4 | 2.49 |
| 8 | E3-3 | 0.36 |
| 9 | DDI-5 | 1.92 |
| 10 | E3-4 | 0.3 |
| 11 | DDI-6 | 1.89 |
| 12 | $Eu_P$ | 1.58 |
| 13 | DDI-7 | 1.91 |

The concentration of Eu and E3 (as measured by TOC) in DDI aliquots DDI-2 to DDI-7 (see Table D.5 of Appendix D) indicate that "carry over" was minimal. The pH remained nearly constant (pH 5±0.2) in the filtrate and retentate fractions, verifying that the modified cleaning protocol did not impact the

pH of the filtered aliquots. These results are similar to those for the PM10 membrane (see Table D.3 of Appendix D).

The E3 polymer treatment had about the same positive impact on Eu rejection by the PM30 membrane as it did for the PM10 membrane. The PM30 rejection results are presented in Table 4.6. Rejection of the Eu-polymer complexes removed 49% of the Eu from the E3-treated sample (mean $R_{PB}$ = 0.49). The average $R_{UF}$ (0.15) did not satisfy, but was close to, the $R_{UF}$ <0.01 criterion. High Eu and E3 recovery values were achieved, which suggests minimal membrane fouling by $Eu(OH)_3$. The mean Eu fractional recoveries were 0.92 and 0.84 for the control sample (without polymer) and the E3-treated sample aliquots, respectively, and the mean E3 fractional recovery was 0.87. The mean $R_P$ value for the PM30 membrane was 0.69 which, similar to the mean $R_P$ value for the PM10 membrane (0.72) [see Table 4.4], did not coincide with the membrane rejection efficiency ($R_P$ = 0.25) expected from the GPC results. Aggregation of the E3 copolymer from hydrogen bonding in the pH 5 test solutions is a possible explanation for the high membrane rejection efficiency.

**Table 4.6.** Eu and E3 Copolymer Rejection by PM30 Membrane

| Sample | Number of Replicates | Results (a) |
|---|---|---|
| Eu without polymer (Control) | 2 | $R_{UF}$ = 0.15±0.09 |
| | | Fractional Eu Recovery = 0.92±0.05 |
| | 1 | $Eu_{Ppt}$ = 0.04 |
| Eu with E3 polymer | 4 | $R_T$ = 0.65±0.03 |
| | | $R_{PB}$ = 0.49±0.03 |
| | | Fractional Eu Recovery = 0.84±0.02 |
| | | $R_P$ = 0.69±0.01 |
| | | Fractional TOC Recovery = 0.87±0.01 |
| | 1 | $Eu_{Ppt}$ = 0.13 |

(a) Individual aliquot data are presented in Table D.6 of Appendix D.

Figure 4.15 is a plot of membrane flux against $R_{PB}$ and $R_P$ and indicates that flux did not influence rejection of either Eu bound to E3 and E3 copolymer by the PM30 membrane. Similar to the PM10 membrane, repeated use of the PM30 membrane using the modified cleaning protocol did not appear to affect the results.

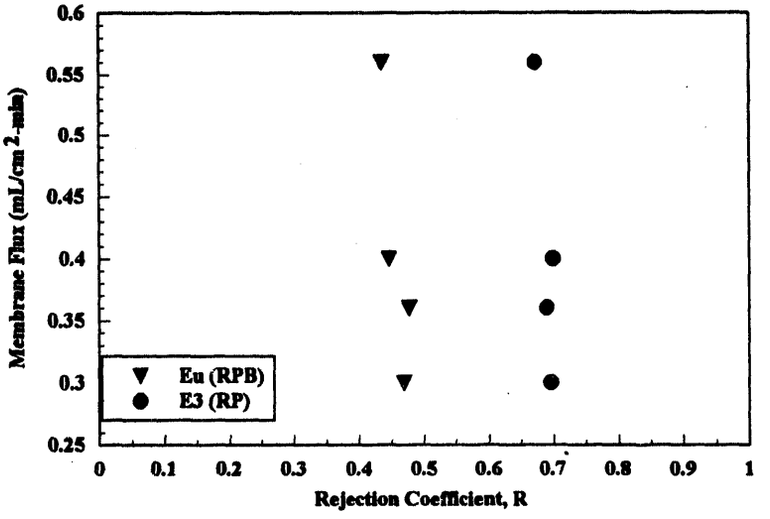



**Figure 4.15.** Effect of Membrane Flux on $R_{PB}$ and $R_P$ for the PM30 Membrane

The data presented for the PM10 and PM30 membranes show that reproducible results could be obtained with the modified membrane cleaning protocol and reuse of membrane coupons. More importantly, the rejection performance of both PM membranes was nearly the same. Poor flux recovery, however, remained a problem for both membranes. This problem is caused by fouling of the membrane by the E3 copolymer and the inability of the cleaning procedure to remove the E3 copolymer.

## 4.5 Final Membrane Cleaning Protocol

Further testing of Eu binding to E3 copolymer and rejection by the PM10 membrane was initiated based on the results of modified cleaning. The PM10 membrane was selected over the PM30 membrane to maximize the possibility of Eu-polymer rejection. Three tests were conducted with the E3 copolymer. Test

Number 1 consisted of Eu control (no polymer) followed by Eu with 3, 35, and 300 μg/mL of E3 copolymer. The same ultrafiltration pressure and aliquot filtration sequence to develop the first modified membrane cleaning protocol were used.

Table 4.7 contains the PM10 membrane flux values for Test 1. The three E3-treated samples are labeled with their corresponding copolymer concentration (i.e., E3-300 represents the sample treated with 300 μg/mL of E3). A comparison of flux values of the DDI aliquot filtered after the E3-300 aliquot (DDI-5) with the first DDI aliquot (DDI-1) shows that the clean water flux decreased by more than 70%. A build-up of E3 copolymer from all of the E3-treated sample aliquots is implicated.

**Table 4.7.** PM10 Membrane Flux for Test Number 1

| Filtration Number | Aliquot | Flux ($mL/cm^2$-min) |
|---|---|---|
| 1 | DDI-1 | 1.74 |
| 2 | $Eu_I$ | 1.33 |
| 3 | DDI-2 | 1.39 |
| 4 | E3-3 | 0.42 |
| 5 | DDI-3 | 1.24 |
| 6 | E3-35 | 0.27 |
| 7 | DDI-4 | 0.93 |
| 8 | E3-300 | 0.38 |
| 9 | DDI-5 | 0.49 |
| 10 | $Eu_F$ | 0.96 |
| 11 | DDI-6 | 1.03 |

The decline in flux over the filtration sequence shown in Table 4.7 raised a concern over whether Eu rejection (without polymer), $R_{UF}$, may also be affected by build-up of the polymer. If so, the contribution of Eu-polymer binding for rejection in each aliquot could not be determined. The initial and final rejection values of Eu without polymer ($R_{uf}$) were 0.12 (filtration number 2) and 0.31 (filtration number 10), respectively. These results show that polymer build-up on the membrane affected the rejection

of Eu and made it necessary to again revamp the cleaning protocol. A 0.1 N NaOH rinse was added to enhance polymer removal.

The steps listed below depict the final membrane cleaning protocol:

1. Filter a polymer-treated solution.
2. Triple-rinse stirred cell and coupon surface with DDI.
3. Add 5 mL of 0.1 N NaOH and stir for at least 20 min.
4. Triple-rinse stirred cell and coupon surface with DDI.
5. Add 5 mL of 0.5% $HNO_3$ and stir for at least 10 min.
6. Triple-rinse stirred cell and coupon surface with DDI.
7. Filter 10 mL of DDI at 55 psi.

It should be noted that after filtering the initial and final control aliquots (Eu without polymer), only the acid rinse was used because these control samples were not polymer-treated.

This refined cleaning protocol was used for the remainder of the experimental work. The success of this cleaning procedure is discussed in Sections 5.1 and 5.2. The results of the second and third tests using the E3 copolymer (Test 2 & 3) are presented in Section 5.2.

# 5.0 Polymer-Enhanced Rejection of Eu

A commercially available polymer (PAA) having a molecular weight of 60,000 was compared with a copolymer (E3) synthesized by PNL to determine if Eu binding improves rejection by the PM10 membrane. These two polymers were evaluated at pH 5 and an ultrafiltration pressure of 55 psi. Each polymer was tested using a single PM10 membrane coupon, with the membrane being cleaned using the protocol described in Section 4.5.

## 5.1 Commercial Polymer

Five PAA concentrations were tried (three in Test 1 and two in Test 2) using a single PM10 membrane coupon with cleaning between each PAA application. The success of the final cleaning protocol was determined by measuring the flux recovery in Test 1 and 2 after filtration of each PAA aliquot. The results are tabulated in Table 5.1. The flux recovery was 89% in Test 1 and 74% in Test 2 (compare flux values of DDI-6 and DDI-11 to DDI-1). Despite the large number of aliquots filtered (20 compared with 10 as recommended by Amicon), the flux recovery was greatly improved by using the 0.1 N NaOH rinse in the final cleaning protocol.

Table 5.2 contains the Eu and PAA rejection results. Test 1 showed that concentrations of 20, 60, and 100 μg/mL PAA achieved 100% rejection of Eu ($R_T = 1$). The average Eu rejection, $R_{UF}$, for the control aliquots (without polymer) was 0.14; therefore, the rejection attributed to the Eu binding to PAA, $R_{PB}$, was 0.86 for all three concentrations. Test 2 was conducted to determine the minimum PAA concentration at which $R_T = 1$. The $R_T$ values were lower at the lower PAA concentrations (5 and 10 μg/mL), and the corresponding $R_T$ values were 0.45 and 0.78, respectively. $R_{PB}$ was calculated by $R_T - R_{UF}$; thus, it was important to note that the average $R_{UF}$ increased somewhat from Test 1 to Test 2. The $R_{UF}$ is of some concern given that it exceeds the arbitrarily selected criterion of 0.10 in Test 2. However, the effect is relatively minor because $R_T$ is large. These results confirm that Eu rejection is dependent on

PAA concentration. The minimum PAA concentration at which Eu is 100% rejected is 20 μg/mL. The effect of PAA treatment on Eu rejection is shown in Figure 5.1.

**Table 5.1.** PM10 Membrane Flux Values for Test 1 and 2

| Test Number | Filtration Number | Aliquot (a) | Flux (mL/cm²-min) |
|---|---|---|---|
| 1 | 1 | DDI-1 | 1.44 |
| | 2 | $Eu_I$ | 1.49 |
| | 3 | DDI-2 | 1.46 |
| | 4 | PAA-20 | 1.39 |
| | 5 | DDI-3 | 1.46 |
| | 6 | PAA-60 | 0.82 |
| | 7 | DDI-4 | 1.44 |
| | 8 | PAA-100 | 0.75 |
| | 9 | DDI-5 | 1.37 |
| | 10 | $Eu_F$ | 1.21 |
| | 11 | DDI-6 | 1.28 |
| 2 | 12 | DDI-7 | 1.29 |
| | 13 | $Eu_I$ | 1.15 |
| | 14 | DDI-8 | 1.23 |
| | 15 | PAA-5 | 1.06 |
| | 16 | DDI-9 | 1.19 |
| | 17 | PAA-10 | 0.99 |
| | 18 | DDI-10 | 1.11 |
| | 19 | $Eu_F$ | 0.84 |
| | 20 | DDI-11 | 1.07 |

(a) The hyphenated PAA aliquot labels indicate the PAA concentration of the aliquot

The average fractional recovery of Eu was 0.94 and 0.86 for the control (without polymer) and PAA-treated aliquots, respectively. The average PAA fractional recovery (as measured by TOC) was 0.96. These recoveries suggest minimal membrane fouling by $Eu(OH)_3$ and effective membrane cleaning between filtrations. All of the PAA rejection ($R_P$) values were greater than or equal to 0.9 except for the lowest PAA concentration (5 μg/mL).

Eu solubility ($Eu_{Ppt}$ values) varied with PAA concentration in the PAA-treated samples. The $Eu_{Ppt}$ values were less than 0.10 for high concentrations of PAA (60 and 100 μg/mL) and greater than 0.10 for low concentrations of PAA (5, 10, and 20 μg/mL). The elevated $Eu_{Ppt}$ values for 5, 10, and 20 μg/mL PAA may have been caused by the retention of Eu-PAA precipitates on the 0.45-μm filter. However, if this were the case, elevated $Eu_{Ppt}$ values for 60- and 100-μg/mL PAA would have been expected. Filtering a second set of aliquots from the 5, 10, and 20 μg/mL PAA samples through 0.45-μm filters yielded the same $Eu_{Ppt}$ values. The low average $Eu_{Ppt}$ for the control aliquots (without polymer) of 0.08 confirms that little formation of $Eu(OH)_3$ occurred.

**Table 5.2.** Effect of PAA on Eu and PAA Rejection by PM10 Membrane

| Test No. | Control (10 μg/mL Eu w/o polymer) Aliquot | $R_{UF}$ | Eu REC | $Eu_{Ppt}$ | [PAA] (μg/mL) | $R_T$ | $R_{PB}$ | Eu REC | $Eu_{Ppt}$ | $R_P$ | TOC REC |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $Eu_I$ | 0.08 | 0.95 | 0.05 | 20 | 1 | 0.86 | 0.81 | 1 | 0.91 | 0.94 |
| | $Eu_F$ | 0.19 | 0.92 | 0.07 | 60 | 1 | 0.86 | 0.89 | 0.06 | 0.96 | 0.91 |
| | **Avg. $R_{UF}$:** | **0.14** | | | 100 | 1 | 0.86 | 0.81 | 0.05 | 0.97 | 0.96 |
| 2 | $Eu_I$ | 0.15 | 0.96 | 0.06 | 5 | 0.45 | 0.26 | 0.9 | 0.29 | 0.77 | 1.03 |
| | $Eu_F$ | 0.22 | 0.92 | 0.12 | 10 | 0.78 | 0.59 | 0.89 | 0.7 | 0.9 | 0.97 |
| | **Avg. $R_{UF}$:** | **0.19** | | | | | | | | | |
| | **Avg. REC & $Eu_{Ppt}$ for the 2 Tests** | | **0.94** | **0.08** | | | | **0.86** | **0.42** | | **0.96** |

The data for Eu and PAA rejection are plotted against PAA concentration in Figure 5.2. PAA rejection decreases slightly below 90% when the PAA concentration falls below 10 μg/mL ($R_P = 0.77$) and Eu rejection decreases when the PAA concentration falls below about 20 μg/mL.

The Eu rejection results can be explained by an Eu binding mechanism in a simple aqueous system at pH 5. The possible binding mechanisms are cation exchange and complexation. The potential for cation exchange of Eu is dependent on the concentration of available exchange sites exhibited by the PAA at pH 5. The exchange sites on PAA are ionized carboxyl groups ($RCO_2^-$). The equilibrium concentration of

$RCO_2^-$ (in meq of negative charge per liter) at pH 5 was calculated for each PAA concentration using the acidity constant of acrylic acid (pKa = 4.25). The ratio of meq $Eu^{3+}$ to meq $RCO_2^-$ was then calculated for each PAA concentration (each solution contained 10 μg/mL of $Eu^{3+}$ which is equivalent to 0.20 meq of positive charge per liter). A ratio greater than 1 would indicate a shortage of exchange sites, while a ratio less than 1 would indicate an overabundance of exchange sites.

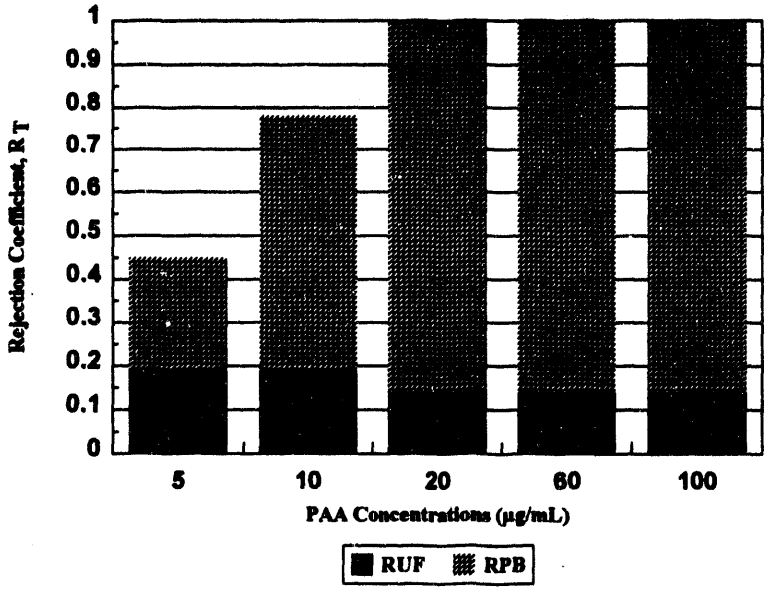



**Figure 5.1.** Effect of PAA Treatment on Eu Rejection

The Eu rejection data ($R_T$) presented in Figure 5.1 are plotted against the $Eu^{3+}$ to $RCO_2^-$ ratio in Figure 5.3 to examine the cation exchange binding mechanism . The results show that the highest Eu rejection occurred when the $Eu^{3+}$ to $RCO_2^-$ ratio was less than 1 (i.e., an overabundance of available cation exchange sites). At an $Eu^{3+}$ to $RCO_2^-$ ratio of about 0.8, Eu rejection began to decrease because of the lack of available cation exchange sites. This suggests that cation exchange is an important mechanism for rejection of Eu in this process.

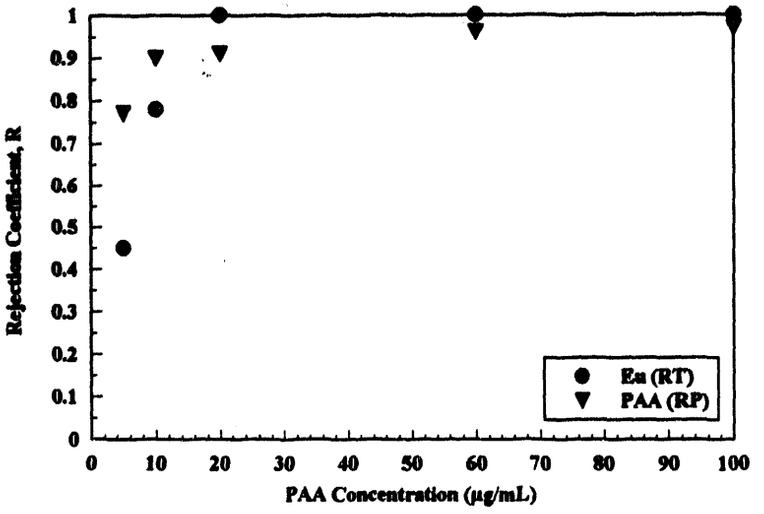



**Figure 5.2.** Eu and PAA Rejection by PM10 Membrane.

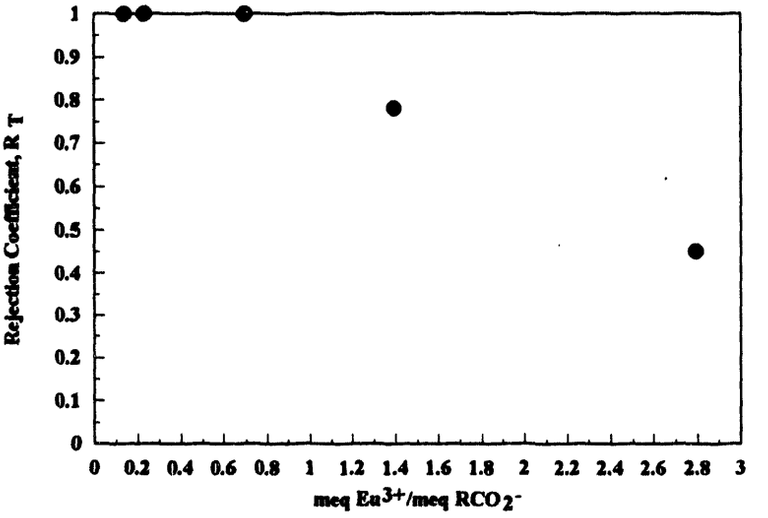



**Figure 5.3.** Effect of Available Cation Exchange Sites of PAA at pH 5 on Eu Rejection

## 5.2 PNL-Synthesized Copolymer

Eight concentrations of the E3 copolymer were tried using three test runs with two PM10 coupons. Test 1 evaluated E3 copolymer concentrations of 3, 35, and 300 µg/mL E3 concentrations. The flux values for the PM10 membrane used in Test 1 were listed earlier (See Table 4.7). As noted in the discussion of Table 4.7 (see Section 4.5), the poor flux recovery for this membrane coupon prompted the

addition of the 0.1 N NaOH rinse for the final membrane cleaning protocol. Thus, a new PM10 coupon was used for Test 2 and 3 with cleaning between each E3 application using the final membrane cleaning protocol. Test 2 investigated E3 concentrations of 20, 60, and 100 μg/mL, and concentrations of 5 and 10 μg/mL were evaluated in Test 3. The flux values for the PM10 membrane used in Tests 2 and 3 are presented in Table 5.3. The flux recovery was 99% in Test 2 and 90% in Test 3 (compare the flux values of DDI-6 and DDI-11 with DDI-1). Hence, the final membrane cleaning protocol helped remove polymer build-up and improved the membrane flux recovery.

**Table 5.3.** PM10 Membrane Flux Values for Test Number 2 and 3

| Test Number | Filtration Number | Aliquot (a) | Flux ($mL/cm^2$-min) |
|---|---|---|---|
| 2 | 1 | DDI-1 | 1.56 |
| | 2 | $Eu_I$ | 1.5 |
| | 3 | DDI-2 | 1.52 |
| | 4 | E3-20 | 0.54 |
| | 5 | DDI-3 | 1.19 |
| | 6 | E3-60 | 0.15 |
| | 7 | DDI-4 | 1.5 |
| | 8 | E3-100 | 0.36 |
| | 9 | DDI-5 | 1.56 |
| | 10 | $Eu_F$ | 1.41 |
| | 11 | DDI-6 | 1.55 |
| 3 | 12 | DDI-7 | 1.64 |
| | 13 | $Eu_I$ | 1.51 |
| | 14 | DDI-8 | 1.57 |
| | 15 | E3-5 | 0.45 |
| | 16 | DDI-9 | 1.41 |
| | 17 | E3-10 | 0.36 |
| | 18 | DDI-10 | 1.41 |
| | 19 | $Eu_F$ | 1.36 |
| | 20 | DDI-11 | 1.41 |

(a) The hyphenated E3 aliquot labels indicate the E3 concentration of the aliquot.

Table 5.4 contains the Eu and E3 rejection results. Test 1 showed that concentrations of 3, 35, and 300 μg/mL E3 achieved 17%, 85%, and 100% rejection of Eu ($R_T$). The excessively high Eu rejection ($R_{UF}$ = 0.31) for the final control aliquot ($Eu_F$) was not included in the mean $R_{uf}$ calculation because it occurred as a result of not using the final membrane cleaning protocol. Therefore, Eu rejection ($R_{UF}$ = 0.12) of the initial control aliquot ($Eu_I$) was used to determine the rejection attributed to Eu binding to E3, $R_{PB}$.

Additional E3 concentrations between 3 and 300 μg/mL were evaluated in Tests 2 and 3. Test 2 showed that E3 concentrations of 20, 60, and 100 μg/mL achieved 63%, 82%, and 100% rejection of Eu ($R_T$), respectively. The average $R_{UF}$ was 0.12. $R_T$ values of 0.23 and 0.35 (for 5 and 10-μg/mL E3, respectively) were obtained from Test 3, as well as an average $R_{UF}$ of 0.09. These tests confirm that Eu rejection is dependent on E3 concentration, and the minimum concentration at which Eu is 100% rejected ($R_T$ = 1) is 100 μg/mL. The effect of treatment using the E3 copolymer is shown in Figure 5.4.

The average fractional recovery of Eu was 0.92 and 0.86 for the control (without polymer) and PAA-treated aliquots, respectively. The average E3 fractional recovery (as measured by TOC) was 0.90. Similar to the PAA results, these good recoveries suggest minimal membrane fouling by $Eu(OH)_3$ and effective membrane cleaning between filtrations. The low average $Eu_{Ppt}$ values (0.06 and 0.11 for the control and E3-treated aliquots, respectively) verify that little formation of $Eu(OH)_3$ occurred. E3 copolymer rejection ($R_P$) was dependent on the E3 concentration, and the $R_P$ values ranged from 0.31 (for 3 μg/mL) and 0.76 (for 300 μg/mL).

**Table 5.4. Effect of E3 on Eu and E3 Rejection by PM10 Membrane**

| Test No. | Control (10 µg/mL Eu w/o polymer) Aliquot | $R_{UF}$ | Eu REC | $Eu_{Ppt}$ | [E3] (µg/mL) | $R_T$ | $R_{PB}$ | Eu REC | $Eu_{Ppt}$ | $R_P$ | TOC REC |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $Eu_f$ | 0.12 | 0.93 | 0.04 | 3 | 0.17 | 0.05 | 0.9 | 0.08 | 0.31 | 1.19 |
| | $Eu_p$ (a) | 0.31 | 0.83 | 0.04 | 35 | 0.85 | 0.73 | 0.85 | 0.08 | 0.69 | 0.9 |
| | **Avg. ($R_{UF}$):** | **0.12** | | | 300 | 1 | 0.88 | 0.83 | 0.04 | 0.76 | 0.85 |
| 2 | $Eu_f$ | 0.07 | 0.95 | 0.04 | 20 | 0.63 | 0.51 | 0.82 | 0.2 | 0.69 | 0.84 |
| | $Eu_p$ | 0.17 | 0.92 | 0.04 | 60 | 0.82 | 0.7 | 0.84 | 0.11 | 0.72 | 0.88 |
| | **Avg. ($R_{UF}$):** | **0.12** | | | 100 | 1 | 0.88 | 0.89 | 0.08 | 0.72 | 0.93 |
| 3 | $Eu_f$ | 0.11 | 0.96 | 0.06 | 5 | 0.23 | 0.14 | 0.9 | 0.12 | 0.52 | 0.84 |
| | $Eu_p$ | 0.08 | 0.92 | 0.12 | 10 | 0.35 | 0.26 | 0.87 | 0.16 | 0.65 | 0.78 |
| | **Avg. ($R_{UF}$):** | **0.09** | | | | | | | | | |
| | **Avg. REC & $Eu_{Ppt}$ for the 3 Tests:** | | **0.92** | **0.06** | | | | **0.86** | **0.11** | | **0.9** |

(a) This $R_{uf}$ value was not included in the average $R_{uf}$ calculation.

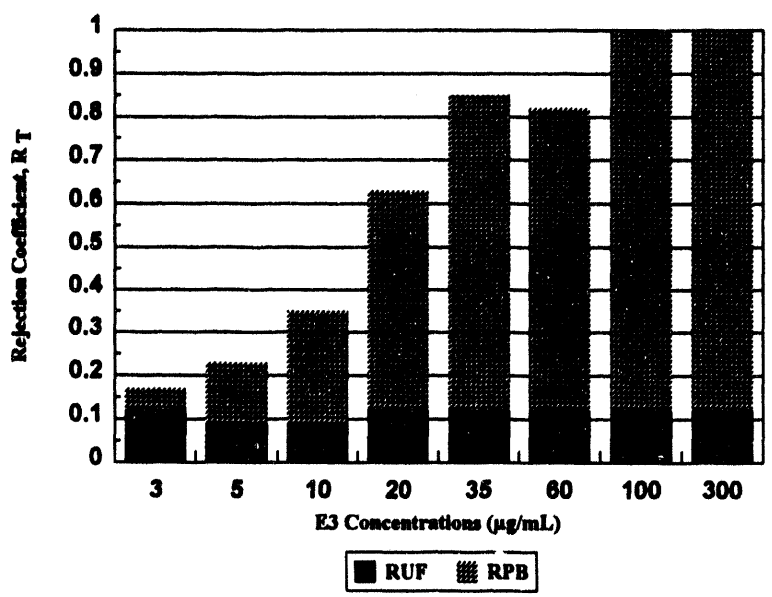



**Figure 5.4.** Effect of E3 Treatment on Eu Rejection

The data for Eu and E3 rejection are plotted against E3 concentration in Figure 5.5. E3 rejection decreased when the E3 concentration fell below about 60 μg/mL, and Eu rejection decreased when the E3 concentration fell below 100 μg/mL. The results presented in Figure 5.5 for the E3 copolymer are similar to those for PAA (see Figure 5.2). It may be concluded that Eu binding by the E3 copolymer accounts for very significant rejection. The cation exchange binding mechanism of the E3 copolymer was evaluated in the same way as for PAA. The ratio of meq Eu to meq $RCO_2^-$ was calculated for each E3 concentration. These calculations were based on the assumption that the average molecular formula for the E3 copolymer was (EO3Me acrylate)$_1$(AA)$_{2.21}$ and the molecular weight of the copolymer was 10,000. The equilibrium concentration of $RCO_2^-$ was calculated for each E3 concentration at pH 5 using pKa = 4.25 for acrylic acid.

The $R_T$ values plotted against the ratio values for each E3 concentration are shown in Figure 5.6. Eu rejection decreased as the amount of available cation exchange sites decreased. The highest $R_{PB}$ values occurred when the ratio values were less than 1. These results are very similar to Eu-PAA binding.

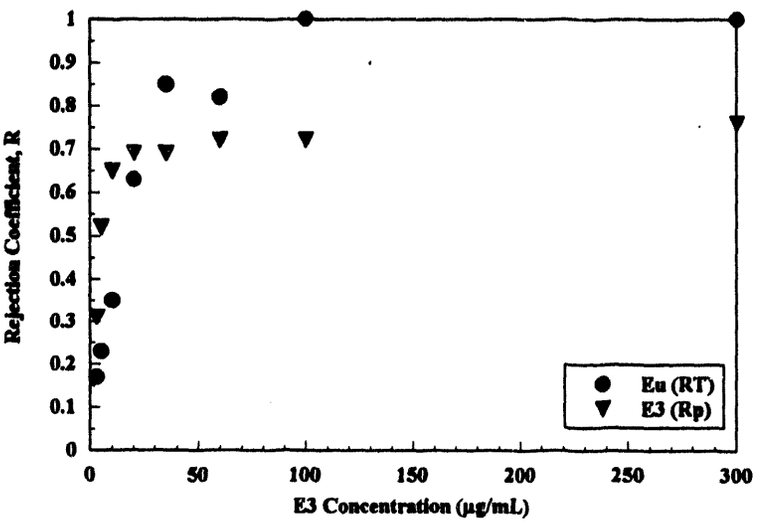



**Figure 5.5.** Eu and E3 Rejection by PM10 Membrane

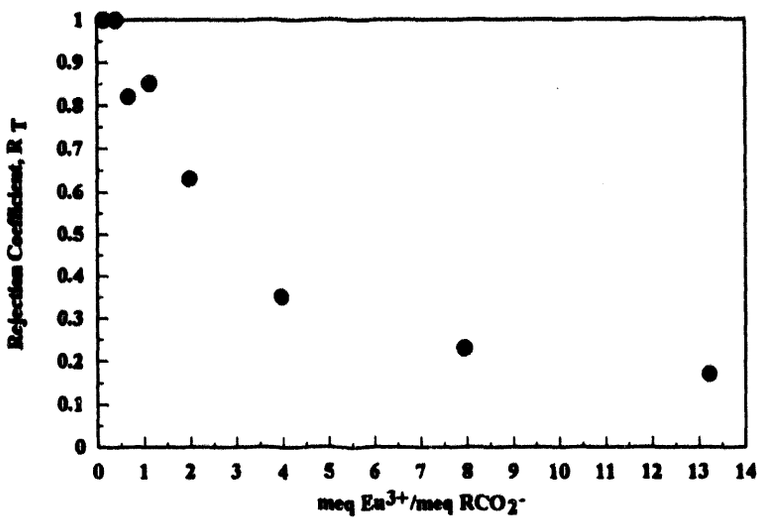



**Figure 5.6.** Effect of Available Cation Exchange Sites of E3 at pH 5 for Eu Rejection

The E3 copolymer rejection decreased for E3 concentrations below 20 μg/mL (see Figure 5.5). The lower $R_p$ value for 3 μg/mL E3 ($R_p$ = 0.31) is close to the expected membrane rejection efficiency for E3 ($R_p$ = 0.25) based on the GPC results (see Section 4.1.1). The increased rejection efficiency at higher E3 concentrations could be due to aggregation of E3 from hydrogen bonding.

## 5.3 Influence of Sodium on Eu Rejection

The influence of Na on membrane rejection of Eu-copolymer and Eu-PAA complexes was investigated to determine if the polymers exhibited a selective binding affinity for Eu. One test run was conducted with control (without polymer) and with PAA- and E3-treated samples using a single PM10 membrane coupon. The Na concentration in the bulk solution (1200 μg/mL Na) was 3 orders of magnitude greater than the Eu concentration (1200 vs. 10 μg/mL). Polymer concentrations (PAA = 20 and E3 = 100 μg/mL) were chosen based on the results of previous tests (Figures 5.1 and 5.4) such that 100% rejection of Eu could be obtained. These polymer concentrations were used in this test run to compare Eu rejection results with and without Na present. The rejection and recovery of Eu, polymer ,and Na was determined for the control (Eu and Na without polymer) and the E3- and PAA- treated samples.

The rejection and recovery results tabulated in Table 5.5 suggest that PAA and E3 have a selective binding affinity for Eu over Na. In the presence of Na, the rejection of Eu ($R_T$) remained at 100%, and the fraction of total rejection due to polymer binding ($R_{PB}$) was 0.89 for both of the polymer-treated samples. The results indicate that Na had no effect on Eu rejection because Eu rejection remained at 100% (for PAA = 20 and E3 = 100 μg/mL) with and without Na present. Thus, it can be concluded that Na did not bind to the PAA and E3 polymers. Lack of Na binding by these polymers is evident by comparing Na rejection with and without polymer treatment; the rejection of Na in the absence of polymer (mean Na $R_{UF}$ = 0.13) was somewhat greater than Na rejection in the presence of polymer (Na $R_T$ = 0.07 and 0.11 for PAA and E3, respectively). Good Eu, Na, and polymer recoveries were achieved for all three of the samples. The polymer rejection ($R_P$) was 90% and 71% for PAA and E3, respectively.

A low Na rejection is to be expected if the cation exchange mechanism is important for Eu rejection. The meq $Na^+$ to meq $RCO_2^-$ ratio was 184 for 20 μg/mL of PAA polymer and 105 for 100 μg/mL of E3 copolymer. Thus, at least 100 times more Na was present than cation exchange sites available for binding. Moreover, Eu is preferred over Na, as is evident from the 100% Eu rejection. Calculation of the meq $Eu^{3+}$ to meq $RCO_2^-$ ratio gave 0.7 for the PAA polymer and 0.4 for the E3 copolymer. Hence, there was an overabundance of cation exchange sites available with respect to Eu, which could explain selective separation of Eu by the cation exchange mechanism.

**Table 5.5.** Eu, Na, and Polymer Rejection by PM10 Membrane

| Sample | Number of Replicates | Results |
|---|---|---|
| Eu & Na without polymer (Control) | 2 | Eu $R_{UF}$ = 0.11±0.06<br>Fractional Eu Recovery = 0.94±0.03<br>Na $R_{UF}$ = 0.13±0.05<br>Fractional Na Recovery = 0.92±0.03 |
| Eu & Na with 20 µg/mL PAA | 1 | Eu $R_T$ = 1.00<br>Eu $R_{PB}$ = 0.89<br>Fractional Eu Recovery = 0.84<br>$R_P$ = 0.90<br>Fraction TOC Recovery = 1.01<br>Na $R_T$ = 0.07<br>Na $R_{PB}$ = 0.00<br>Fractional Na Recovery = 0.94 |
| Eu & Na with 100 µg/mL E3 | 1 | Eu $R_T$ = 1.00<br>Eu $R_{PB}$ = 0.89<br>Fractional Eu Recovery = 0.82<br>$R_P$ = 0.71<br>Fraction TOC Recovery = 0.87<br>Na $R_T$ = 0.11<br>Na $R_{PB}$ = 0.00<br>Fractional Na Recovery = 0.94 |

# 6.0 Conclusions and Recommendations

The research presented in this report suggests that Eu removal from aqueous solutions at pH 5 was possible using organic polymers in conjunction with ultrafiltration. Both the commercially available PAA with a molecular weight of 60,000 and PNL's synthesized E3 copolymer effectively enhanced the rejection of Eu by the Amicon PM10 membrane operated at 55 psi. The optimum polymer concentrations (i.e., for 100% removal of 10 μg/mL Eu) were 20 μg/mL of PAA and 100 μg/mL of E3. These optimal polymer concentrations indicated that the Eu to polymer concentration ratios were 1:2 and 1:10 for PAA and E3, respectively. In addition to enhancement of rejection, the polymers selectively bound Eu over Na; this is an indication that selective separation of Eu was possible.

The pH was important for both Eu solubility and binding of Eu with the polymers. The acceptable pH range for effective polymer-enhanced Eu rejection was between 4.25 and 6. At pH greater than 6, Eu precipitated as $Eu(OH)_3$. Eu binding to polymers may be explained by either complexation or cation exchange. Cation exchange binding of Eu was important and maximum Eu rejection occurred when an overabundance of cation exchange sites were present. The ratio of meq $Eu^{3+}$ to meq $RCO_2^-$ was 1:1.43 and 1:2.5 for 20 μg/mL PAA and 100 μg/mL E3, respectively.

Ultrafiltration, without polymer treatment, was effective for rejecting Eu from the bulk solution at pH 5 using the YM1 and YM10 Amicon membranes (close to 100% Eu rejection was achieved). Membrane rejection of Eu not bound to polymer (i.e., without polymer treatment) was found to be dependent on pH (i.e., rejection decreased with decreasing pH) and membrane cleaning protocol. Once an effective cleaning protocol was established, the Eu rejection was reduced to less than 20% for the PM10 and PM30 membranes. An effective cleaning protocol was important for reusing the PM10 and PM30 membranes. Consistent Eu and polymer rejection was achieved only when an effective cleaning protocol was used between sample filtrations.

The narrow pH required for the process evaluated here limits its application for Hanford tank waste. A pH adjustment of the alkaline tank waste (pH >13) would be required. Further evaluation of its applicability is warranted, however, because this process does not generate solids (e.g., hydroxide precipitates) and has the potential for selectively separating high-energy $^{241}Am$ from the bulk of the tank waste. Effective separation would result in a concentrated fraction of high-level waste, thus, reducing the volume of high-level waste requiring vitrification, a very expensive, energy-intensive process. Because of the potential cost savings associated with this process, the use of binding agents and membranes effective under conditions similar to the tank waste (e.g., very alkaline and high ionic strength) should continue to be investigated.

The cost associated with handling and disposal of metal-bearing wastes have driven industry to consider alternative treatment methods to minimize waste generation. This process has many potential waste minimization applications for industrial process streams containing regulated metals because it does not generate a solids stream (preventing solids handling and disposal requirements) and concentrates target species (e.g., regulated toxic metals), thus minimizing the volume of waste streams requiring treatment, storage, and disposal. Therefore, use of the polymers evaluated in this study and other high molecular weight materials as binding agents for regulated toxic metals (e.g., Hg, Ni, Cd, Cr, Pb, and Cu) should also be further investigated.

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# 8.0 Appendices

## Appendix A. Derivation of Equations to Calculate Average Membrane Rejection Coefficient

The following discussion presents a detailed derivation of membrane rejection Eqs. (2) and (3) given in Section 3.4.2. Eq. (2) was derived from the following rejection coefficient (R) equation:

$$R = 1 - \frac{C_P}{C_B} \qquad (A1)$$

The flow across the membrane coupon is

$$\frac{dV}{dt} = -Q \qquad (A2)$$

and the mass balance around the membrane is

$$\frac{d\left(V \bullet C_B\right)}{dt} = -QC_P = -Q(1 - R)C_B \qquad (A3)$$

Using the chain rule and separating variables simplifies equation (A3) to

$$\frac{d\left(V \bullet C_B\right)}{dt} = -R\frac{dV}{V} \qquad (A4)$$

Integrating Eq. (A4) yields the following average rejection coefficient equation for describing membrane rejection in batch mode (i.e., Eq. 2 in Section 3.4.2):

$$\overline{R} = \frac{Ln\left(\frac{C_r}{C_i}\right)}{Ln\left(\frac{V_i}{V_r}\right)} \qquad (A5)$$

The integration intervals are as follows:

at $t = 0$; $C_B = C_i$ and $V = V_i$

at $t = t_f$(total filtration duration); $C_B = C_r$ and $V = V_r$.

To calculate $\overline{R}$ using the filtrate concentration, $C_f$, Eq. (A5) is modified assuming that $V_f = V_i - V_r$ and the solute mass balance is $V_iC_i = V_fC_f + V_rC_r$. The resulting equation is (i.e., Eq. 3 of Section 3.4.2):

$$\bar{R} = \frac{Ln\left[\frac{V_i}{V_r} - \frac{C_f}{C_i}\left(\frac{V_i}{V_r} - 1\right)\right]}{Ln\left(\frac{V_i}{V_r}\right)} \qquad \text{(A6)}$$

# Appendix B. GPC Analysis of E3 Copolymer

**Table B.1.** E3 Copolymer Chromatogram Peak Report

| Peak Number | Retention Time (min) | Peak Area | % of Total Peak Area |
|---|---|---|---|
| 1 | 26.6 | 1,833,041 | 0.25 |
| 2 | 35.7 | 2,569,620 | 0.35 |
| 3 | 38.1 | 1,511,093 | 0.21 |
| 4 | 48.6 | 1,417,842 | 0.19 |
| | **Total Area:** | 7,331,596 | |

## Appendix C. Rejection of Eu by YM Series Membranes

**Table C.1.** Effect of Pressure on Rejection of Commercial Polymers by YM1 Membranes

| Polymer | Pressure (psi) | $R_p$ |
|---|---|---|
| PAA | 10 | 0.61 |
| | 20 | 0.63 |
| | **30** | **0.64** |
| | 40 | 0.73 |
| | 50 | 0.64 |
| | 60 | 0.72 |
| PEG | 10 | 0.93 |
| | 20 | 0.65 |
| | **30** | **0.81** |
| | 40 | 0.5 |
| | 50 | 0.43 |
| | 60 | 0.67 |
| PEG/PAA | 10 | 0.81 |
| | 20 | 0.83 |
| | **30** | **0.83** |
| | 40 | 0.77 |
| | 50 | 0.81 |
| | 60 | 0.87 |

**Table C.2.** Eu Solubility and Eu and Polymer Rejection by YM1 Membranes at pH 2 with 100-μg/mL Polymer Concentrations

| Polymer Treatment | $Eu_{Ppt}$ | $R_{PB}$ | Eu REC | $R_P$ | TOC REC |
|---|---|---|---|---|---|
| PEG | 0.02 | 0.24 | 0.96 | 0.77 | 0.99 |
| PAA | 0.04 | 0.06 | 0.96 | 0.63 | 0.94 |
| PEG/PAA | 0.03 | 0.07 | 0.96 | 0.71 | 0.99 |
| E3 | 0.03 | 0.03 | 0.96 | 0.59 | 1.02 |

**Table C.3.** Eu Solubility and Eu and Polymer Rejection by YM1 Membranes at pH 2 with 1000-μg/mL Polymer Concentrations

| Polymer Treatment | $Eu_{Ppt}$ | $R_{PB}$ | Eu REC | $R_P$ | TOC REC |
|---|---|---|---|---|---|
| PEG | 0.02 | 0 | 0.96 | 0.89 | 0.96 |
| PAA | 0.02 | 0.08 | 0.95 | 0.71 | 0.97 |
| PEG/PAA | 0.01 | 0.06 | 0.95 | 0.84 | 0.96 |
| E3 | 0.03 | 0.02 | 0.95 | 0.7 | 0.91 |

**Table C.4. Effect of pH on $R_{UF}$ and REC for YM3, YM10, YM30, and YM100 Membranes**

| Membrane | pH | $R_{UF}$ | Eu REC |
|---|---|---|---|
| YM3 | 10 | 1 | 0.79 |
| | 8 | 1 | 0.62 |
| | 6 | 1 | 0.21 |
| | 4 | 1 | 0.54 |
| | 3 | 0.14 | 0.99 |
| | 2 | -0.56 | 1.18 |
| YM10 | 10 | 1 | 0.66 |
| | 8 | 1 | 0.62 |
| | 6 | 1 | 0.67 |
| | 4 | 0.85 | 0.73 |
| | 3 | -0.71 | 1.11 |
| | 2 | -0.1 | 1.03 |
| YM30 | 10 | 1 | 0.73 |
| | 8 | 1 | 0.61 |
| | 6 | 1 | 0.76 |
| | 4 | 1 | 0.81 |
| | 3 | -0.17 | 1.06 |
| | 2 | -0.12 | 1.01 |
| YM100 | 10 | 1 | 0.8 |
| | 8 | 1 | 0.74 |
| | 6 | 1 | 0.61 |
| | 4 | 0.62 | 0.67 |
| | 3 | -1.07 | 1.45 |
| | 2 | -0.15 | 1.02 |

## Appendix D. Rejection of Europium by PM Series Membranes

**Table D.1.** Effect of pH on Eu Rejection and Recovery for PM10 and PM30 Membranes

| Membrane | pH | $R_{UF}$ | Eu REC |
|---|---|---|---|
| PM10 | 10 | 1 | 0.9 |
| | 8 | 0.92 | 0.76 |
| | 6 | 0.05 | 0.94 |
| | 4 | 0.17 | 0.94 |
| | 2 | 0..13 | 0.96 |
| PM30 | 10 | 1 | 0.85 |
| | 8 | 0.96 | 0.87 |
| | 6 | 0.11 | 0.92 |
| | 4 | 0.09 | 0.86 |
| | 2 | 0.3 | 0.96 |

**Table D.2.** Test 1 and Test 2 Results of pH Effect on $R_{UF}$ and REC for PM10 and PM30 Membranes

| Membrane | Test No. | pH | $R_{UF}$ | Eu REC |
|---|---|---|---|---|
| PM10 | 1 | 4 | 0.1 | 0.9 |
| | | 5 | 0.05 | 0.94 |
| | | 6 | 0.15 | 0.96 |
| | 2 | 4 | 0.62 | 0.9 |
| | | 5 | -0.07 | 0.94 |
| | | 6 | 0.06 | 0.96 |
| PM30 | 1 | 4 | 0.17 | 0.91 |
| | | 5 | 0.11 | 0.93 |
| | | 6 | 0.09 | 0.88 |
| | 2 | 4 | 0.06 | 0.95 |
| | | 5 | 0.01 | 0.96 |
| | | 6 | 0.05 | 0.94 |

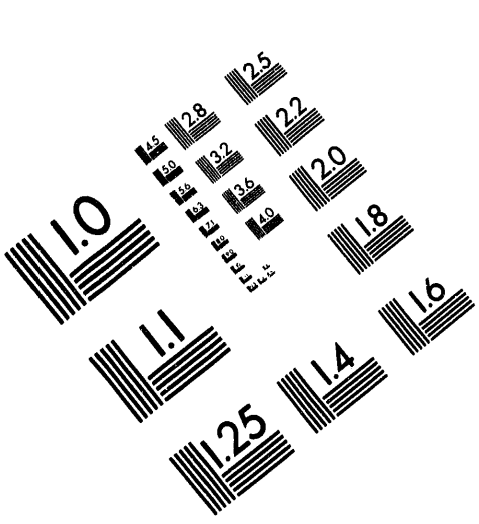
**Table D.3.** Europium and TOC Concentrations in DDI Aliquots for the PM10 Membrane

| DDI Aliquot | [Eu] (μg/mL) | [TOC] (μg/mL) |
|---|---|---|
| DDI-2 | 0.19 | 1.88 |
| DDI-3 | 0.16 | 3.06 |
| DDI-4 | ND | 1.92 |
| DDI-5 | 0.25 | 2.26 |
| DDI-6 | ND | 1.78 |
| DDI-7 | 0.51 | 1.63 |

ND: not detectable

**Table D.4.** Europium and E3 Rejection with 35-μg/mL E3 and PM10 Membrane

| Control (Eu w/o polymer Aliquot | $R_{UF}$ | Eu REC | E3 Aliquot | $R_T$ | $R_{Eu}$ | Eu REC | $R_P$ | TOC REC |
|---|---|---|---|---|---|---|---|---|
| $Eu_I$ | 0.05 | 0.97 | 1st | 0.59 | 0.5 | 0.91 | 0.71 | 0.89 |
| $Eu_F$ | 0.12 | 0.92 | 2nd | 0.6 | 0.51 | 0.9 | 0.71 | 0.87 |
| **Average:** | **0.09** | **0.94** | 3rd | 0.63 | 0.55 | 0.87 | 0.73 | 0.87 |
| **Std Deviation** | **0.05** | **0.03** | 4th | 0.62 | 0.54 | 0.86 | 0.71 | 0.88 |
| | | | **Average:** | **0.61** | **0.53** | **0.88** | **0.72** | **0.88** |
| | | | **Std Deviation** | **0.02** | **0.02** | **0.02** | **0.01** | **0.01** |



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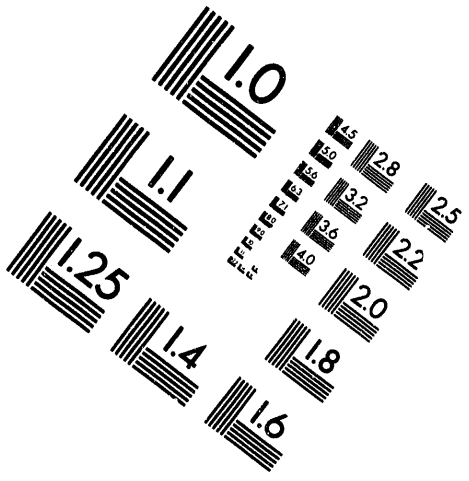


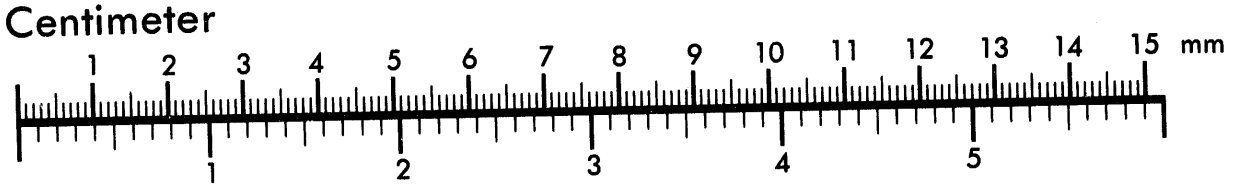


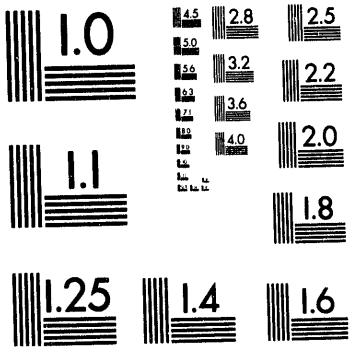


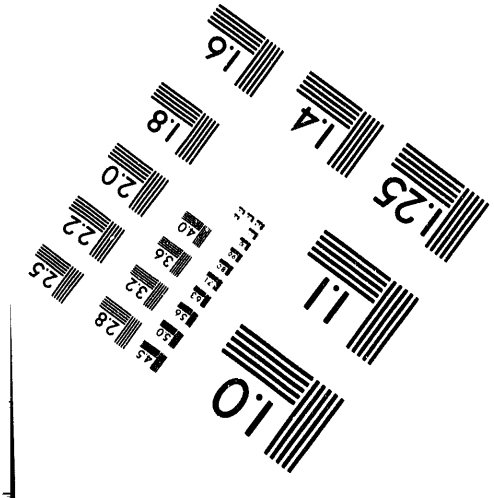


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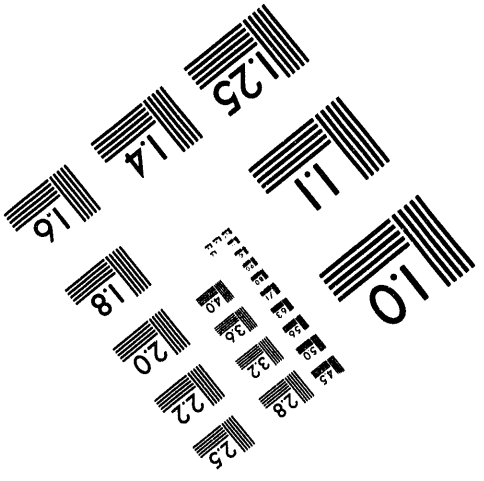

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**Table D.5.** Europium and TOC Concentrations in DDI Aliquots for the PM30 Membrane

| DDI Aliquot | [Eu] (µg/mL) | [TOC] (µg/mL) |
|---|---|---|
| DDI-2 | 0.19 | 1.68 |
| DDI-3 | 0.16 | 2.1 |
| DDI-4 | ND | 2.05 |
| DDI-5 | 0.42 | 1.96 |
| DDI-6 | ND | 1.51 |
| DDI-7 | 0.48 | 1.19 |

ND: not detectable

**Table D.6.** Europium and E3 Rejection with 35-µg/mL E3 and PM30 Membrane

| Control (Eu w/o polymer) | $R_{UF}$ | Eu | E3 | $R_T$ | $R_{Eu}$ | Eu | $R_P$ | TOC |
|---|---|---|---|---|---|---|---|---|
| Aliquot | | REC | Aliquot | | | REC | | REC |
| $Eu_I$ | 0.05 | 0.97 | 1st | 0.59 | 0.5 | 0.91 | 0.71 | 0.89 |
| $Eu_F$ | 0.12 | 0.92 | 2nd | 0.6 | 0.51 | 0.9 | 0.71 | 0.87 |
| **Average:** | **0.09** | **0.94** | 3rd | 0.63 | 0.55 | 0.87 | 0.73 | 0.87 |
| **Std Deviation** | **0.05** | **0.03** | 4th | 0.62 | 0.54 | 0.86 | 0.71 | 0.88 |
| | | | **Average:** | **0.61** | **0.53** | **0.88** | **0.72** | **0.88** |
| | | | **Std Deviation** | **0.02** | **0.02** | **0.02** | **0.01** | **0.01** |

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