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UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

**TECHNICAL AND ECONOMIC FEASIBILITY STUDY OF
POLYELECTROLYTE-ENHANCED ULTRAFILTRATION (PEUF)
FOR THE REMOVAL OF MULTIVALENT IONS FROM WATER**

A Dissertation

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

Doctor of Philosophy

By

AHMADALI TABATABAI

Norman, OK

1998

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**TECHNICAL AND ECONOMIC FEASIBILITY STUDY OF
POLYELECTROLYTE-ENHANCED ULTRAFILTRATION (PEUF)
FOR THE REMOVAL OF MULTIVALENT IONS FROM WATER**

**A Dissertation APPROVED FOR THE
SCHOOL OF CHEMICAL ENGINEERING
AND MATERIALS SCIENCE**

John Scamhorn
Robert Shabany
Jim Harwell
Lance Lobban
Sheila D. Plimpton

To my parents

Thanks for all that you have done

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ABSTRACT

This investigation has demonstrated the effectiveness of polyelectrolyte-enhanced ultrafiltration (PEUF) as a viable technique for water softening. It is shown that PEUF is effective in the rejection of up to 99.7% of hardness ions (calcium and magnesium) from aqueous streams. It is further shown that in the presence of low concentrations of added salt, the rejection is still quite high. The effect of temperature is negligible on rejection of multivalent ions. However, an increase in temperature increases flux of solution across the ultrafiltration membrane.

The results of this work were modeled using an ion-binding model based on a two-phase approximation theory to predict rejection of the hardness ions. The model is highly accurate in prediction of rejections at low concentrations of added salt. However, at higher salt concentrations the model deviates from experimental results.

Recovery of the polyelectrolyte was also investigated to determine the effectiveness of colloid recovery as well as optimize the PEUF process to minimize its cost in a commercial process. Of the recovery processes considered, three provided the greatest promise. These included 1. addition of sodium carbonate to precipitate the bound multivalent ions, 2. addition of sodium chloride to replace the bound multivalent ions with sodium ions, and 3. addition of hydrochloric acid to replace the bound multivalent ions with hydrogen ions. The optimum recovery occurred when the least amount of an additive (sodium carbonate, sodium chloride, or hydrochloric acid) was used and the highest multivalent ion rejection was obtained using the regenerated polyelectrolyte.

It was also observed that maximum rejection of multivalent ions using regenerated polyelectrolyte was always less than maximum rejection using fresh polyelectrolyte.

The results of multivalent ion rejection were used in conjunction with the polyelectrolyte recovery results to develop a model to determine optimum parameters to minimize the cost of PEUF. The experimental ultrafiltration results were scaled up for large scale applications. The PEUF process as a water softening technique was compared with two conventionally used water softening processes, lime softening and ion exchange. The PEUF process was analyzed using the three polyelectrolyte recovery methods mentioned above. A cradle to grave scenario was developed to account for all costs associated with water softening.

The economic analysis results showed that as the flowrate increased, so did the cost of the PEUF process. Furthermore, an optimum percent of the feed recovered results in a minimum cost for the PEUF process. At low recovery of the feed stream, the PEUF cost is too high due to the small amount of product. At higher recovery of the feed stream, the retentate stream becomes too concentrated leading to increased concentration polarization and therefore a higher cost of operation for the PEUF process.

When compared with lime softening and ion exchange, the PEUF process is shown to be effective for specific situations. For example, the PEUF process is nearly competitive with

lime softening at low flow rates. In comparison with ion exchange for the removal of only multivalent ions, the PEUF process is not nearly as economically feasible. However, when the comparison is for a feed stream containing both multivalent ions as well as bacteria and viruses, PEUF becomes more competitive with ion exchange.

The results of this study provide a basis for determining commercialization potential of the PEUF process for water treatment. Additionally, these results clarify areas where further research and development might improve the PEUF process. While this process is not economically attractive, at least for the water softening process considered, the PEUF process can have potential in specific areas. Its applicability might be well enhanced as alternative ultrafiltration membranes and polyelectrolytes are developed.

**TECHNICAL AND ECONOMIC FEASIBILITY STUDY OF
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Chapter 1: INTRODUCTION

With the advent of the industrial revolution, there has been an ever increasing introduction of pollutants into the environment. In many instances, the effects of the pollution have not been immediately obvious. In the meanwhile, scientists have obtained greater knowledge about the consequences of the pollutants in the environment. With this greater knowledge, the public has taken a more decisive role in the industrial age as it has demanded creation of the Environmental Protection Agency (EPA) or similar agencies around the globe. In the process, the public has been able to some extent control disposal and treatment of waste into the environment. As a result of the society's demands, the EPA has set at times strict standards for many facets of the industry forcing the industries to comply.

To comply with the new standards, the industries have had to redesign many of their processes. In some situations, new processes had to be developed to clean up areas already contaminated. It was also determined that some of the pollutants were of economic value and their recovery could lead to potential savings. An example is the recovery of certain heavy metals from mining operations. The new demand by the

government and industry created an arena for a large number of novel processes. Given the exorbitant costs of waste removal and remediation projects, there was (and still is) a tremendous incentive to develop processes which would reduce the treatment costs. Environmental remediation costs have generally been a major part of the capital and operating costs for many plants. As a result, both the government and the industry established funds to devise and implement waste treatment processes.

Some of the funding provided for research of new techniques of waste treatment. Any new technique that could reduce waste at a low cost would have great importance both environmentally and economically. These included methods for the removal of various forms of pollutants from air, water, and soil. The pollutants to be removed included organic, ionic or a combination of both. The methods have included extraction, oxidation, precipitation, electromagnetic fields, incineration, biodegradation, and filtration, to name a few.

One novel process that was introduced some ten years ago by investigators in our labs is one form of colloid-enhanced ultrafiltration (CEUF) (1-17), specifically polyelectrolyte-enhanced ultrafiltration (PEUF). In this process, shown in Figure 1, an anionic polyelectrolyte is added to an aqueous stream containing contaminants, specifically positively charged metal ions. The multivalent ions bind to the negatively charged polyelectrolyte. The stream is then allowed to flow across an ultrafiltration membrane. Since the pore size of the membrane is much smaller than the polyelectrolyte chain, the

polyelectrolyte as well as the multivalent ions bound to it are retained by the membrane. Therefore, this process produces two streams, the retentate containing almost all of the polyelectrolyte and the multivalent ions and the permeate being a relatively pure stream of water. One of the major advantages of this process is that the retentate volume is much smaller than the permeate. Disposal and/or treatment of a smaller volume of the retentate is far easier to handle and economically more appealing.

The effectiveness of the CEUF method has been shown for a number of contaminants, both organic and ionic. In fact, it has been shown that CEUF is effective in rejecting in excess of 99% of the contaminant. However, to establish the CEUF process as viable, it must also prove to be economically feasible. To achieve this goal, a complete analysis of the CEUF process for specific situations must be performed. The complete analysis of the CEUF process must take regeneration and recycling of the colloid into account in order to minimize operating costs. This is particularly important in CEUF since the colloid is generally expensive. Therefore to fully explore the viability of the CEUF process, its use for a specific application had to be investigated. The study would determine technical and economic feasibility of the CEUF process and make comparisons with other conventional methods of treatment for a similar process. The results of this work would also allow clarification of bottlenecks that need to be addressed in the future in order to make the process more feasible. Therefore, it was proposed that the CEUF process would be used as a water softening method to remove water hardness (dissolved calcium and magnesium salts) from water.

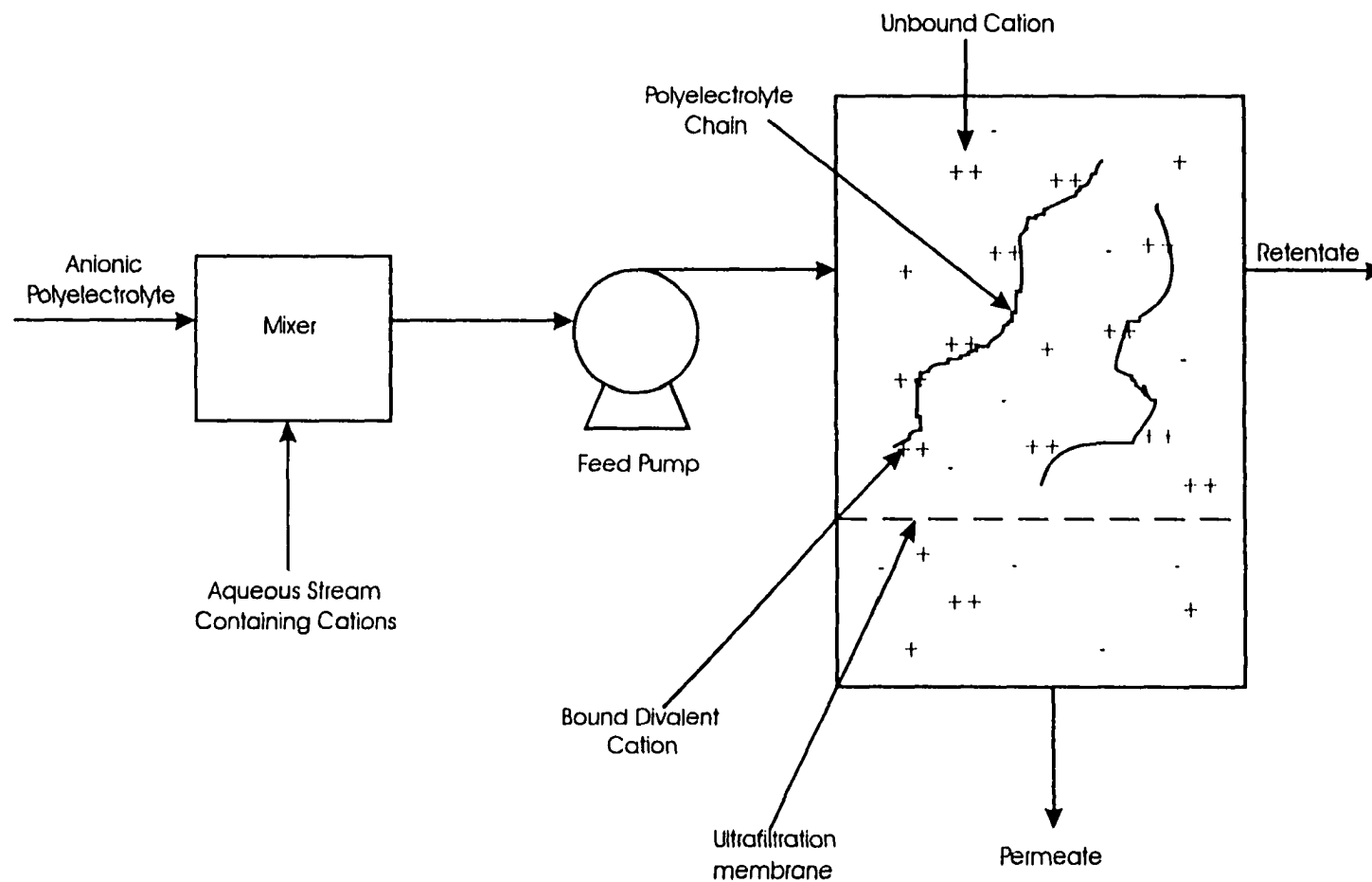


Figure 1: Schematic of polyelectrolyte-enhanced ultrafiltration for the removal of multivalent metal ions.

It is important to note that before the environmental pollution prevention laws were set into motion, there was a great reluctance by the industry, understandably due to higher costs, to accept the new standards. However, in the process of developing efficient pollution prevention methods, the industry has come to recognize its own inefficiencies and therefore has corrected them. In some cases this has led to greater profits for the industry. The environmental movement has also led to development of engineers who are generally more conscious of the environment.

This work sets to establish the following three areas of research: 1. technical feasibility of CEUF, 2. colloid recovery as applied to CEUF, and 3. economic feasibility of CEUF. This is a unique study in the fact that all three of these elements are addressed in conjunction with one another to optimize the process and show the effectiveness of the CEUF process. Chapter 2 presents a brief background of the ultrafiltration process as applied to the CEUF process. The experimental methods utilized in this work are presented in Chapter 3. The technical feasibility of CEUF process as a method of water softening is presented in chapter 4. Chapter 5 explores methods for recovery of the colloids used in this work. Based on the results from chapters 4 and 5, a model for economic analysis is developed to determine economic feasibility of the CEUF process as shown in chapter 6. Chapter 7 presents conclusions and recommendations based on the findings of this investigation.

It should also be noted that this work does not address toxicological effects of the colloid as used in this process.

Chapter 2: BACKGROUND

2.1 Introduction

One of the major areas of pollution prevention is that of water treatment. Since water is such a basic necessity to living beings and since water has played such a decisive factor in the development of human civilization, it is imperative that it is used and maintained properly. This reality becomes more profound in view of the ever-growing population and demands of the population for various uses of water. Therefore with the industrial transformation of the society, the uses of larger quantities of cleaner water have become extremely important. Water is used in processes where it is grossly contaminated. At the same time, ultrapure water is needed for consumption as well as for the development of new technologies and applications. Therefore in an effort to utilize water more effectively, a number of water treatment methods for the removal of various forms of contaminants have been studied. This has included removal of dissolved minerals and salts, organics, and biological elements such as bacteria from water.

However, in view of the growing need for fast and cheap treatment of large quantities of water to remove multiple forms of contaminants and to obtain ultrapure water, new processes continue to be developed. One group of proposed processes is colloid-enhanced ultrafiltration (CEUF) for the removal of both multivalent ions and dissolved organics.

2.2 Colloid-Enhanced Ultrafiltration.

The CEUF processes (1-17) are a class of separation techniques in which a colloid (e.g., polyelectrolyte or micelle-forming surfactant) is added to water containing organic or metal species. The ultrafiltration of bound metal with soluble polyelectrolytes has been studied at least since 1968 (18). Since then many studies have been performed to investigate the ultrafiltration of soluble polyelectrolyte/bound metal ions for various applications (9, 12, 14, 16-17, 19-23). The use of surfactant-enhanced ultrafiltration was first introduced in 1979 (24) for the removal of phenol from water. Depending on the type of surfactant used, phenol rejections of 26% to 99.5% of phenol were obtained. In early 1980's, an initiative was made by investigators in our laboratories to systematically study the use of micellar-enhanced ultrafiltration (MEUF) for the removal of dissolved organics and multivalent ions. This work would determine effects of various parameters on the feasibility of the MEUF process and determine optimum conditions for operation of MEUF. The conditions included surfactant type, concentration, contaminant type, ratio of surfactant to contaminant, molecular weight cutoff of ultrafiltration membrane, pressure, temperature, stirring rate (as in the case of batch stirred cell) as well as a comparison between batch versus continuous operation. Later, this work was extended to investigate the use of polyelectrolytes as colloids for the CEUF process. It was generally found that rejections of up to 99.9% were possible depending on circumstances and contaminants used. A mixture of surfactant and polyelectrolyte was also used as the colloid for the CEUF process (16).

In the CEUF processes, dissolved organics or multivalent ionic species bind onto or solubilize into the colloid due mainly to electrostatic attraction and/or hydrophobic bonding. The colloidal solution containing the solubilized organic and/or bound multivalent metal ion is filtered under pressure through an ultrafiltration membrane with pore sizes smaller than the size of the colloid. The colloid and the bound organic/metal ion species are retained by the membrane resulting in a purified water stream referred to as the permeate and a concentrated stream containing almost all of the colloid and the organic/metal ion species, the retentate. Figure 2 shows a schematic of the CEUF process where a mixture of surfactant and polyelectrolyte is used as the colloid.

2.2.1 Rejection of contaminant. Effectiveness of the CEUF process is measured in terms of rejection of the contaminant, that is the ratio of the amount of the contaminant passing through the membrane to that retained by the retentate. The retentate-based rejection, R_i , of a given species in a solution is defined as:

$$R_i(\%) = (1 - \frac{[per]_i}{[ret_{bulk}]_i}) \times 100 \quad (2-1)$$

where $[per]_i$ and $[ret_{bulk}]_i$ are the concentration of species i in the permeate and retentate streams, respectively. As will be discussed later, an extremely low concentration of colloid inevitably passes through the membrane into the permeate.

2.2.2 Choice of colloid. The colloid can be either a surfactant, a polyelectrolyte, or a mixture of both. The process containing surfactant as the colloid is referred to as

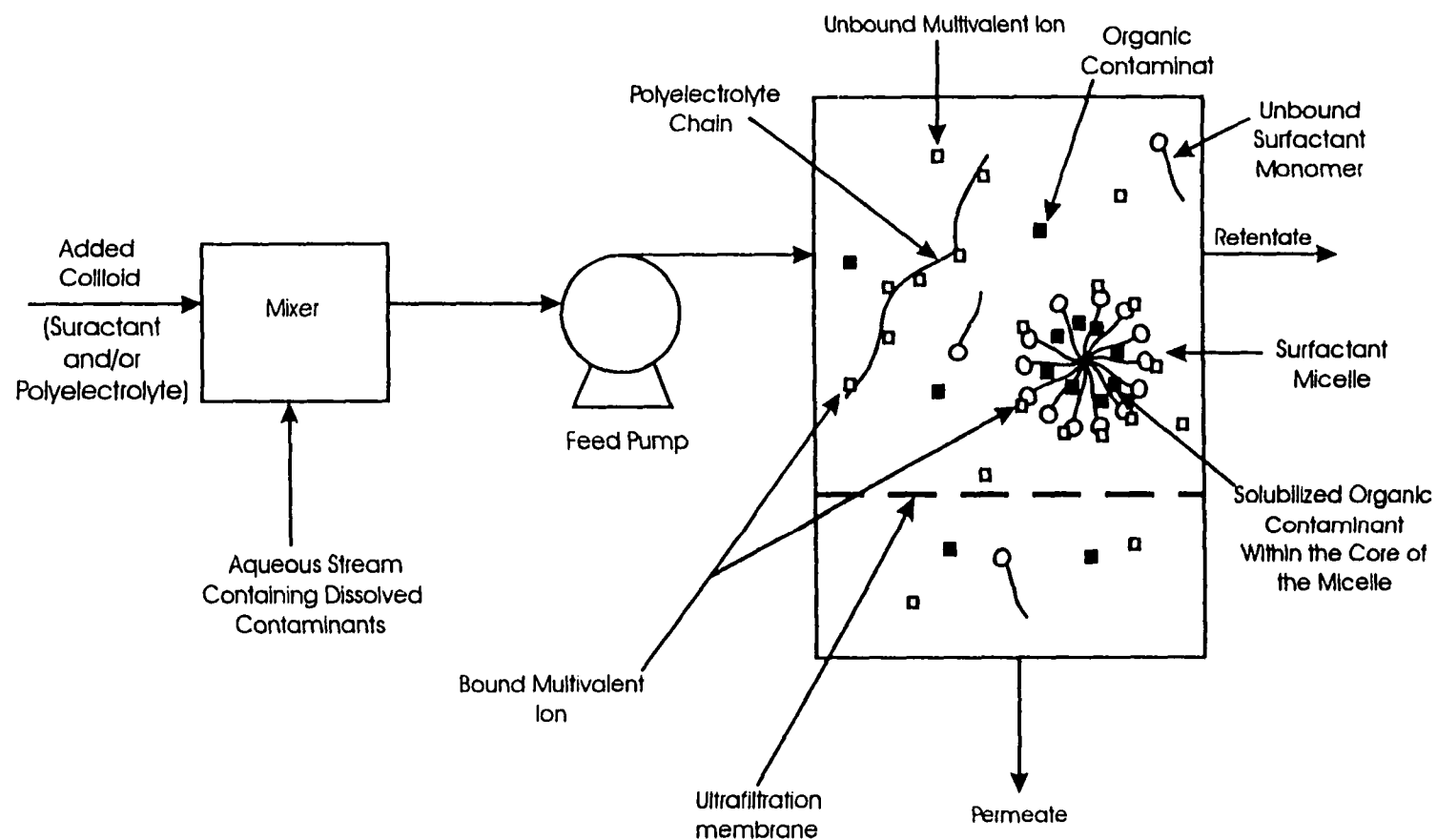


Figure 2: Schematic of colloid-enhanced ultrafiltration using a mixture of polyelectrolyte and surfactant for the removal of dissolved organics and multivalent ions.

micellar-enhanced ultrafiltration (MEUF), whereas a process with a polyelectrolyte as the colloid is polyelectrolyte-enhanced ultrafiltration (PEUF). The optimum colloid for the CEUF process would be one with a low cost which would result in minimum loss of colloid through the membrane and contribute as little as possible to concentration polarization while binding with ions and organics as effectively as possible. In PEUF, the polyelectrolyte molecules must be sufficiently large to be retained by the ultrafiltration (UF) membrane. However, any commercial polyelectrolyte has a distribution of molecular weight cut-off (MWCO) chains covering a fairly large spectrum. This means that the lower MWCO chains can pass through the UF membrane thereby defeating the purpose of the PEUF process. In order to eliminate the lower MWCO chains, the polyelectrolyte solution can be pretreated so to remove almost all of the lower MWCO chains. This is achieved by washing the polyelectrolyte which means adding water to and filtering the polyelectrolyte solution through an ultrafiltration (UF) membrane with pore sizes considerably larger than that used in the actual process. For example, a 70,000 MWCO polyelectrolyte can be pretreated using a 30K MWCO UF membrane to remove chains that are 30K or smaller. The pretreated polyelectrolyte solution would then contain molecules ranging from 30K and larger. If this solution is now used in a process using a 10K MWCO membrane, almost no polyelectrolyte would pass through the membrane. The polyelectrolyte molecule can dissociate into smaller chains as a result of shear stress due to the flow of the polyelectrolyte in pipes and pumps. However, the dissociation is generally negligible. Therefore, after pretreatment of the

polyelectrolyte, practically no polyelectrolyte passes through the ultrafiltration membrane.

In micellar-enhanced ultrafiltration, the surfactant monomer in excess of the critical micelle concentration (CMC) forms spherical or cylindrical shaped micelles large enough to be easily retained by a UF membrane. However, the micelle in equilibrium with the monomer is continuously going through a transition where surfactant monomers associate and dissociate with and from the micelle. Therefore, an incrementally small amount of surfactant monomer passes through the membrane.

It should be noted, however, that surfactants are a better group of colloids for the removal of organics from an aqueous stream since the organic contaminant solubilizes within the micelle core. In the case of polyelectrolytes, the organic contaminant can not bind or solubilize within the polyelectrolyte.

2.3 Polyelectrolytes

As the name suggests, polyelectrolytes are a group of chemicals with flexible chains containing many ionizable groups. When dissolved in solution, the counter ions of the polyelectrolyte dissociate from the polyvalent chain. Due to the large number of ions present on the polyelectrolyte chains, a strong electric field is produced which retains the

counterions in the vicinity of the polyelectrolyte chain (25). This unique property allows the use of polyelectrolytes for many applications.

Most polyelectrolytes are present in solution as long flexible straight chains. The polyelectrolyte is initially present in solution as a coiled cylindrical or spherical shaped molecule. The counter ion is present in the close vicinity of the coiled shape. However, as concentration of the polyelectrolyte increases or as other additives are added to the solution, the polyelectrolyte chain becomes more extended (or straight) due to the repulsive effect of the increased charge present in solution. Therefore, the counter ion is pushed further away from the polyelectrolyte chain. This can explain an effect observed in PEUF where for the same ratio of polyelectrolyte to added multivalent ions, as the concentration of the polyelectrolyte is reduced, rejection of the multivalent ions increases. Additionally, when the polyelectrolyte is in a coiled shape, it can be retained better by an ultrafiltration membrane. An extended polyelectrolyte chain can pass through an ultrafiltration membrane much easier which can lead to loss of polyelectrolyte and lower rejection of multivalent ions as may have been intended.

As multivalent ions are added to a polyelectrolyte solution, they can compete for the available sites with monovalent ions present in solution. Since the multivalent ions have higher affinity than monovalent ions for the available sites, the multivalent ions bind to the polyelectrolyte.

2.4 Ultrafiltration Membranes.

Filtration including ultrafiltration is the process by which two or more components are selectively separated in a given stream according to their sizes. Figure 3 shows the spectrum of the membrane technology (26) including the range where an ultrafiltration membrane is effective. An ultrafiltration membrane can separate particles in the range of approximately 0.005 micron to 0.5 micron. Since its introduction in 1963 (27), ultrafiltration membranes have been successfully used in many processes (1-16, 19-21, 24, 29-33). Some of these industries have included the food industry, pharmaceutical processes, electronics manufacturing to name a few.

Since UF membranes have been used so extensively in such a wide range of applications, their behavior has been well established. In addition, a number of membranes have been developed to best apply to a particular application. The membrane can be chosen according to its size and material. Membrane sizes are classified according to their molecular weight cutoff size (MWCO). This represents the average size of molecules that are retained by the membrane. Commercial filtration membranes are available ranging from 500 to 100,000 MWCO. As MWCO size is decreased, smaller molecules can be retained. However, since membranes of smaller MWCO size have smaller pore size, flux of solution across the membrane is also lower which leads to a higher capital and operating cost.

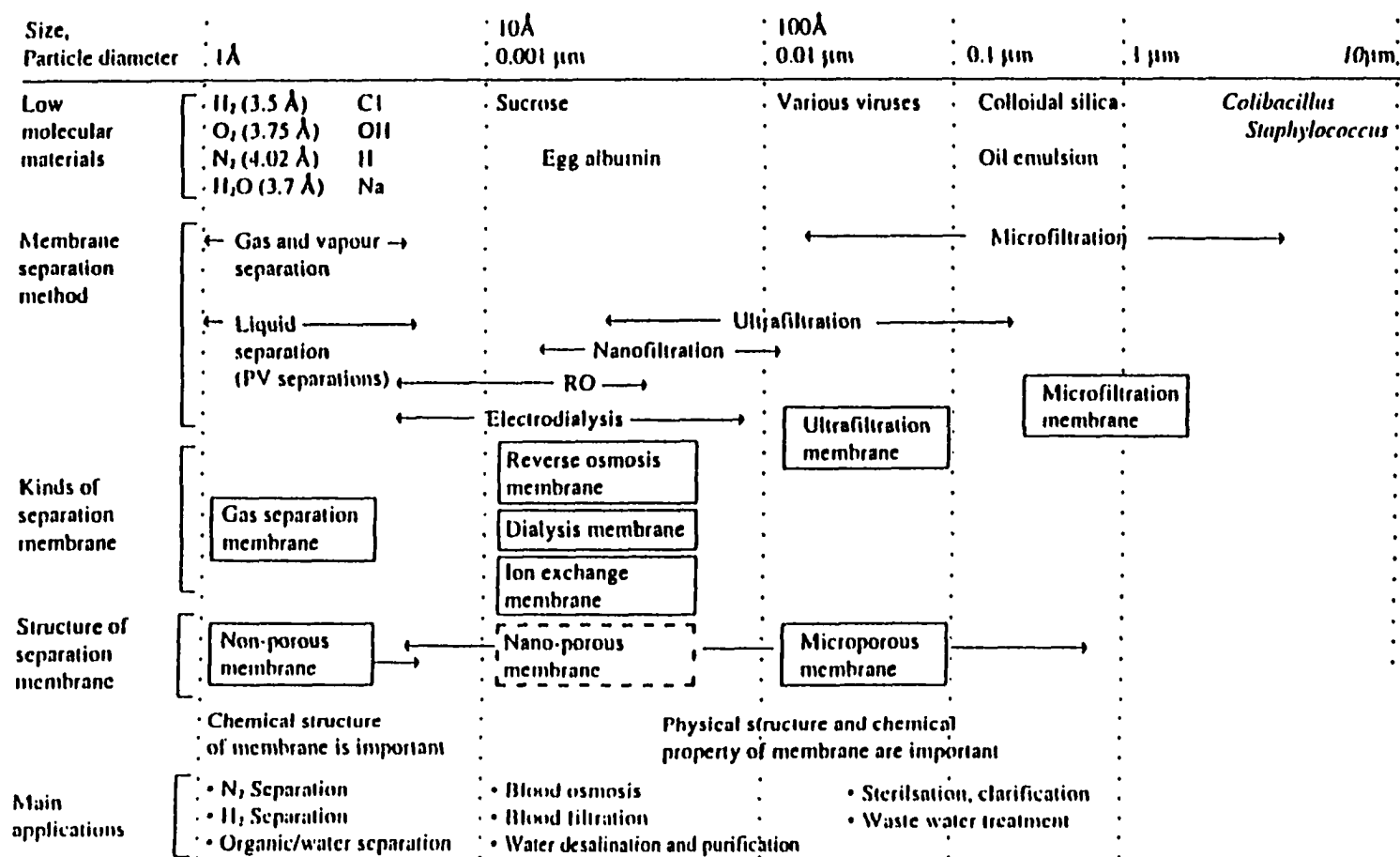


Figure 3: Schematic of Membrane Separation Technology Spectrum.
(Reproduced from K. Scott, Handbook of Industrial Membranes)

The UF membrane material affects several factors in the ultrafiltration process including particulate adsorption at the surface of the membrane, temperature range, and pH and chemical sensitivity (33). There are several materials of membranes in use today including cellulose acetate. The cellulose acetate has a limited temperature range (up to 30°C) and can not be exposed to extremely acidic conditions for extended periods and is biodegradable. However, cellulose acetate allows for a high flux across the membrane and excellent salt rejection properties which minimizes adsorption on the surface of the membrane. On the other hand, polysulfone membranes can tolerate a wide range of temperature up to 75°C and wide pH range (1-12). However, polysulfone membranes can not withstand large pressures (ranging from 25 - 100 psig depending on the ultrafiltration configuration) leading to lower flux across the membrane and are more prone to adsorption on their surface. For example, Cytochrome C adsorption losses are 0.8 % for cellulose acetate membrane versus 11.3 % for polysulfone membranes (27).

Another factor that has a great impact on the performance of the ultrafiltration process is the configuration of the ultrafiltration module. The type of configuration can affect concentration polarization (discussed in the next section) as a result of extent of mixing, fouling of the membrane and therefore the need for additional maintenance and replacement of membrane as well as cost of membrane. There are four widely used types of configurations in the industry: tubular, hollow fiber, plate and frame, and spiral wound. While each of these configurations has certain advantages and disadvantages, the one providing the most overall effective performance is the spiral wound

configuration. This is due to its low cost/area ratio, high flux (higher pressures), relatively low energy consumption, and ease of operation (27).

It is obvious from these observations, that using a particular membrane for a given application requires a great deal of optimization of temperature, pressure, and solution concentration, and module type.

2.4.1 Effect of concentration polarization on flux in CEUF. One of the factors that adversely affects the feasibility of CEUF is concentration polarization at the boundary layer of the ultrafiltration (UF) membrane. Figure 4 shows the zone of concentration polarization on the UF membrane. The anisotropic membrane used in ultrafiltration processes has a very thin skin aimed at reducing resistance to flow of solution through the membrane. The membrane with a uniform pore size distribution prevents passage of molecules larger than the pore size while allowing passage of molecules smaller than the pore size. Initially the solutes in the bulk feed are uniformly distributed throughout the solution. As more species are retained by the membrane and therefore the solute concentration in the retentate increases, more solutes accumulate at the surface of the membrane, leading to formation of a boundary layer. Eventually, enough solute accumulates at the surface of the membrane so that a gel layer is formed. This effect, known as concentration polarization, has an adverse effect on flux and rejection (26, 27, 33). Flux through a membrane can be defined according to:

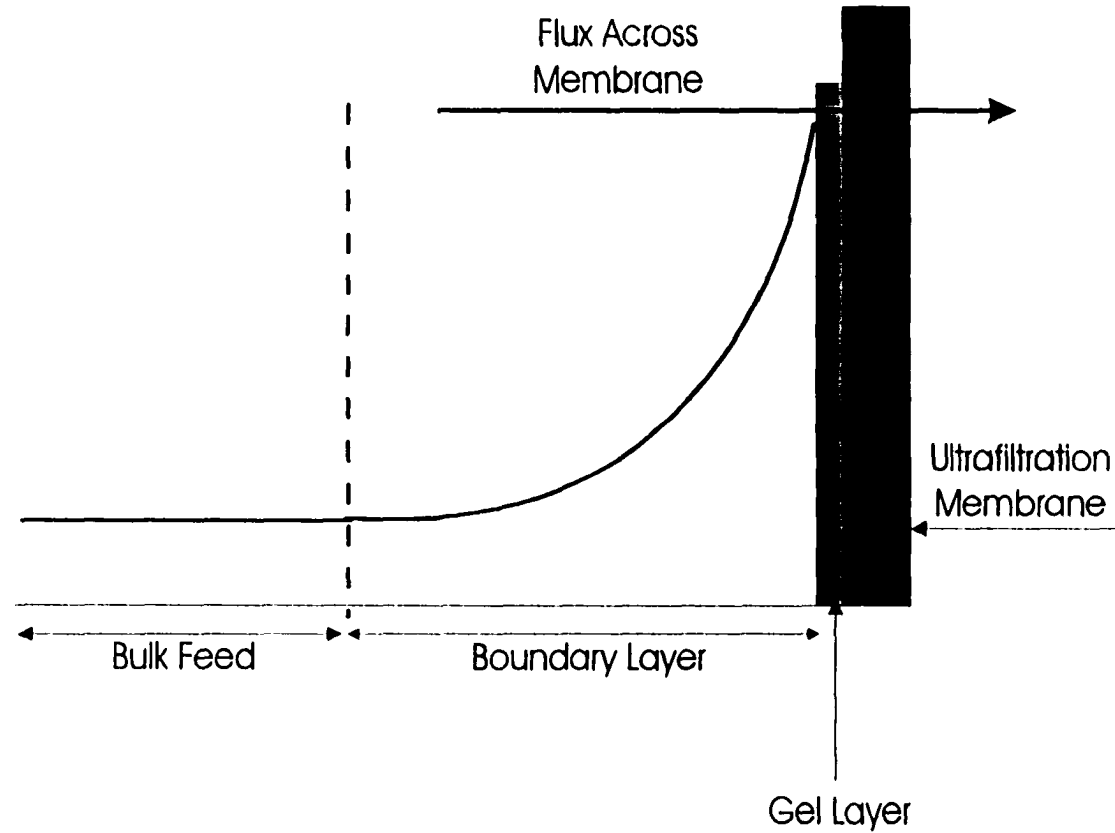


Figure 4: Schematic of Concentration Polarization Due to the Formation of Gel Layer.

$$J = \frac{\Delta P}{R_c + R_m} \quad (2-2)$$

where, J is the solution flux across the membrane, ΔP is the transmembrane pressure drop across the membrane, R_m and R_c are the resistances to flux due to the membrane thickness and gel (or cake) layer, respectively. As the gel layer increases in thickness, the solution must pass through a thicker layer of resistance and therefore, flux is reduced dramatically. Eventually, a point is reached at which flux reduces to zero. This point is known as the gel point.

A useful parameter for flux studies is relative flux (RF), that is flux of a given solution divided by flux of pure water at the same temperature and pressure. A decrease in flux or relative flux has an adverse effect on the cost of an ultrafiltration membrane process. To offset the reduced flux and obtain a higher flux, one can use a larger membrane surface area. However, larger surface area leads to higher capital and operation costs.

The concentration polarization phenomenon can also affect calculation of rejection (5, 27). This is due to the fact that as concentration at the surface of the membrane increases, the surface concentration no longer represents the bulk concentration. The rejection is now represented by:

$$R_i (\%) = (1 - \frac{[per]_i}{[ret]_i}) \times 100 \quad (2-3)$$

where $[ret.]_i$ refers to the contaminant concentration at the surface of the membrane. This suggests that the rejection calculated would be higher than the true rejection which might lead to erroneous conclusions.

The formation of the gel layer can be reduced by a more uniform mixing of the solution so that the colloid diffuses back into the bulk solution. However, the mixing must be optimized so that turbulence at the membrane surface does not become counterproductive. The formation of a gel layer can also be reduced by using a membrane where solute adsorption on the surface of the membrane is minimal. As a particle adsorbs on the surface of the membrane, it can plug the membrane pore and reduce rejection (34-35). However, with time the particles adsorbing at the surface of the membrane flocculate. Eventually the size of the flocculated particles becomes so large that the particles are rejected by the membrane. Therefore, flocculation actually increases rejection, however at the cost of increased concentration polarization, reduced flux and increased capital and operating costs. Furthermore, a colloid having lower molecular interactions at the surface can contribute to minimizing concentration polarization.

Other factors that affect the concentration polarization are pH of the solution, concentration of the solutes, solute size, and ionic strength of the solution (36). Each of these factors can change the steric effect at the surface of the membrane which therefore affects flux across the membrane and concentration polarization. It is therefore quite

important to choose a membrane with minimal adsorption at its surface. Cellulose acetate membranes, as used in this investigation, reflect low adsorption at their surface.

2.4.2 Effect of temperature on CEUF. Temperature can also affect flux across membrane. Generally as temperature increases, the membrane pores swell and allow greater flux across the membrane. However, higher temperatures require added energy costs, unless the incoming stream is already heated. It should be added that excessively high temperatures can lead to degradation of the membrane surface coating. In the case of the membranes used in this study, temperatures in excess of 30°C can lead to degradation of the anisotropic layer.

2.4.3 Effect of pressure on CEUF. Previous investigation (5) has shown that increasing the pressure increases flux. The increase in pressure generally has no detrimental effect on the flux or permeate purity, at least in the non-gel-polarized regime. However, an ultrafiltration membrane has a physical limit for pressure beyond which it can become compressed and damaged. Therefore, the highest flux allowed by physical limitations of the membrane is suggested for the CEUF process.

2.5 Colloid Recovery

Due to the relatively high cost of the colloid, its recovery is imperative in order to make the CEUF process economically feasible. Previous works have shown the use of electrolysis for depositing nickel ions on an electrode. However, results have shown that

only 0.5% of the current across the electrolyzer cell was effective in deposition of the nickel (21, 32, 37). Therefore, electrolysis is a poor choice for the regeneration of the polyelectrolyte. Thermal regeneration of the polyelectrolyte has also investigated to break the polymer/metal bond. However, this method has proven to be highly energy intensive and not effective for many systems (32). Previous investigations have shown that regeneration of the polyelectrolyte by addition of chemicals is the most feasible method for the recovery of the polyelectrolyte (21,32,38,39). It was generally found that the most effective method was acidification of the polyelectrolyte/metal solution and its subsequent ultrafiltration to remove the unbound metal ion.

The general methods of colloid recovery investigated in this study include precipitation of the contaminant bound to the colloid, precipitation of the colloid, or exchanging the contaminant ion bound to the colloid with a less noxious ion. The latter method would be achieved by addition of either a strong acid such as HCl or NaCl. For the precipitation methods, an additive would be added such that the additive complexing with the hardness ions would result in a compound with an extremely low solubility product thereby forcing the hardness ion to precipitate.

2.6 The Need For Economic Analysis of CEUF.

While many investigations have shown excellent feasibility of CEUF for various applications, only one previous study (15) has considered economic analysis of these

processes for a commercial application. In that study, it is shown that MEUF is nearly competitive with conventional methods for the removal of chlorinated hydrocarbons from aqueous streams. In order to further establish the effectiveness of CEUF processes for commercial applications, additional economic evaluations must be performed.

It was proposed that PEUF would be used as a water softening method. The results would then allow a convenient comparison with conventionally used water softening methods, specifically, lime softening and ion exchange. Such a study would determine economic feasibility of PEUF and determine bottleneck areas where PEUF and CEUF in general may need additional improvements. The reason that the PEUF method was chosen over the MEUF method for the water softening process was due to the fact that polyelectrolyte ions do not dissociate into smaller species to any noticeable degree (as do surfactant micelles as discussed earlier) and therefore they do not pass through the membrane in measurable concentrations. The PEUF process would therefore allow for a more ultrapure stream of water. Furthermore, at the same colloid concentration, polyelectrolytes have a higher relative flux than surfactants (9) leading to lower capital and operation costs.

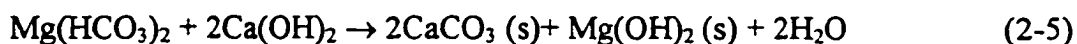
2.7 Water Softening.

Water softening is the process by which hardness present in water is removed. Water hardness includes calcium and magnesium, iron, and manganese present in water.

However, since raw water includes only very low concentrations of iron and manganese, water hardness generally refers to calcium and magnesium. The U. S. Geological Survey (USGS) classifies soft water as water containing 0 - 60 mg/L (ppm) of hardness (as CaCO_3) (40). The presence of calcium and magnesium in water is at times undesirable for several reasons (40,41). These include taste, aesthetics, and economics. When combined with carbonate and bicarbonate ions, hardness ions contribute to the formation of scale on the inside of pipes. The scales can act as insulation in the pipes and lead to undesirable heat transfer effects as well as clogging of pipes in heat exchangers. The scales forming in the pipes can eventually lead to corrosion of pipes. There are also many industries which demand extremely soft water for their applications since the presence of any excess ions can affect the reliability of their processes and products. Examples of such industries include pharmaceutical and electronics industries. High concentrations of calcium and magnesium also leads to undesired precipitation of surfactants present in detergents which means a loss of the detergent. Additionally, a large concentration of magnesium in water has a laxative effect (40). Therefore, there is clearly potential for economic gain as a result of water softening.

2.7.1 Addition of lime for water softening. A water softening process was first introduced in 1841 (41). In this process, lime, calcium hydroxide, reacts with the carbonate hardness to precipitate calcium carbonate and magnesium hydroxide according to the following equations:





The CaCO_3 and $\text{Mg}(\text{OH})_2$ are very fine particles and can take a long time to settle to the bottom of the tank which can slow down the process of water softening. In order to expedite the process, a coagulant, aluminum sulfate (alum), is added to help settle the particles. The coagulated particles are disposed of in a drying pond. It should be noted the softened water at this point still contains fine particles of calcium carbonate and magnesium hydroxide. Furthermore, the reactions do not occur stoichiometrically. Therefore, excess amount of lime must be added to remove the hardness ions. However, even in spite of excess amounts of lime, residual amounts of hardness ions still remain in the water (41). Although lime softening is an effective method for water softening and is used extensively in many local water treatment facilities, it is not an effective method for production of ultrapure water.

2.7.2 Use of ion exchange for water softening. The first commercial application of ion exchange was for the purpose of water softening and still continues to be one of the most important (41, 42). In the ion exchange process, the hardness ions present in the hardwater are replaced with sodium ions of the cation exchange bed. The soft water produced contains only NaHCO_3 , NaCl and, Na_2SO_4 . These compounds have a very high solubility in water and will dry only if all of the water is evaporated. Therefore, the presence of these compounds does not contribute to scale formation in pipes. The cation exchange bed material is a strong acid cation exchange resin such as polystyrene sulfonic

acid. Due to the nature of the ion exchange process, no chemicals precipitate on the bed and therefore the pores of the bed are generally not clogged. However, particulates present in the water entering the ion exchange bed can plug the bed pores. However, the pores can be cleared by backwashing the exchange bed with cleaning agents. Once the exchange resin capacity for exchanging hardness ions is exhausted, it can be regenerated using a 5 -10 wt% sodium chloride solution (42) followed by a wash cycle with water to remove the residual sodium chloride from the exchange bed. The resins are quite durable and have a long service life. The ion exchange process is an extremely efficient and reliable water softening technique providing soft water containing nearly zero hardness (41).

2.7.3 Use of PEUF for water softening. In using PEUF for water softening, a negatively charge polyelectrolyte is added to a stream containing the hardness ions. The hardness ions replace the negatively charged ions of the polyelectrolyte. The solution is then filtered through an UF membrane. The polyelectrolyte and the hardness ions are retained by the UF membrane while an ultrapure stream of softened water passes through the UF membrane. The polyelectrolyte solution is then regenerated using a number of possible methods as discussed earlier in this chapter.

2.8 Purpose of This Study

The purpose of this study is to determine the effectiveness of polyelectrolyte-enhanced ultrafiltration (PEUF) as an alternative method for the removal of hardness ions, calcium and magnesium, from water. The economic feasibility of PEUF process is then compared to two conventionally utilized water softening techniques, specifically, lime softening and ion exchange softening for a range of conditions. This study investigates a cradle to grave scenario to account for all costs associated with PEUF, lime softening, and ion exchange for the same set of conditions. The economic analysis utilizes a program (in FORTRAN 77) that compares the PEUF process with lime softening and ion exchange softening.

CHAPTER 3: EXPERIMENTAL PROCEDURES

3.1 Introduction

This section describes the experimental procedures performed as well as materials and analytical techniques utilized in this study. The initial phase of the experiments was to determine the effectiveness of the PEUF process. This included studying effects of polyelectrolyte, hardness ions, and added salt concentration as well as temperature on PEUF runs using the stirred cell. In the second phase of the experiments, the effectiveness of polyelectrolyte recovery methods were studied.

3.2 Types and Treatment of Materials

3.2.1 Polyelectrolytes. Shown in Figure 5 are the two representative anionic polyelectrolytes used in this study. The first with an average molecular weight cutoff (MWCO) of 70,000 (Aldrich), was sodium polystyrene sulfonate (PSS), $\text{NaC}_8\text{H}_7\text{SO}_3$ (FW: 206.19), obtained from Aldrich Chemical Co. and National Starch and Chemical Company. The second with a MWCO of 25,000 (43) was poly(methyl vinyl ether/maleic acid) (PMVEMA), commercially known as Gantrez S-95, $\text{H}-[\text{-CH}(\text{OCH}_3)\text{-CH}_2\text{-CH}(\text{COOH})\text{-CH}(\text{COOH})\text{-}]_n\text{-H}$ (FW: 175.2, CAS#: 25153-40-6), manufactured by GAF and obtained from GAF Chemicals Company. The bound hardness ions replace the sodium and hydrogen ions on PSS and PMVEMA, respectively.

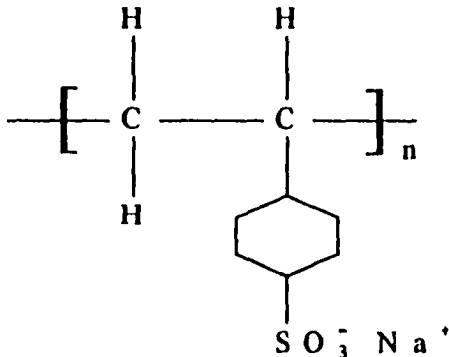
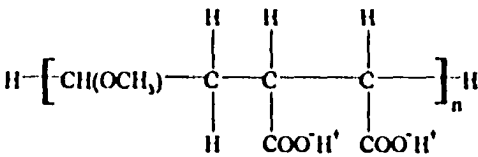
Anionic Polyelectrolyte	MWCO	Formula Weight	Vendors	Molecular Structure
Poly sodium styrene sulfonate PSS	70,000	206.19	Aldrich National Starch & Chemical Company	
Poly (methyl vinyl ether/maleic acid) Gantrez S-95	25,000	176.2	Aldrich GAF Chemical Company	

Figure 5: Structure of anionic polyelectrolytes PSS and Gantrez S-95.

The polyelectrolyte solutions were pretreated to remove smaller molecular weight chains. The pretreatment minimized loss of polyelectrolyte across the membrane (an average of 5×10^{-7} M or 0.1 ppm). This pretreatment was achieved by filtering the pure polyelectrolyte solution through a 10K MWCO spiral wound membrane (cellulose acetate, type C) (Spectrum) in a continuous ultrafiltration unit so that the lower molecular weight chains passed through the UF membrane. In the continuous flow spiral wound unit, the solution goes through a large pocket of membrane wrapped around a central perforated tube. The perforations in the tube allow purified water filtering through the large membrane envelope to leave through the tube. Since the surface area of the membrane envelope is relatively large (5 m^2)(44), it allows a much larger flow of solution across the membrane. The retentate leaving through an exit perforation recirculated back into the spiral wound module so to maximize the removal of lower molecular weight chains from the solution. Details on operation of the spiral wound unit are provided elsewhere (15).

The polyelectrolyte solution retained by the membrane contained molecular weight chains larger than 10K and was subsequently used for the PEUF process. As a result of the pretreatment process, it was found that molecular weight chains smaller than 10K account for about up to 7 mole % of the polyelectrolyte in the initial solution. The polyelectrolyte solution was circulated through the spiral wound ultrafiltration module for 7 to 10 hours to complete the polyelectrolyte pretreatment process.

No toxicological studies for the polyelectrolytes were performed in this work.

3.2.2 Miscellaneous Chemicals. Extra pure calcium chloride dihydrate crystals, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (FW: 147.02) (EM Science) and reagent grade magnesium chloride, 6-hydrate crystals, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (FW: 203.30) (J.T. Baker) were used to simulate calcium and magnesium in hard water. Sodium chloride, NaCl (FW: 58.44) (Fisher Scientific) was used to determine the effect of salinity on the process. For the recovery studies, certified hydrochloric acid and sodium hydroxide solutions (0.001 - 12 N) (Fisher Scientific) as well as certified ACS anhydrous sodium carbonate crystals, Na_2CO_3 (Fisher Scientific) were used. Also used were granular dihydrate barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (FW: 244.28) (Mallinckrodt) and certified ACS dibasic anhydrous sodium phosphate, Na_2HPO_4 (FW: 141.96) (Fisher Scientific). For the analysis of calcium, magnesium, sodium, and barium by atomic absorption, 1000 ppm standard solutions were obtained from Fisher Scientific.

3.3 Techniques and Equipment

3.3.1 UF experimental runs. The glassware were acid washed using sulfuric acid with Nochromix. The glassware were then rinsed with distilled deionized water several times and allowed to dry. The polyelectrolyte stock solutions were prepared by dissolving the polyelectrolyte in distilled deionized water. The solutions were heated for 15-25 minutes at about 30°C in order to completely dissolve the polyelectrolyte into solution. Initial pH

of PSS was about 5.0 while that of PMVEMA was about 2.5 - 3.1. Experimental runs for PMVEMA were initially performed at a pH of 2.5. However, since rejections obtained were so low, the pH of the PMVEMA solution was adjusted to approximately 7 before its use in the PEUF process. The pH of the solutions were measured using a Markson handheld pH meter.

The experimental runs were performed in a batch stirred cell reactor as shown in Figure 6. The stirred cell parts were cleaned after each use by washing them in distilled deionized water. A 76 mm diameter cellulose acetate membrane, type C (Spectrum Medical Industries) used in a 400 ml batch stirred cell reactor (Spectrum) was soaked overnight in distilled water. The purpose of using cellulose acetate membrane was to minimize adsorption on the surface of the membrane. Due to the fragile nature of the ultrafiltration membrane, special precautions were taken in its handling. These included holding the membrane by the outer edges and avoiding touching the membrane surface. Also, before and after each run the membrane was checked for the presence of scratches on its surface.

Since the ultrafiltration membranes are anisotropic, flux across each membrane can be slightly different. Therefore, to standardize and compare flux across different membranes, flux of distilled deionized water is measured across each membrane. Flux of a given solution across a given membrane is then divided by that of the distilled deionized water across the same membrane to give the relative flux of the solution. The

relative flux provides a useful parameter for comparing flux of different solutions across different membranes. For experiments above room temperature, the temperature around the cell was controlled using a GCA Precision Scientific water circulator. For experiments below room temperature, the temperature was controlled using a Brinkmann mgw Lauda RM-20 coolant bath.

A 300 mL solution of the polyelectrolyte, calcium chloride, and/or magnesium chloride was placed in the stirred cell reactor. The solution temperature was controlled by circulating water from a constant temperature bath through flexible Tygon tubing wrapped around the cell. The experiments were run at 5.5°C, 15°C, and 30°C. The solution was stirred at a speed of 845 rpm (45) with a pressure drop of 60 psi (using gaseous nitrogen) across the membrane. The values of 845 rpm and 60 psig were values determined in previous studies to result in optimum flux and reduction of concentration polarization. Depending on the required solution temperature, from 30 minutes to several hours was required to achieve temperature equilibrium. Approximately 200 mL of the solution was filtered through the membrane to produce eight samples of approximately 25 mL each, obtained at known times. The permeate samples were weighed and the fluxes calculated. The feed as well as the permeate samples were analyzed for concentrations of polyelectrolyte, calcium, and/or magnesium. The rejection was determined by analyzing the sample at the midpoint of each run, that is, the point at which 100 mL of the solution had passed through the membrane. After each

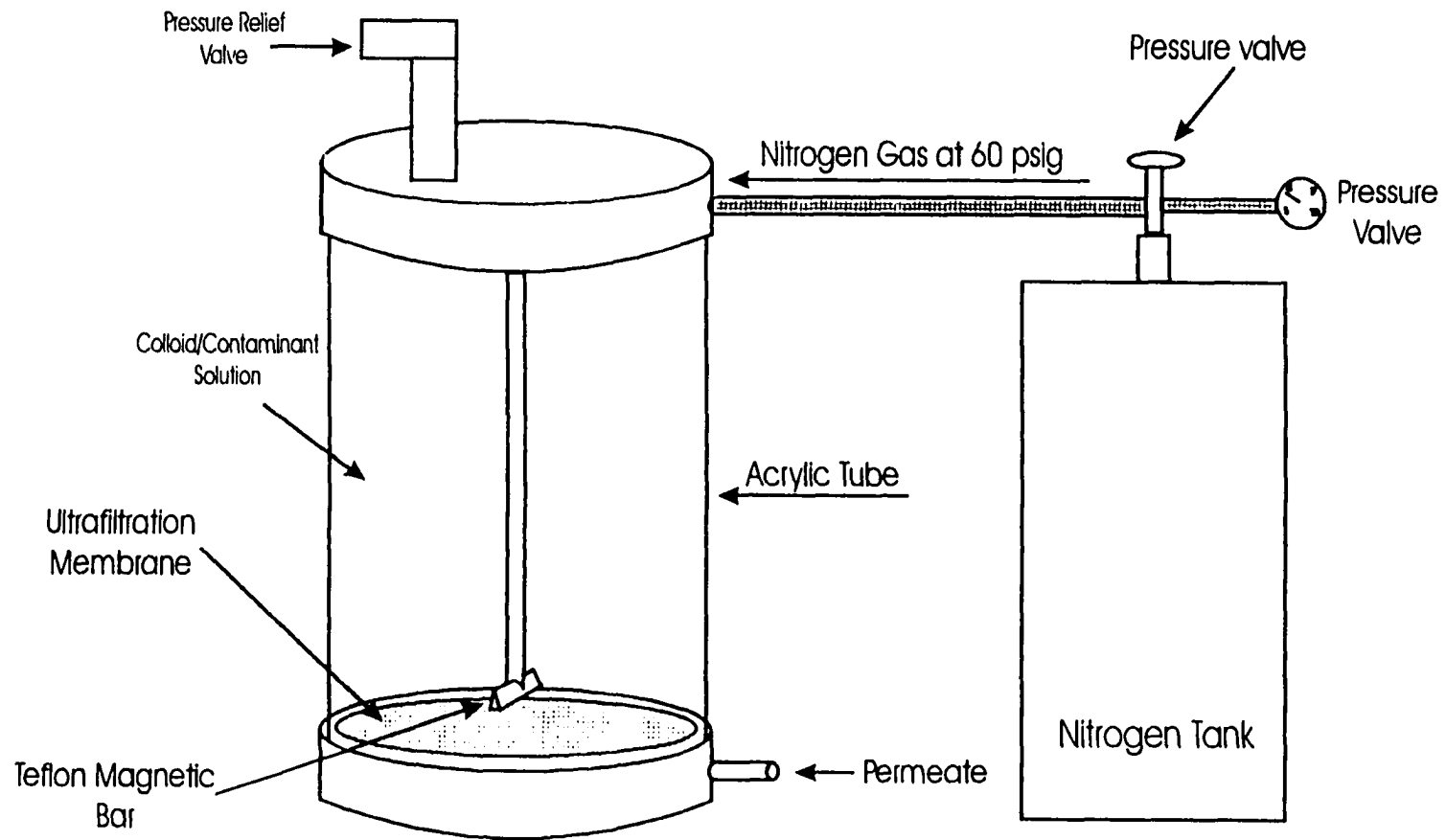


Figure 6: Schematic of stirred cell ultrafiltration unit.

use, all the elements of the stirred cell were soaked and cleaned with distilled deionized water.

3.3.2 Viscosity and density measurements. The density was measured using a 10 mL pycnometer. The 10 mL volume was first measured gravimetrically. The density of the solution was then calculated by dividing the mass of the 10 mL solution (in grams) by 10 mL. The viscosity of the solutions were measured using a Canon-Fenske capillary #50 viscometer. This size has a range of 0.8 to 4 cSt for kinematic viscosity. The time required for a particular volume of the solution to pass through the viscometer was measured. The time was then multiplied by the viscometer constant (0.004 cSt/sec) to obtain the kinematic viscosity. The viscosity was calculated by multiplying the density by kinematic viscosity. The viscosity and density values were to be used to calculate the Reynolds number based on the experimental flux data of the polyelectrolyte solution through the membrane module and scale up the PEUF process for an industrial unit accordingly. However, in discussions with membrane manufacturers, it was later determined that UF modules can be scaled up almost linearly. Therefore, the viscosity and density data reported here have not been used for any calculations. However, the values are provided for interested readers in Table 1.

3.4 Polyelectrolyte Recovery Methods.

For the regeneration processes considered, the purpose was to recover as much of the polyelectrolyte as possible for reuse while maximizing hardness rejection using the

Table 1: Viscosity and density of PSS solution at 25.5 °C. Approximation constant=0.004 cSt/sec using a size #5 Canon-Fenske viscometer.

Liquid Solution	Time (sec)	Kinematic Viscosity (cSt)	Density (g/mL)	Viscosity (cp)
Distilled DI Water	243	0.9720	0.9969	0.9690
0.001 M PSS	257	1.0280	0.9971	1.0250
0.01 M PSS	326	1.3040	0.9973	1.3005
0.1 M PSS	596	2.3840	1.0027	2.3904

regenerated polyelectrolyte. The following provides a brief description of the methods used for the two polyelectrolytes used in this study, PSS and PMVEMA.

3.4.1 Recovery of PSS.

1. Precipitation of the PSS by addition of barium chloride, followed by precipitation of barium phosphate and subsequent dissolution of the polyelectrolyte by addition of sodium phosphate: PSS recovery was the only polyelectrolyte tested using this method. Upon addition of barium chloride, the solution was centrifuged to remove the barium polystyrene sulfonate. The supernatant was analyzed for the presence of hardness ions and polyelectrolyte. Sodium phosphate was then added to the solution to replace the barium ions with sodium ions and produce a precipitate of barium phosphate and bring the PSS into solution. Since the PSS did not readily dissolve into solution, nitric acid

was added to improve dissolution of PSS. The supernatant was then analyzed for PSS and hardness metal ions.

2. Precipitation of the hardness ions by addition of sodium hydroxide, sodium phosphate, or sodium carbonate: sodium hydroxide, sodium phosphate, or sodium carbonate was added to precipitate hardness ions as calcium hydroxide and magnesium hydroxide, calcium phosphate and magnesium phosphate, or calcium carbonate and magnesium carbonate, respectively. Excess sodium hydroxide, sodium phosphate, or sodium carbonate was added so that hardness ion concentration in the supernatant was below a few ppm. After centrifuging the solution, the supernatant was removed and analyzed for hardness ions. Excess amount of the additives had to be added since stoichiometric ratios were not sufficient to attain the desired precipitation. The pH of the supernatant was then adjusted with hydrochloric acid to approximately 5. The solution was placed in a stirred cell and rinsed with distilled deionized water in a UF stirred cell several times so that excess HCl and salts formed were removed from the solution. Calcium chloride and/or magnesium chloride were again added to the regenerated polyelectrolyte solution. The regenerated PSS/calcium (and/or magnesium) solution was then treated again in an ultrafiltration stirred cell to determine the effectiveness of the regenerated solution in binding calcium and magnesium ions.

3. Exchange of hardness ions with sodium or hydrogen by addition of sodium chloride or hydrochloric acid, respectively: an excess quantity of sodium chloride or hydrochloric

acid was added to the spent PSS solution to exchange the hardness ions bound to the PSS with sodium or hydrogen, respectively. The solution was then placed in a ultrafiltration stirred cell and rinsed with distilled deionized water until the hardness ion concentration in the permeate was reduced considerably (almost to zero). However, the polyelectrolyte in the retentate still retained at least about 1% of the hardness ion concentration initially added to it. The solution was then removed from the stirred cell and the pH adjusted to 7. Calcium chloride and/or magnesium chloride was then added to the regenerated PSS solution to determine the effectiveness of the regenerated solution in a stirred cell PEUF experiment.

3.4.2 Recovery of PMVEMA.

To study the recovery of PMVEMA, the pH of a 300 mL solution of PMVEMA and calcium was adjusted to about 7. The solution was then ultrafiltered. The pH of the retentate was lowered to about 1 to regenerate the PMVEMA. The retentate was then washed with 150 mL of distilled deionized water five times to remove calcium and excess hydrogen ions. The pH of the retentate was adjusted to about 7 again and calcium chloride added to it. This solution was then ultrafiltered to determine the rejection of calcium ions with the regenerated PMVEMA.

3.5 Analytical Techniques

The concentration of the metal ions was determined using a Varian SpectrAA-20 atomic absorption (AA) flame spectroscope with multiwavelength spectrometer with GTA-96 graphite tube atomizer (for detection of low (ppb) metal concentrations). The GTA-96 was equipped with a PSC-56 Programmable Sample Changer. The gases used for the AA were house air, AA grade acetylene and nitrous oxide. A 1000 ppm standard solution of the particular metal was diluted to the desired range. The diluted standard solutions were then used to calibrate the detector. The standard solutions were prepared to simulate the experimental solutions as much as possible. For example, for a set of samples containing PSS and calcium, standards were prepared to contain similar PSS concentrations to those in the samples. This was to maximize the signal obtained from the UV detector in the AA. Table 2 shows the lamp current, spectral band pass, optimum working range, fuel and supporting fuel for the metals used in this work.

Table 2: Parameters Used for the Metal Lamps in the Analysis of the Metals Using the Atomic Absorption Spectroscopy

Metal Lamp	Wave-length (nm)	Lamp Current (mA)	Band Pass	Optimum Range (ug/ml)	Fuel	Fuel Support
Calcium	422.7	3.5	0.5	1-4	Acetylene	Nitrous Oxide
Magnesium	285.2	3.5	0.5	0.1-0.4	Acetylene	Air
Barium	553.6	20	0.5	10-40	Acetylene	Nitrous Oxide

Due to the ring structure in PSS, a UV spectrophotometer could be used for analysis of PSS. Therefore the concentration of PSS was determined using a Hewlett Packard 8452A diode array UV spectrophotometer at a wavelength of 226 nm. PMVEMA, on the other hand, has two carboxylic acid groups per repeating monomer unit. The two carboxylic acid groups allow for two equivalence points at pH=5.8 and 10.3 (43). Initially an effort was made to determine the concentration of PMVEMA using titration with NaOH. However, titration did not provide an accurate measurement of PMVEMA even at large concentrations. The concentration of PMVEMA was therefore analyzed using a DOHRMANN DC-180 total organic carbon (TOC) analyzer. Using titration, PMVEMA concentration of a feed stock was determined to be 0.1463 M whereas DC-180 TOC analysis yielded a concentration of 0.1206 M. Titration would have been far more difficult and far less accurate at low PMVEMA concentrations (as would have been obtained in the permeate) than TOC measurements which provided far more accurate and reproducible results. The TOC analyzer operates by UV-promoted persulfate oxidation and nondispersive infrared detection of CO₂ product (produced by oxidizing carbonaceous materials). Theoretically, TOC analysis has capability of analyzing from 10 ppb through 30,000 ppm. A full description for operation of the Varian AA and DOHRMANN DC-180 are provided in the system manuals.

Chapter 4: TECHNICAL FEASIBILITY OF POLYELECTROLYTE- ENHANCED ULTRAFILTRATION (PEUF) FOR WATER SOFTENING.

4.1 Introduction

Water frequently contains numerous solutes, many of which are not desirable either for residential or industrial purposes. One category of solutes are the cations of calcium and magnesium, which are responsible for water hardness. Some of the consequences of water hardness are the formation of residues in pipes and boilers resulting in poor energy transfer and corrosion, precipitation of chemicals such as soaps, spots and stains, and undesirable taste in drinking water(41). At present, the major processes available for water softening are ion exchange and lime softening. A new class of techniques that may be useful in decreasing hardness are the colloid-enhanced ultrafiltration processes. These methods operate continuously at low pressure and low temperature providing a very clean stream of water. Previous experimental studies have shown that colloid-enhanced ultrafiltration techniques are effective methods of removing a wide variety of solutes from aqueous streams, but the emphasis in earlier research has been on polluted water clean-up, not improvement of drinking water.

In this chapter, it is shown that the PEUF process can be used for the effective removal of dissolved calcium and magnesium from water in the presence of low concentration of sodium chloride at several temperatures. This chapter also utilizes a modified Oosawa

model (25), the ion-binding model which gives an excellent prediction of the hardness concentration in the permeate stream of the ultrafiltration process.

4.2 Ion-Binding Model

It is desirable to model the experimental results so that the permeate metal concentration can be predicted when the retentate metal and colloid concentrations are known.(12) This is achieved by using the two phase approximation theory by Oosawa (25) to determine the fraction of each ion that is bound to the polyelectrolyte or is free in the bulk by relating the counterion binding to the surface potential of the polyelectrolyte. Such a model requires use of material and charge balances for the electrolyte species in the solution. It is assumed that the thermodynamic activity of each electrolyte passing through the ultrafiltration membrane is the same in the permeate as in the retentate; for example, for a compound such as CaCl_2 , the activity product $a_{\text{Ca}^{2+}} \cdot a_{\text{Cl}^-}^2$ will be the same in the permeate and the retentate. This assumption has been experimentally confirmed in studies(9,12) of heavy metal removal using PEUF. For a solution containing PSS, CaCl_2 , and, MgCl_2 , the equations describing activity equilibrium reduce to:

$$a_{\text{CaCl}_2, \text{ret}} = a_{\text{CaCl}_2, \text{per}} \quad (4-1)$$

$$a_{\text{MgCl}_2, \text{ret}} = a_{\text{MgCl}_2, \text{per}} \quad (4-2)$$

where a is the thermodynamic activity, and, per and ret denote permeate and retentate, respectively. In the absence of sodium chloride, the ionic strength is low enough so that

the activity coefficient terms may be taken to be unity. Therefore, equations 1 and 2 can be expressed in terms of species concentration as follows:

$$[\text{Ca}^{2+}]_{\text{ret}} [\text{Cl}^-]_{\text{ret}}^2 = [\text{Ca}^{2+}]_{\text{per}} [\text{Cl}^-]_{\text{per}}^2 \quad (4-3)$$

$$[\text{Mg}^{2+}]_{\text{ret}} [\text{Cl}^-]_{\text{ret}}^2 = [\text{Mg}^{2+}]_{\text{per}} [\text{Cl}^-]_{\text{per}}^2 \quad (4-4)$$

where the concentrations are those of the unbound ions. The charge balance for both the retentate and the permeate streams must also be satisfied according to:

$$[\text{PSS}^-] + [\text{Cl}^-] = [\text{Na}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] \quad (4-5)$$

where $[\text{PSS}^-]$ is zero in the permeate. To predict the permeate concentration, the concentration of the ions bound to the polyelectrolyte in the retentate must be determined. Assuming that PSS has an extended, rodlike configuration (46), the Oosawa approximation treats counterions as either bound to the polyelectrolyte or free in the bulk aqueous solution. The extent of the counterion binding of the monovalent and divalent ions is related to the equilibrium surface potential of the polyelectrolyte. In the case of the rodlike PSS, the Oosawa model leads to the following expressions for the logarithms of the concentration ratios (bound/free) for the monovalent and the divalent ions:

$$\ln \left[\frac{(1-\beta)}{\beta} \right] = \ln \left[\frac{\phi}{(1-\phi)} \right] + (\beta q + \beta' q') z Q \ln \left[\frac{1}{\phi} \right] \quad (4-6)$$

$$\ln \left[\frac{(1-\beta')}{\beta'} \right] = \ln \left[\frac{\phi}{(1-\phi)} \right] + (\beta q + \beta' q') z' Q \ln \left[\frac{1}{\phi} \right] \quad (4-7)$$

where β and β' are the apparent degrees of dissociation for the monovalent and the divalent ions, respectively, f is the fraction of the total solution volume in which the bound ions are located, q and q' are the fractions of the free ion charge carried by the two types of counterions, z and z' are the absolute values of the counterion charges (1 for Na^+ , 2 for Ca^{2+} and Mg^{2+}), and Q is the dimensionless potential parameter, important in determining the extent of binding of counterions. For PSS, f is taken to be equal to 0.2 L/mol (12), the apparent molar volume of the styrenesulfonate, multiplied by the total molarity of styrenesulfonate units in solution. The variables β , β' , z , z' , q , and q' in equations 6 and 7 can be represented in terms of known concentrations of sodium and PSS to yield:

$$\ln\left(\frac{[\text{Na}]_{br}}{[\text{Na}]_{fr}}\right) = \ln\left(\frac{\phi}{1-\phi}\right) + \frac{[\text{PSS}] - [\text{Na}]_{br} - 2[\text{metal}]_{br}}{[\text{PSS}]} Q \ln\left(\frac{1}{\phi}\right) \quad (4-8)$$

$$\ln\frac{[\text{metal}]_{br}}{[\text{metal}]_{fr}} + \ln\left(\frac{\phi}{(1-\phi)}\right) = 2 \ln\left(\frac{[\text{Na}]_{br}}{[\text{Na}]_{fr}}\right) \quad (4-9)$$

where $[\text{Na or Metal}]_{br}$ and $[\text{Na or Metal}]_{fr}$ denote the sodium or divalent metal ions bound and free in the retentate, respectively, and metal indicates total calcium and magnesium.

It is the binding of the divalent cations responsible for hardness to the highly-charged polyelectrolyte anions which immobilizes these cations, preventing them from passing through the membrane.

4.3 Results and Discussion

The experiments were performed with two polyelectrolytes, PSS and PMVEMA. However, the PSS proved to be more effective for the water softening experiments. This was due to several factors: 1. PMVEMA tended to degrade after a few days which meant its regeneration was not as reliable as that of the PSS, 2. PSS was cheaper than PMVEMA, and 3. PMVEMA was more toxic than PSS. Nevertheless, the PEUF results for PMVEMA is also presented to show its potential capability. The ion-binding model analysis, however, was applied only to PSS.

The removal efficiency of the calcium and magnesium is represented by rejection, R (%), as defined by:

$$R = \left[1 - \frac{[TotalMetal]_{per}}{[TotalMetal]_{ret}} \right] * (100\%) \quad (4-10)$$

The results of the PEUF runs using PSS are shown in Tables 3, 4, and 5. Table 3 shows the results of PEUF using PSS with calcium in the presence and in the absence of added salt. Table 4 shows the use of PEUF using PSS with magnesium in the absence of added salt. Table 5 shows the PEUF runs using PSS with both calcium and magnesium in the presence and in the absence of added salt. Table 6 shows the PEUF runs using PSS,

Table 3: PEUF using PSS and calcium. All concentrations in molarity (M).

Feed Concentratio Calcium	PSS/Total Metal Ratio	Temp(C)	Metal,ret*	PSS,ret	NaCl,Feed	Metal,per** Experimental	%Rejection Experimental
1.19E-03	7.86E+00	5.5	1.80E-03	1.41E-02		6.52E-06	9.96E+01
1.14E-03	8.35E+00	15	1.70E-03	1.42E-02		6.00E-06	9.96E+01
1.02E-03	9.11E+00	15	1.51E-03	1.38E-02		8.23E-06	9.95E+01
2.50E-03	3.88E+00	30	3.68E-03	1.43E-02		1.32E-04	9.64E+01
1.16E-03	8.26E+00	30	1.78E-03	1.47E-02		1.21E-05	9.93E+01
2.16E-03	6.50E-01	30	2.39E-03	1.55E-03		1.69E-03	2.93E+01
3.01E-03	2.86E+01	30	4.41E-03	1.26E-01		1.30E-05	9.97E+01
1.75E-04	6.48E+00	30	2.77E-04	1.80E-03		7.49E-07	9.97E+01
1.12E-03	6.15E+00	30	1.24E-03	7.65E-03		1.12E-05	9.91E+01
2.11E-03	5.24E+00	30	2.51E-03	1.51E-02		8.76E-05	9.65E+01
4.76E-03	3.26E+00	30	4.76E-03	1.55E-02		3.31E-04	9.30E+01
4.31E-03	1.28E+01	30	6.15E-03	7.93E-02		3.27E-05	9.95E+01
4.34E-03	1.23E+01	30	6.69E-03	8.23E-02	3.42E-04	4.60E-05	9.93E+01
4.19E-03	1.26E+01	30	6.07E-03	7.64E-02	3.42E-03	5.12E-05	9.92E+01
4.41E-03	1.22E+01	30	6.60E-03	8.04E-02	8.55E-03	8.99E-05	9.86E+01
1.91E-03	5.06E+00	30	2.81E-03	1.42E-02	8.90E-04	1.52E-04	9.46E+01
2.08E-03	4.87E+00	30	3.01E-03	1.47E-02	8.55E-03	3.47E-04	8.85E+01
2.29E-03	4.45E+00	30	3.26E-03	1.45E-02	1.69E-02	4.90E-04	8.50E+01
3.15E-03	3.52E+00	30	4.07E-03	1.43E-02	3.42E-02	1.37E-03	6.64E+01

*ret: retentate

**per: permeate

Metal: Calcium and/or Magnesium

Table 4: PEUF using PSS and Magnesium. All concentrations in molarity (M).

Concentratio Magnesium	PSS/Total Metal Ratio	Temp(C)	Metal,ret*	PSS,ret	Metal,per** Experimental	%Rejection Experimental
1.03E-03	8.98E+00	5.5	1.55E-03	1.39E-02	7.82E-06	9.95E+01
4.53E-03	2.25E+00	30	6.18E-03	1.39E-02	9.17E-04	8.52E+01
2.26E-03	4.26E+00	30	3.48E-03	1.48E-02	9.30E-05	9.73E+01
2.21E-04	4.36E+00	30	3.33E-04	1.45E-03	8.18E-06	9.75E+01
1.21E-03	7.77E+00	30	2.08E-03	1.61E-02	1.30E-05	9.94E+01
1.90E-03	5.15E+00	30	2.85E-03	1.46E-02	6.55E-05	9.77E+01

*ret: retentate

**per: permeate

Metal: Calcium and/or Magnesium

Table 5: PEUF using PSS with calcium and magnesium. All concentrations in molarity.

Initial Feed Calcium	Concentration Magnesium	PSS/ Total Metal Ratio	Temp (C)	Metal,ret* Experimental	PSS,ret Experimental	NaCl,Feed	Metal,per** Experimental	%Rejection Experimental
6.89E-04	7.10E-04	6.74	5.5	2.11E-03	1.42E-02		1.28E-05	99.39
6.74E-04	7.12E-04	6.67	15	2.07E-03	1.38E-02		1.18E-05	99.43
5.69E-03	4.20E-03	5.37E+00	30	1.46E-02	7.84E-02		5.60E-04	9.62E+01
5.69E-03	2.08E-03	6.82E+00	30	1.14E-02	7.81E-02		2.49E-04	9.78E+01
1.71E-04	1.32E-04	3.62E+00	30	4.91E-04	1.78E-03		7.33E-06	9.85E+01
6.39E-04	5.98E-04	7.54E+00	30	1.87E-03	1.41E-02		1.91E-05	9.90E+01
2.16E-04	1.41E-04	4.12E+00	30	4.68E-04	1.93E-03	8.78E-03	1.54E-04	6.71E+01
9.68E-04	6.50E-04	6.01E+00	30	2.35E-03	1.41E-02	8.81E-03	9.40E-05	9.60E+01

*ret: retentate

**per: permeate

Metal: Calcium and/or Magnesium

Table 6. Polyelectrolyte-Enhanced Ultrafiltration of Calcium and/or Magnesium with PSS. All concentrations in molarity (M).

PSS/Total Metal Ratio	Temp (°C)	Metal,ret* Experimental	PSS,ret Experimental	NaCl,Feed	Metal,per** Experimental	Metal,per Model	%Rejection Experimental	%Rejection Model
8.98E+00	5.50E+00	1.55E-03	1.39E-02		7.82E-06	4.96E-06	9.95E+01	9.97E+01
6.74E+00	5.50E+00	2.11E-03	1.42E-02		1.28E-05	1.36E-05	9.94E+01	9.94E+01
7.86E+00	5.50E+00	1.80E-03	1.41E-02		6.52E-06	7.86E-06	9.96E+01	9.96E+01
8.35E+00	1.50E+01	1.70E-03	1.42E-02		6.00E-06	6.54E-06	9.96E+01	9.96E+01
9.11E+00	1.50E+01	1.51E-03	1.38E-02		8.23E-06	4.64E-06	9.95E+01	9.97E+01
6.67E+00	1.50E+01	2.07E-03	1.38E-02		1.18E-05	1.34E-05	9.94E+01	9.94E+01
2.25E+00	3.00E+01	6.18E-03	1.39E-02		9.17E-04	1.34E-03	8.52E+01	7.84E+01
3.88E+00	3.00E+01	3.68E-03	1.43E-02		1.32E-04	1.41E-04	9.64E+01	9.62E+01
4.26E+00	3.00E+01	3.48E-03	1.48E-02		9.30E-05	9.73E-05	9.73E+01	9.72E+01
8.26E+00	3.00E+01	1.78E-03	1.47E-02		1.21E-05	7.20E-06	9.93E+01	9.96E+01
6.50E-01	3.00E+01	2.39E-03	1.55E-03		1.69E-03	1.69E-03	2.93E+01	2.89E+01
2.86E+01	3.00E+01	4.41E-03	1.26E-01		1.30E-05	1.82E-05	9.97E+01	9.96E+01
5.37E+00	3.00E+01	1.46E-02	7.84E-02		5.60E-04	6.53E-04	9.62E+01	9.55E+01
6.82E+00	3.00E+01	1.14E-02	7.81E-02		2.49E-04	3.00E-04	9.78E+01	9.74E+01
6.48E+00	3.00E+01	2.77E-04	1.80E-03		7.49E-07	2.85E-07	9.97E+01	9.99E+01
6.15E+00	3.00E+01	1.24E-03	7.65E-03		1.12E-05	5.94E-06	9.91E+01	9.95E+01
4.36E+00	3.00E+01	3.33E-04	1.45E-03		8.10E-06	1.37E-06	9.75E+01	9.86E+01
7.77E+00	3.00E+01	2.08E-03	1.61E-02		1.30E-05	1.06E-05	9.94E+01	9.95E+01
5.15E+00	3.00E+01	2.85E-03	1.46E-02		6.55E-05	4.11E-05	9.77E+01	9.86E+01
5.24E+00	3.00E+01	2.51E-03	1.51E-02		8.76E-05	2.31E-05	9.65E+01	9.91E+01
3.62E+00	3.00E+01	4.91E-04	1.78E-03		7.33E-06	6.84E-06	9.85E+01	9.86E+01
7.54E+00	3.00E+01	1.87E-03	1.41E-02		1.91E-05	9.05E-06	9.90E+01	9.95E+01
3.26E+00	3.00E+01	4.76E-03	1.55E-02		3.31E-04	3.61E-04	9.30E+01	9.24E+01
1.28E+01	3.00E+01	6.15E-03	7.93E-02		3.27E-05	5.05E-05	9.95E+01	9.92E+01
1.23E+01	3.00E+01	6.69E-03	8.23E-02	3.42E-04	4.60E-05	6.31E-05	9.93E+01	9.91E+01
1.26E+01	3.00E+01	6.07E-03	7.64E-02	3.42E-03	5.12E-05	6.63E-05	9.92E+01	9.89E+01
1.22E+01	3.00E+01	6.60E-03	8.04E-02	8.55E-03	8.99E-05	1.06E-04	9.86E+01	9.84E+01
4.12E+00	3.00E+01	4.68E-04	1.93E-03	8.78E-03	1.54E-04	5.46E-05	8.71E+01	8.83E+01
6.01E+00	3.00E+01	2.35E-03	1.41E-02	8.81E-03	9.40E-05	7.70E-05	9.60E+01	9.67E+01
5.06E+00	3.00E+01	2.81E-03	1.42E-02	8.90E-04	1.52E-04	4.99E-05	9.46E+01	9.82E+01
4.87E+00	3.00E+01	3.01E-03	1.47E-02	8.55E-03	3.47E-04	1.47E-04	8.85E+01	9.51E+01
4.45E+00	3.00E+01	3.26E-03	1.45E-02	1.69E-02	4.90E-04	3.15E-04	8.50E+01	9.03E+01
3.52E+00	3.00E+01	4.07E-03	1.43E-02	3.42E-02	1.37E-03	9.24E-04	6.64E+01	7.73E+01

*ret. retentate

**per. permeate

Metal, Calcium and/or Magnesium

Model Values Based on $Q=2.10 \pm 0.09$

calcium and/or magnesium in the presence and in the absence of added salt. In addition, Table 6 provides a comparison of the experimental as well as the ion-binding model values.

4.3.1 Effectiveness of PEUF using PSS for water softening. The PEUF runs performed at [PSS] to [total metal] ratios of 3.5 and 6.7 in the absence of added salt are shown in Figure 7. The percent rejection of total metal is plotted against the total metal concentration in the retentate. Total metal represents calcium plus magnesium. As the ratio of [PSS] to [metal] increases, the rejection increases. This is because an increase in the availability of the negatively charged sites on the PSS chains increases the magnitude of the PSS surface electrical potential and therefore enhances binding of the positively charged ions. It is also noted that at a constant ratio of [PSS] to [total metal], as the concentration of PSS and metal are reduced simultaneously, the concentration of metal in the permeate decreases, resulting in increased rejections, as predicted by the model (12). This effect is especially useful in a situation where a low concentration of hardness is present in water and ultrapure water is desired.

Figure 8 shows the effect of [PSS] to [total metal] ratio on rejection. The theoretical stoichiometric ratio of PSS to either calcium or magnesium is 2 to 1. The actual ratio needed for effective ultrafiltration may be higher than the stoichiometric ratio. In this study, a PSS to metal ratio of at least 6 is required to obtain rejections higher than 99%. The calcium and magnesium rejections obtained are as high as 99.71% for a PSS to

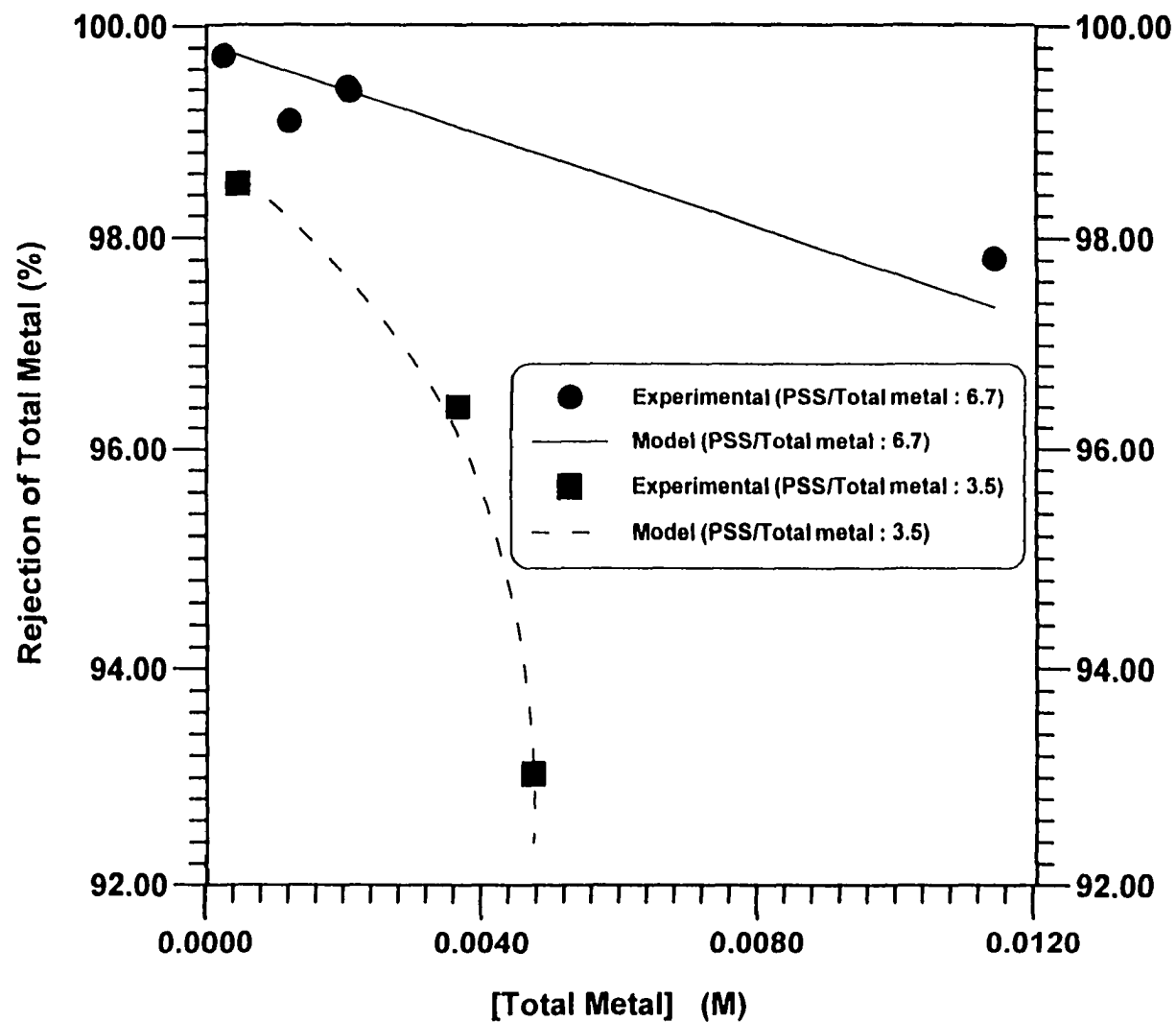


Figure 7: Rejection of total metal versus total metal present in the retentate in the absence of added salt
PSS/Total metal ratios of 3.5 and 6.7

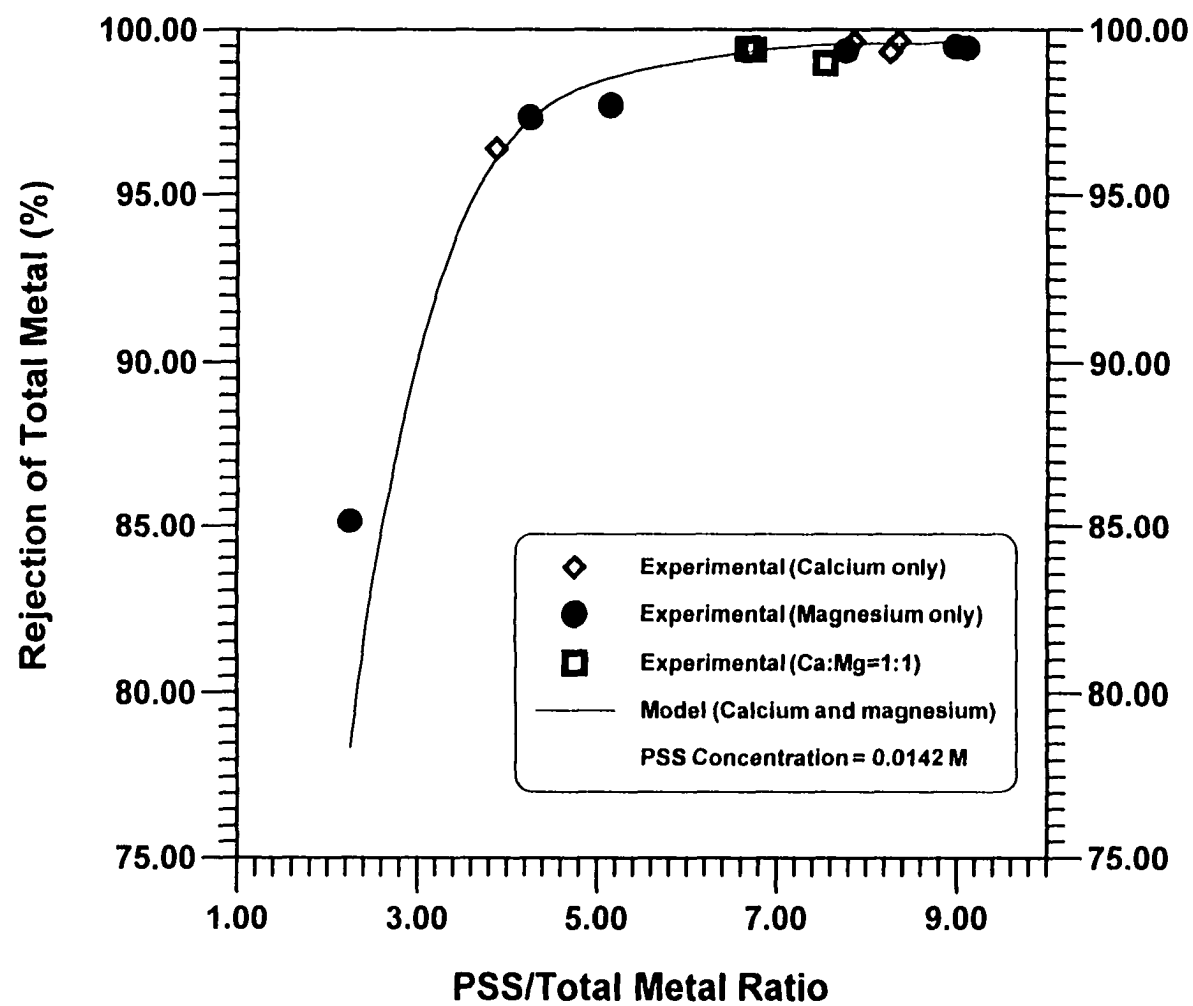


Figure 8: Rejection of total metal as a function of PSS/total metal ratio at a constant PSS concentration.

metal ratio of 28.6 and as low as 29.27% for a PSS to metal ratio of 0.65. Also, under similar conditions calcium and magnesium are removed with the same rejection. Rejections predicted by the model agree quite well with the observed rejections.

4.3.2 Effect of added salt. The ionic strength of the aqueous stream greatly affects the effectiveness of the PEUF process. Increasing the salt concentration and therefore the ionic strength of the stream leads to compression of the electric double layer and therefore the electrostatic attraction between the positively charged calcium and magnesium ions and the negatively charged PSS ions is greatly reduced. As a result, the unbound calcium and magnesium in the stream pass through the ultrafiltration membrane leading to poor rejection of these ions. Figure 9 shows the effect of salt concentration on the permeate calcium concentration. As the salt concentration is increased, the concentration of metal in the permeate increases. In the presence of 2000 ppm (0.0342 M) of sodium chloride, calcium rejection is only 66%, while in the presence of only 20 ppm (0.00034 M) of sodium chloride, a rejection of nearly 99% is possible. At a higher concentration of PSS, however, better rejections are possible. The presence of salt also causes deviation between the model predictions and the experimental results. This is especially true at higher salt concentrations and lower PSS to metal ratio. Deviations from the model in the presence of salt could be somewhat decreased by introducing a parameter explicitly accounting for added monovalent salt concentration (12). Activity coefficient correlations might also be made to improve the correlation of data.

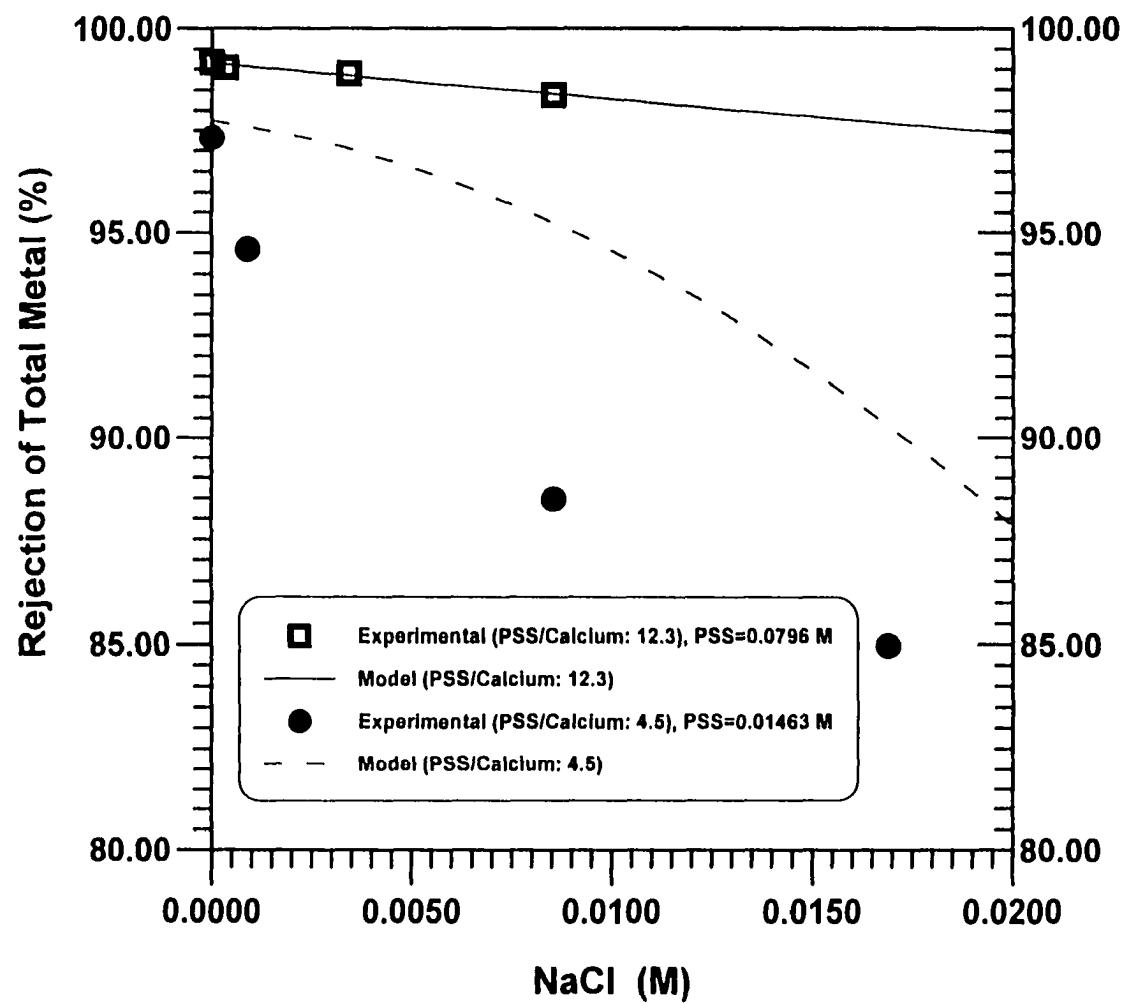


Figure9: Effect of added NaCl concentration on permeate metal concentration.

4.3.3 Effect of temperature. The PEUF process was run at PSS to total metal ratio of 6.7 and 9.1 at 5.5°C, 15°C, and, 30°C. As shown in Figure 10, temperature has negligible effect on the metal concentration in the permeate at these ratios. The flux of the aqueous stream of the permeate, however, was reduced from 89.8 L/hr.m² at 30°C to 49.6 L/hr.m² at 5.5°C as shown in Figure 11. The decrease in flux at low temperatures may be attributed to the increased viscosity of the aqueous stream as well as contraction of the ultrafiltration membrane pores.

4.3.4 Effectiveness of ion-binding model. A single adjustable parameter, Q , is required to predict permeate concentrations of the divalent metal ions from the known values of the metal and polyelectrolyte ion concentrations in the retentate. By means of a non-linear least squares regression analysis (6,12) it is possible to obtain the optimum or best fit value of Q for fitting the entire collection of data in Table 6. The value of Q is determined to be 2.10 ± 0.09 . This value corresponds to a mean relative error of 42.8% in the predictions. This error is partly due to the wide range of PSS, metal, and salt concentrations employed in the experimental runs. The inclusion of data at high salt concentrations in the analysis also contributes greatly to the overall error as is indicated by the relatively large deviation between experimental results and model predictions in Figure 9.

The model is highly effective in predicting the permeate concentration in the absence of added salt and in the presence of low concentrations of added salt.

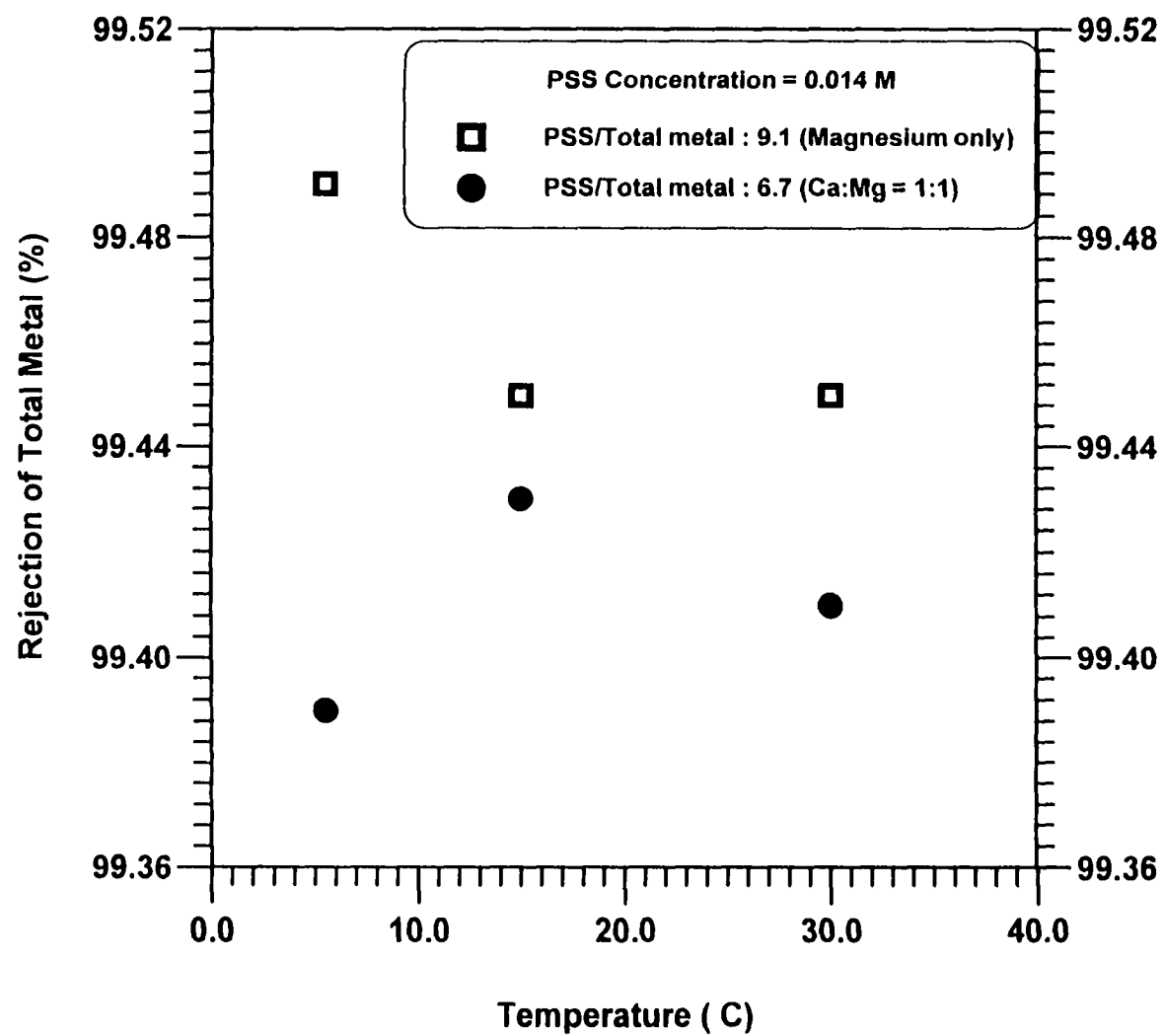


Figure 10: Effect of temperature on total metal rejection

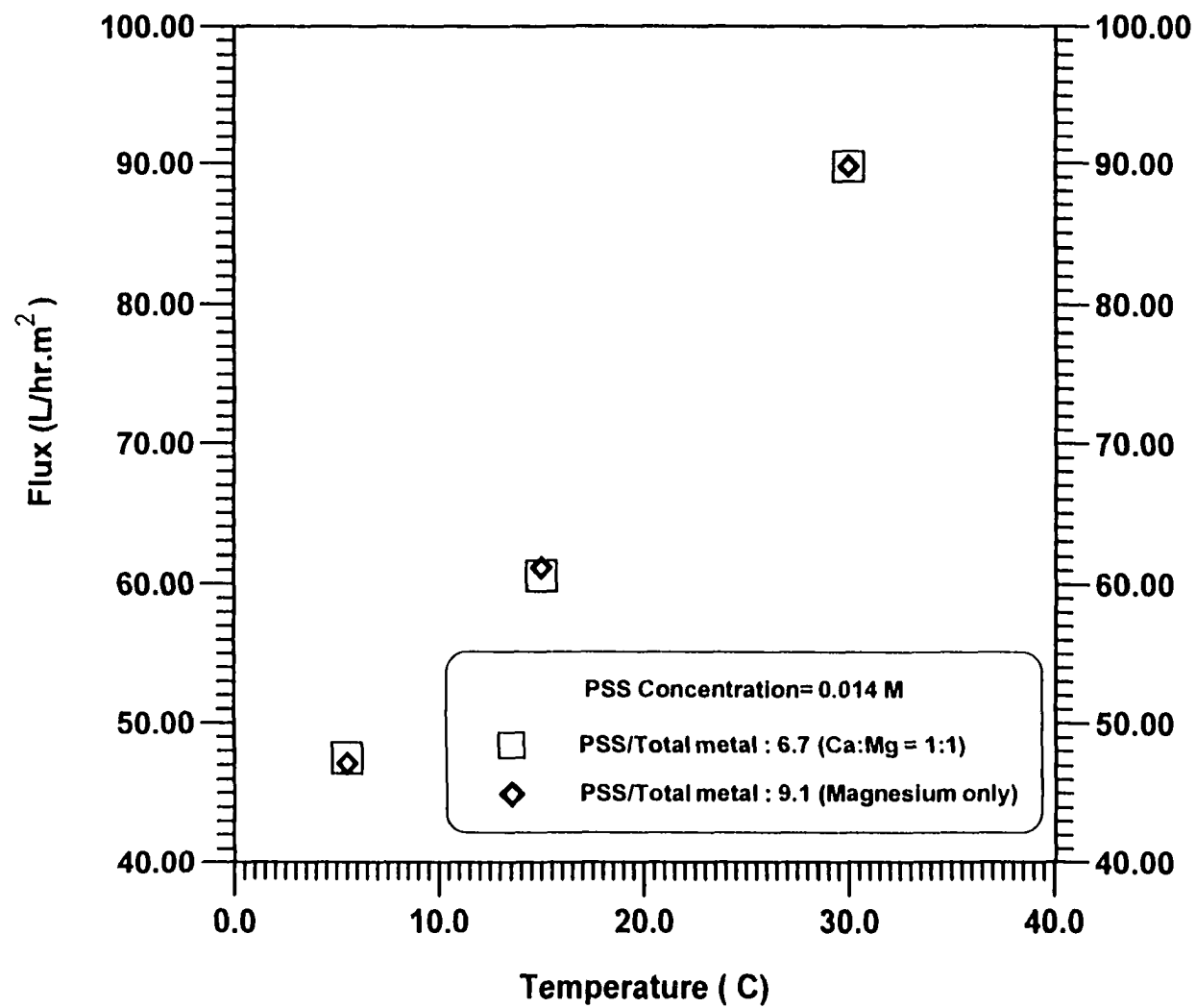


Figure 11: Effect of temperature on PEUF flux.

4.3.5 Effectiveness of PEUF using PMVEMA for water softening. The results of the PEUF runs using PMVEMA and calcium are shown in Table 7. Runs were performed at PMVEMA to calcium ratios of 1:1, 2:1, and 10:1 at two different pH values. PMVEMA has two carboxyl groups each of which can be hydrolyzed. PMVEMA solution has a natural pH of about 2.7-3.1. As shown in Figure 12, the use of PMVEMA at a pH of 2.8 results in very poor rejections of from 32.1 to 59.5%. However, as the pH is increased to about 6.8, the two carboxyl groups are hydrolyzed resulting in the PMVEMA solution having a much better affinity for the calcium ions. This results in better rejection of the calcium ions. It is also worth noting that at a ratio of 2:1, the PMVEMA is already very effective in rejecting close to 97 % of the calcium ions. To achieve such a rejection with PSS, a ratio of PSS to calcium of nearly 4 is required. Therefore, considering only its binding effectiveness, PMVEMA is a superior polyelectrolyte compared to PSS. However, its rather quick degradation and toxicity make it an unlikely candidate for the PEUF process.

4.3.6 Effect of other parameters. Other parameters of importance in ultrafiltration are membrane pore size, pressure, and solute and colloid concentration. These parameters were not studied in this work. However, other investigators (9) have found that as the pore size of the membrane is increased, so does the flux across the membrane. Additionally an increase in pressure results in an increase in flux (5). In the non-gel polarized regime, an increase in pressure generally has no detrimental effect on the flux or permeate purity.

Table 7: PEUF runs using Gantrez and calcium. All concentrations in molarity (M).

Concentration Calcium	Gantrez/Total Metal Ratio	pH	Temp(C)	Metal,ret*	Gantrez,ret	Metal,per** Experimental	%Rejection Experimental
5.00E-03	1	2.81	30	6.14E-03	1.22E-02	4.17E-03	32.11
1.00E-03	2	2.88	30	6.51E-03	3.26E-02	3.89E-03	40.23
5.00E-03	10	2.9	30	1.51E-03	2.34E-02	6.11E-04	59.5
5.00E-03	1	6.8	30	1.11E-02	1.29E-03	1.20E-03	89.19
5.00E-03	2	6.84	30	1.37E-02	2.47E-02	3.74E-04	97.27
1.00E-03	10	6.88	30	2.42E-03	2.35E-02	9.98E-06	99.59

*ret: retentate

**per: permeate

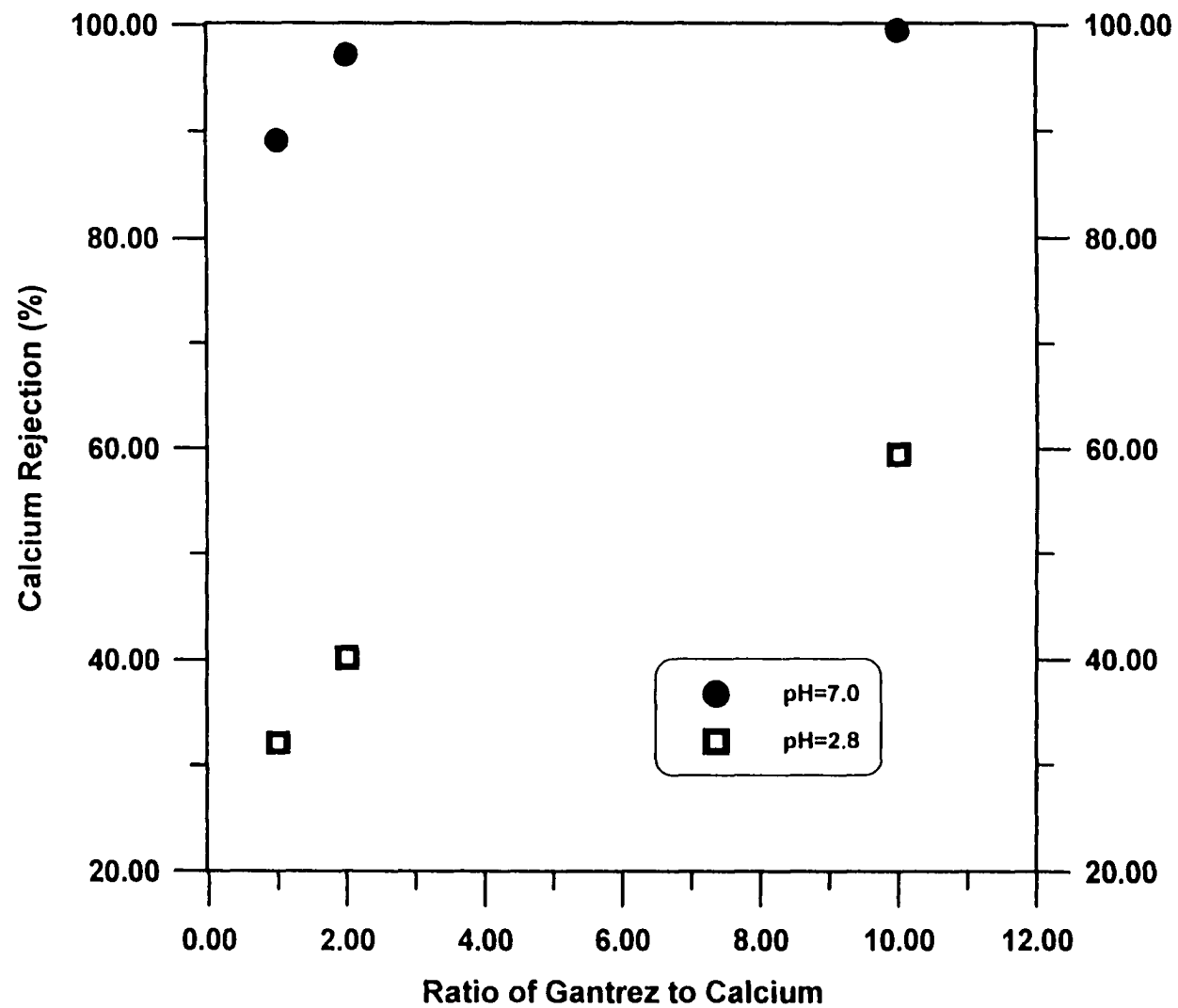


Figure 12: Effect of initial pH of Gantrez on the rejection of calcium

4.4 Conclusions

1. The polyelectrolyte-enhanced ultrafiltration process, operating at a relatively low pressure and temperature, is highly effective in the removal of hardness from aqueous streams resulting in rejection of up to 99.7%.
2. Increasing the PSS or PMVEMA to metal ratio leads to higher rejections.
3. Using PSS as the polyelectrolyte, calcium and magnesium are removed with the same rejection under similar conditions.
4. At constant ratio of PSS to total metal, decreasing the PSS and metal concentration simultaneously leads to lower metal concentration in the permeate and therefore higher rejection.
5. Increasing the pH of the PMVEMA solution from 2.8 to approximately 7 increases calcium binding and therefore rejection from 32.1 - 59.5% to 89.2 - 99.5% for the PEUF process.
6. PEUF is also effective in hardness removal in the presence of very low concentration of added salt. At higher salt concentrations, however, the rejection decreases dramatically.
7. Moderate temperature changes have a negligible effect on the rejection of calcium and magnesium. The permeate flux, however, is reduced at a lower temperature.
8. The ion binding model provides an excellent prediction of metal ion concentrations in the permeate in the absence of added salt or in the presence of a low concentration of

salt. The presence of high salt concentration, however, results in moderate to extreme deviations of the model predictions from observed data.

This study has demonstrated the technical feasibility of PEUF to soften water.

Chapter 5: RECOVERY OF POLYELECTROLYTE FROM POLYELECTROLYTE-ENHANCED ULTRAFILTRATION (PEUF) FOR REUSE.

5.1 Introduction

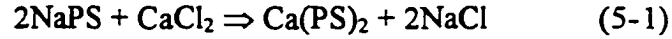
There are numerous applications requiring removal of multivalent ions and/or nonionic organics from water. These include clean up of polluted wastewater or groundwater and purification of drinking water. Colloid-enhanced ultrafiltration (CEUF) processes have the advantage of operating at relatively low pressures and temperatures resulting in excellent rejection of multivalent metals and organics while reducing the initial waste volume significantly (1-17). Due to the relatively high cost of the colloid, its recovery is imperative in order to make the CEUF process economically feasible.

This chapter investigates the regeneration and reuse of the polyelectrolytes used in for water softening. The two types of polyelectrolytes used in this study were PSS and PMVEMA which have proven to be effective in PEUF and are commercially available. This study helps to identify problems associated with selection and use of a polyelectrolyte.

5.2 Experimental Results

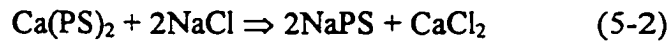
5.2.1 Recovery of PSS

In the PEUF softening process using PSS as the colloid, calcium ion binds to the polystyrene sulfonate (PS) according to:



The polyelectrolyte solution is allowed to pass through an ultrafiltration membrane. The polyelectrolyte and the bound calcium ions are retained by the membrane while a relatively pure stream of water passes through the membrane. The retentate is then treated to regenerate the spent polyelectrolyte solution. The following describe the regeneration processes investigated in this study.

5.2.1.1 Addition of NaCl. In this process, excess NaCl was added to the calcium polystyrene sulfonate solution to replace the Ca^{2+} ions according to:



The solution was washed with distilled deionized water to remove the excess NaCl and calcium ions from the solution. Concentrations of NaCl in excess of stoichiometric ratio were needed due to the fact that Ca^{2+} and Mg^{2+} ions have a higher electronegativity and have greater tendency to bind to the polyelectrolyte than Na^+ . Therefore, compared to sodium ions, calcium and magnesium ions have a strong attraction for the polyelectrolyte. As a result, excess amounts of sodium chloride was needed to saturate the solution and force the calcium and magnesium ions away from the PSS solution. Results are shown in Table 8.

Table 8: Use of NaCl for the recovery of PSS.

[PSS]	[Calcium]	[PSS]/[Ca ²⁺]	[NaCl]	[NaCl]/[Ca ²⁺]	PSS Recovered (%)	Ca ²⁺ Rejection(%) w/regenerated PSS	Ca ²⁺ Rejection (%) w/fresh PSS
0.0100	0.0028	3.57	0.0045	1.61	99.96	93.0	97.0
0.0152	0.0028	5.47	0.014	4.96	99.89	98.4	99.0
0.0152	0.0027	5.62	0.050	18.6	99.90	98.0	99.0

5.2.1.2 Addition of HCl. In this process, excess HCl acts to replace the calcium ion bound to the calcium polystyrene sulfonate with a hydrogen ion according to:



As with NaCl, the solution was rinsed with distilled deionized water to remove the calcium chloride and excess HCl from the solution. The solution pH was increased back to 5 by adding NaOH. The regenerated PSS solution was then used for another PEUF process. Table 9 shows the results of PSS regeneration using HCl.

5.2.1.3 Addition of Na₂CO₃. The addition of Na₂CO₃ to the calcium polystyrene sulfonate complex resulted in the precipitation of calcium carbonate according to the following reaction:



The calcium carbonate precipitates due to its low solubility product ($K_{sp} = 4.96 \times 10^{-9}$ at 25°C) (47). The precipitate was removed by centrifuging the solution and removing the supernatant from the solution. The supernatant was analyzed for PSS and Ca²⁺ concentration. As shown in Table 10, it was observed that there was a decrease of about 5% in the concentration of PSS. One possibility is that the PSS has adsorbed onto the calcium carbonate precipitate. Addition of sodium carbonate caused an increase in the pH of the solution. The pH was adjusted back to 5 by addition of HCl. The solution was then rinsed with distilled deionized water to remove the excess sodium carbonate from the solution.

Table 9: Use of HCl for the recovery of PSS.

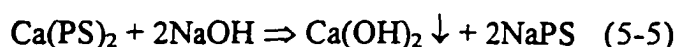
[PSS]	[Calcium]	[PSS]/[Ca ²⁺]	pH after HCl addition	[HCl]/[Ca ²⁺]	PSS Recovered (%)	Ca ²⁺ Rejection (%) w/ regenerated PSS	Ca ²⁺ Rejection (%) w/fresh PSS
0.0149	0.00276	5.4	1.62	2.04	99.87	79.72	98.9
0.0126	0.00233	5.02	1.33	6.64	99.73	86.29	98.5
0.0148	0.00275	5.38	1.08	9.01	99.78	98.62	98.9
0.0186	0.00244	7.61	1.20	13.54	99.93	92.94	99.5
0.0142	0.00234	6.08	1.24	14.17	99.82	93.88	99.1
0.0162	0.00229	7.07	0.91	24.85	99.90	90.94	99.3

Table 10: The use of Na_2CO_3 for the recovery of PSS.

[PSS]	[Calcium]	[PSS]/[Ca ²⁺]	[Na ₂ CO ₃]	[Na ₂ CO ₃]/[Ca ²⁺]	PSS Recovered (%)	Ca ²⁺ Rejection (%) w/ regenerated PSS	Ca ²⁺ Rejection (%) w/ fresh PSS
0.0099	0.0027	3.67	0.0067	2.47	96.8	89.62	96.5
0.0409	0.0115	3.56	0.0402	3.49	93.4	92.6	96.5
0.0500	0.0052	9.54	0.0254	4.85	96.2	98.6	99.7
0.0123	0.0025	4.92	0.0131	5.23	94.9	98.8	98.6

Previous work (48) has shown the effectiveness of precipitation of the contaminant and regeneration of the polyelectrolyte in a system containing a cationic polyelectrolyte, poly(dimethyl ammonium chloride) or PDMDAAC and negatively charged ions, CrO_4^{2-} .

5.2.1.4 Addition of NaOH. One of the methods tested was the addition of NaOH to the calcium polystyrene sulfonated to cause precipitation of calcium hydroxide. The reaction would be as follows:



Since Ca(OH)_2 has a low solubility product ($K_{sp} = 4.68 \times 10^{-6}$ at 25°C) (47), it would precipitate and sodium would replace the calcium as bound counterion on the polyelectrolyte. Table 11 shows the results of adding NaOH to the calcium polystyrene sulfonate. Unacceptably large concentrations of NaOH had to be present in the solution to cause complete precipitation of the calcium. Therefore, other methods of PSS recovery were pursued.

5.2.1.5 Addition of Na_2HPO_4 . One of the methods used to recover the PSS was to added sodium hydrogen phosphate to the Ca(PS)_2 complex. The calcium bound to the styrene sulfonate would complex with the phosphate and precipitate ($K_{sp, \text{Ca}_3(\text{PO}_4)_2} = 2.07 \times 10^{-33}$ at 25°C) (47) according to:



The regenerated PSS solution was then washed with distilled deionized water to remove excess phosphate and calcium ions from the solution. The washing of the polyelectrolyte

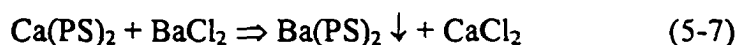
solution entailed repeated additions of distilled deionized water to the solution and filtering the solution through an ultrafiltration membrane. In this process, any unbound

Table 11: Use of NaOH for the recovery of PSS.

[PSS]	[Calcium]	[PSS]/[Calcium]	[NaOH]/[Calcium]	% Calcium precipitated
0.0085	0.0065	1.31	19.2	27.7
0.0085	0.0065	1.31	44.3	76.2
0.0085	0.0065	1.31	64.9	84.4
0.0085	0.0065	1.31	102.8	89.3

ions would also pass through the membrane and leave a relatively pure PSS solution. This regeneration method required that excessive amounts of phosphate to be used to remove the bound calcium ions. In washing the regenerated PSS solution, the excess phosphate would have to be disposed of properly since direct emission of phosphate into the environment is not an acceptable option. Therefore, it was decided this method would not be pursued for the recovery of PSS.

5.2.1.6 Addition of BaCl₂ followed by addition of Na₃PO₄. Another method used for the recovery of PSS was to add BaCl₂ to the Ca(PS)₂ complex. This would result in complexation and precipitation of Ba²⁺ with styrene sulfonate and leave the calcium chloride in solution in the supernatant according to:



The PSS was then recovered by addition of sodium phosphate, Na_3PO_4 to precipitate barium phosphate according to:



Addition of barium chloride to the calcium/styrene sulfonate complex resulted in a white precipitate. The supernatant was analyzed for the PSS concentration. The difference in PSS concentration before and after addition of barium chloride was considered to be due to the incorporation of PSS in the white precipitate. The results shown in Table 12 were obtained.

Table 12: Addition of BaCl_2 followed by addition of Na_3PO_4 for the recovery of PSS.

[BaCl_2]	PSS precipitated (%)	[Barium] / [PSS]
0.100	88.7	10
0.164	90.0	16.4
0.330	92.5	33
0.679	95.0	68

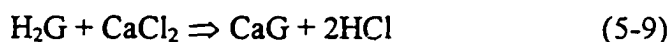
It was expected that upon addition of sodium phosphate, barium would bind with the phosphate and precipitate due to the low solubility product of barium phosphate ($K_{sp}=3.4 \times 10^{-23}$ (between 18°C and 25°C)) (49). This would have allowed the PSS to dissolve into solution and to be used again in the PEUF process. However it was observed that the PSS did not dissolve to any appreciable degree. Therefore, nitric acid was added to the PSS solution to improve dissolution of the PSS. However, upon addition of nitric acid, the PSS could no longer be detected on the UV

spectrophotometer. It is possible that the nitric acid might have damaged the PSS structure. Due to problems with dissolution of PSS, this method of PSS recovery was not pursued any further.

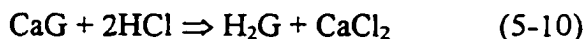
5.2.2 Recovery of PMVEMA

Due to the problems with degradation of the PMVEMA, the use and recovery of PMVEMA was not investigated extensively. Only one method of recovery by addition of HCl was studied to show that generally regeneration and reuse of PMVEMA was possible.

Using PMVEMA as the colloid in the PEUF softening process, calcium ions bind to PMVEMA(G) according to:

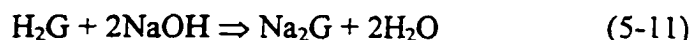


5.2.2.1 Addition of HCl. Addition of HCl to the used calcium/PMVEMA complex results in the following reaction:



The results show that lowering the pH of the retentate to 1.0 and washing it with distilled deionized water is highly effective in regeneration of the PMVEMA. The retentate solution was washed six times with distilled deionized water. The permeate sample after each wash was analyzed to insure that metal concentration had reduced

considerably. The permeate showed lowering of calcium concentration from 175 ppm of calcium to 112, 100, 63, 45, 26, and 20 ppm, respectively. In general, it is almost impossible to regenerate the polyelectrolyte completely to its initial capacity. Therefore, after six wash cycles, the retentate was removed and tested for another PEUF run. 99.8% of the PMVEMA was recovered. The pH of the retentate was adjusted to about 7 by addition of NaOH according to the following reaction:



The regenerated PMVEMA used in the next PEUF run resulted in excellent rejections. With an initial calcium concentration of 376 ppm, the permeate concentration of calcium ranged from 9 to 6 ppm, resulting in calcium rejection of more than 99%. It is important to note that rejection values using regenerated PMVEMA are not as high as those obtained using fresh PMVEMA (up to 99.6%). In spite of this fact, rejection of 99.12% for regenerated PMVEMA versus that for fresh PMVEMA is excellent.

An important aspect of all of the recovery methods investigated in this study is that excessive amounts of additives must be added to recover the polyelectrolyte. As a result the regenerated solution must be washed with distilled deionized water to remove excess additive from the solution. However, it is not possible to achieve the same rejections after addition of the additive since even with excessive washing of the polyelectrolyte solution, the additive is still present in small concentrations in the solution. In addition, a residual amount of the hardness ions will remain bound to the polyelectrolyte.

Therefore, it is almost impossible to attain the initial exchange capacity of the polyelectrolyte.

5.3 Conclusions

The cost of colloid is generally a major part of the PEUF process. For example, the cost of PSS is \$3.39/lb as quoted by National Starch and Chemical Co. and the cost of PMVEMA as quoted by GAF Chemical Corp. is \$4.03/lb. The three recovery methods which offered the greatest promise were addition of NaCl or HCl to ion exchange with the hardness ions on the polyelectrolyte, and Na₂CO₃ for precipitation of hardness ions as CaCO₃ or MgCO₃. The purpose was to recover as much of the PSS as possible and to achieve maximum hardness rejection using the regenerated PSS. An excess amount of NaCl, HCl, or Na₂CO₃ had to be added to the spent PSS solution to achieve its regeneration.

Figure 13 shows the effect of NaCl/hardness, HCl/hardness, and Na₂CO₃/hardness ratio on hardness metal rejection using the regenerated PSS. The optimum ratios of NaCl/hardness, HCl/hardness, and Na₂CO₃/hardness for PSS regeneration were 5, 9, and 5.3, respectively. The optimum ratio is the smallest ratio of the added NaCl, HCl, or Na₂CO₃ to the hardness ion which results in the largest hardness rejection. For each case, hardness rejection using the regenerated PSS was not improved greatly or was in fact reduced beyond the optimum ratio of added electrolyte/hardness. The decrease in rejection beyond the optimum ratio could be due to an insufficient rinsing of the

regenerated PSS solution prior to its repeated use. The regenerated PSS resulted in approximately 99% rejection of hardness ions when PSS was regenerated with NaCl, HCl, and Na_2CO_3 . The PSS regeneration might be improved further by more effective rinsing of the PSS in a continuous process. The maximum rejection obtained using fresh polyelectrolyte (99.7%) is shown on Figure 13 by a dashed line.

With NaCl and HCl addition, almost complete recovery of the PSS was possible whereas with Na_2CO_3 addition, only about 95% of the PSS was recovered. The PSS loss in the case of Na_2CO_3 addition may be due to the adsorption of PSS on the calcium carbonate and/or magnesium carbonate precipitate. Figure 14 shows the percent of PSS recovered as a function of molar ratio of additive added.

The feasibility for recovery of PMVEMA was also shown in this study. The recovered PMVEMA was effective in the rejection of more than 99% of the hardness ions.

It is important to note that rejection of hardness ions using regenerated polyelectrolyte is generally lower than when using fresh polyelectrolyte. However, the rejections are still close to 99%. Therefore, this study suggests that regenerated polyelectrolyte is effective in rejection of hardness ions.

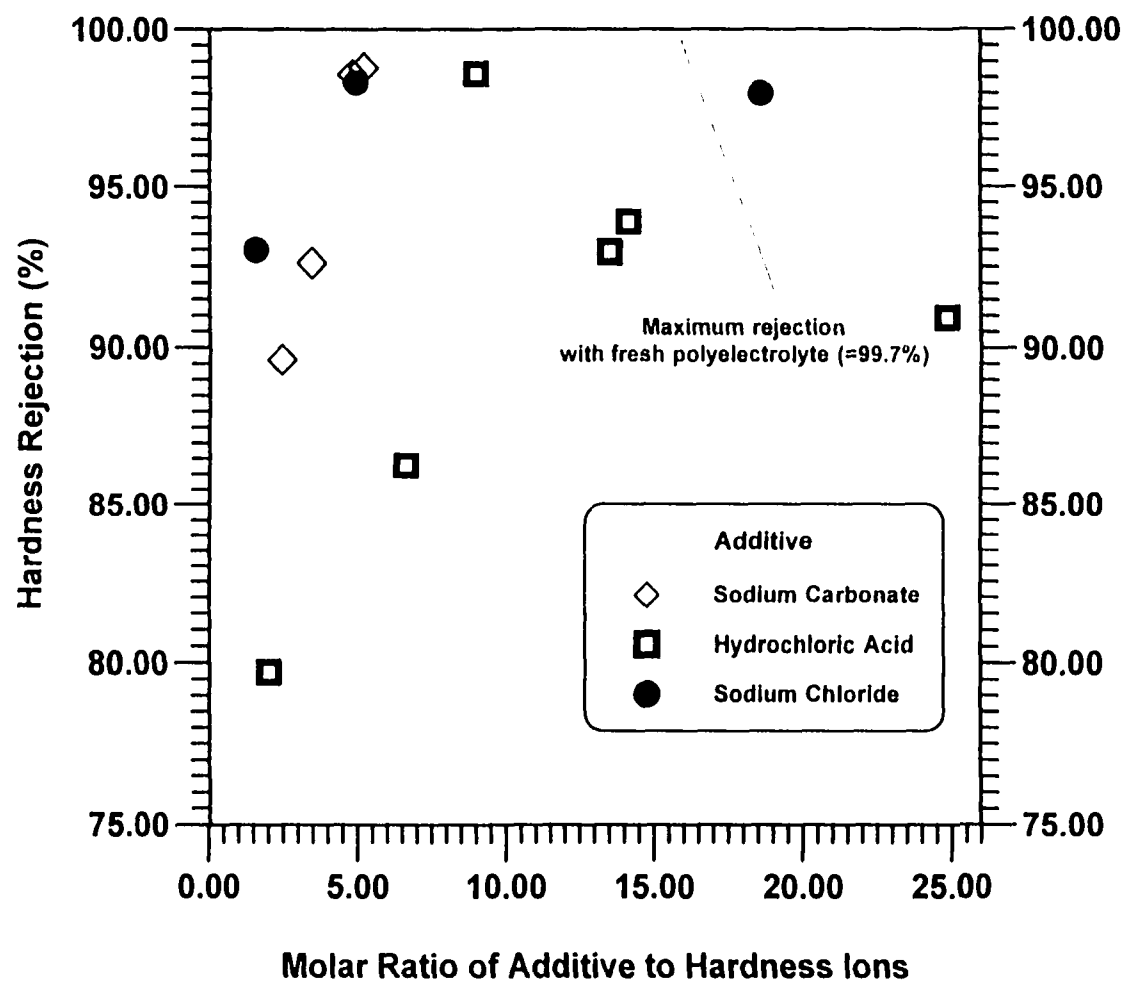


Figure 13: Effect of amount of additive on hardness rejection using regenerated PSS for PEUF.

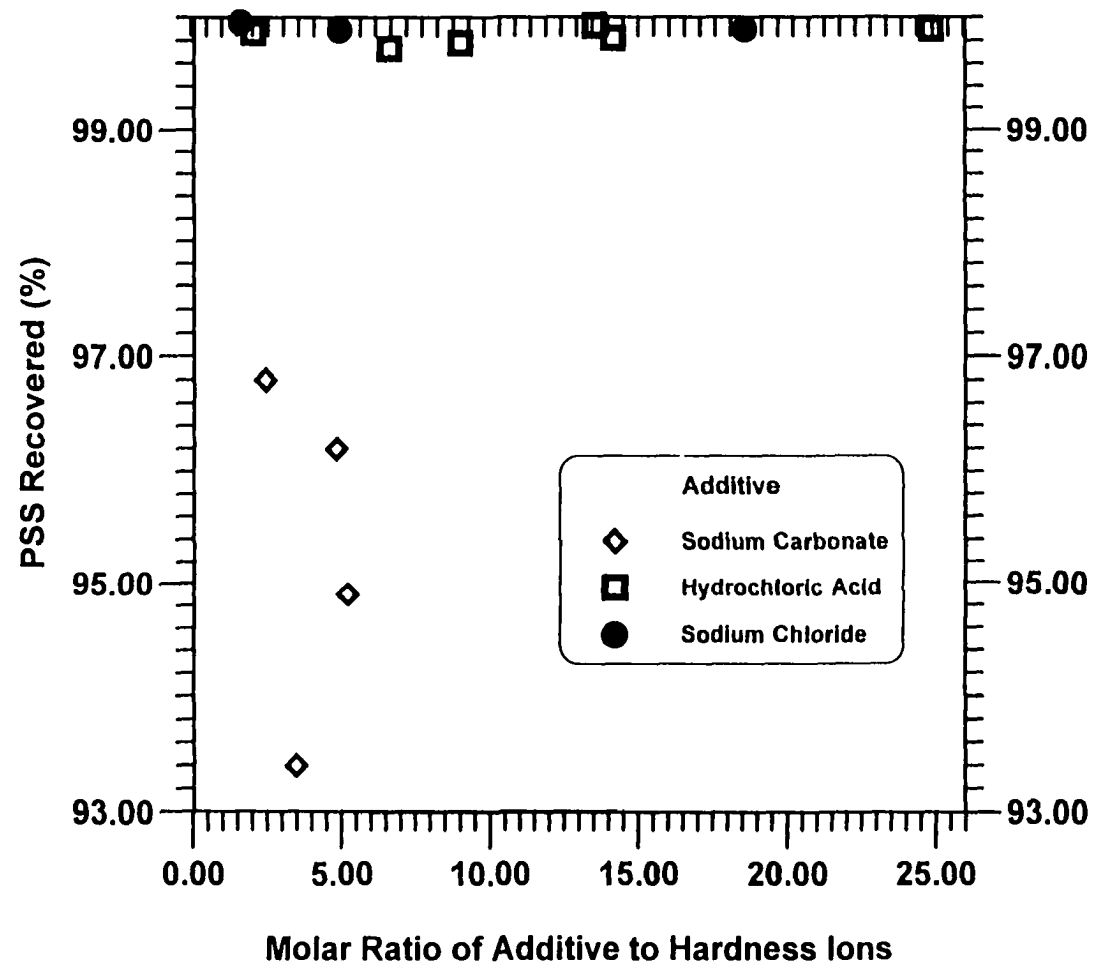


Figure 14: Effect of amount of additive on PSS Recovery.

Chapter 6: ECONOMIC FEASIBILITY STUDY OF POLYELECTROLYTE-ENHANCED ULTRAFILTRATION (PEUF) FOR WATER SOFTENING.

6.1 Introduction

The colloid-enhanced ultrafiltration processes (CEUF) have proven their effectiveness for the removal of dissolved organics and multivalent ions from aqueous streams. However, to determine the commercialization potential of these processes, an extensive economic analysis must be performed to compare these processes with other conventional processes presently used in the industry. A previous economic analysis (15) has shown that micellar-enhanced ultrafiltration (MEUF), one form of CEUF, is nearly competitive with other conventional methods for the removal of chlorinated hydrocarbons from aqueous streams.

The purpose of this study is to determine the economic effectiveness of polyelectrolyte-enhanced ultrafiltration (PEUF), another form of CEUF, as an alternative method for the removal of hardness ions (calcium and magnesium) from water. In this study, the PEUF ultrafiltration data are used with the polymer recovery data to perform an economic analysis of this water softening process. Results are compared to traditional water softening techniques. This study develops a computer model to optimize the PEUF process based on the best hardness ion rejection and most effective polyelectrolyte recovery method to determine bottlenecks within the PEUF system and suggests new areas of research and development. Under some conditions, the PEUF process is shown

to be economically competitive with lime softening. It should be noted that the use of PMVEMA for the economic analysis was not investigated. This is due to reasons mentioned in Chapter 4. This analysis uses only the PSS data for the PEUF process.

6.2 Process Flow Diagrams For PEUF Water Softening.

Three continuous water softening processes using PEUF with different schemes for recovery of the polyelectrolyte, polystyrene sodium sulfonate (PSS), were studied.

6.2.1 NaCl addition for recovery of the PSS (PEUF/NaCl). In this process shown in Figure 15, the stream containing hardness ions and PSS is filtered under pressure through a bank of spiral wound ultrafiltration membrane modules arranged in parallel, producing a softened water stream as permeate. Each module contains several vessels as needed to accommodate the required product flowrate and each vessel contains two to four membranes. The modules are set up such that at any time one is being bypassed to be cleaned while the remaining modules are used in the ultrafiltration process. The purpose of the cleaning is to reduce membrane fouling and therefore extend its lifetime as well as minimize resistance to flux across the membrane. The cleaning also reduces contamination of treated water due to the presence of impurities such as bacteria on the membrane [27,33]. The cleaning is done by periodic backwashing as well as forward flushing of the membranes with proper chemicals such as chlorine from a chemical tank as necessary.

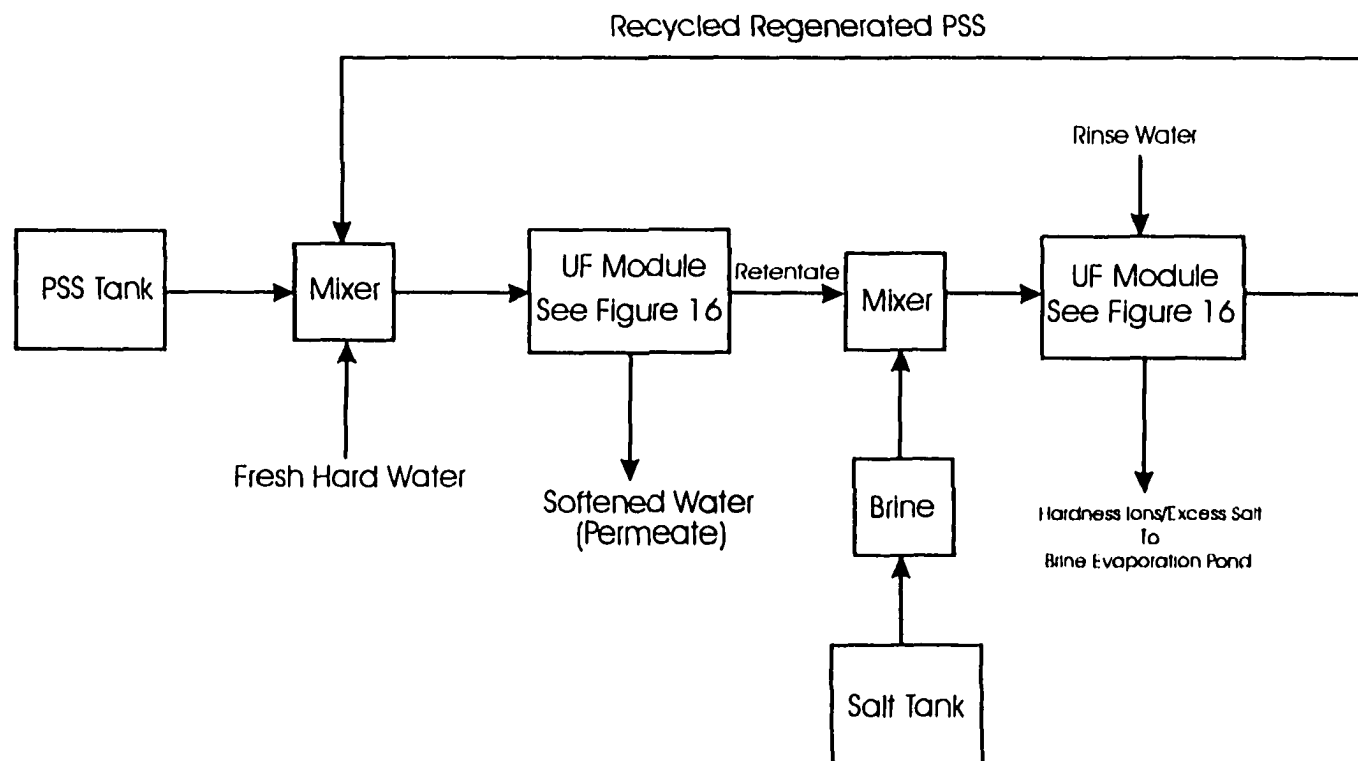


Figure 15: PEUF with PSS regeneration using NaCl.

Figure 16 shows the schematic of an ultrafiltration module. The use of spiral wound membranes in preference to other membrane configurations is due to their relatively low cost, good flux, and low membrane fouling (27). The fraction of feed water recovered is controlled by adjusting the recirculation rate (rate at which retentate is recycled back into the feed stream). The PSS/hardness ion rich retentate stream goes to a PSS recovery step where it mixes with an excess amount of brine solution in a PVC static mixer. The brine is prepared in a tank by a metering pump at a predetermined rate. The sodium ions of the salt replace the calcium and magnesium ions bound to the PSS. The stream is then filtered through a second ultrafiltration unit, where the PSS solution is rinsed with water. The softening of the hard water as well as rinsing of the PSS/salt stream could also be achieved in a single UF unit, but the process would then be batch, not continuous. In order to have a continuous process, the second UF unit is added into the envisioned process. The calcium and magnesium, as well as excess sodium ions, leave in the permeate while the regenerated PSS is recycled and mixed in a static mixer with fresh hard water feed as well as fresh PSS to account for PSS lost through the UF membrane. The permeate leaving the second UF unit, where PSS is rinsed, is sent to a brine evaporation lagoon for final disposal.

6.2.2 HCl addition for recovery of the PSS (PEUF/HCl). As seen in Figure 17, this process is similar to the PEUF/NaCl addition, except for the use of HCl instead of NaCl. After the PSS/hardness ion rich retentate stream leaves the UF unit, it is mixed with HCl in a static mixer where hydrogen ions replace the calcium and magnesium ions. This stream is then rinsed with water in a second UF unit where the calcium, magnesium

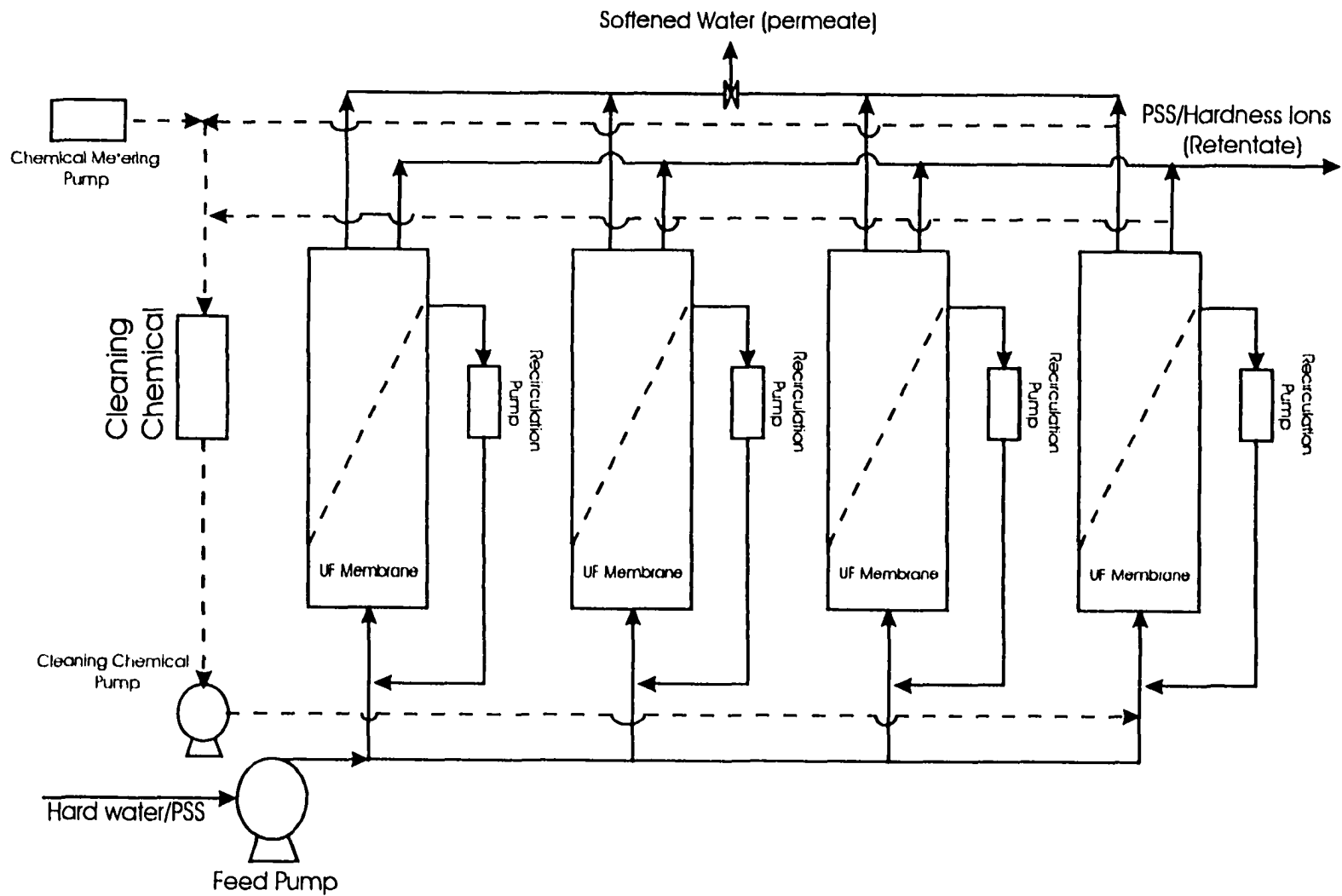


Figure 16: Schematic of ultrafiltration module with chemical cleaning cycle.

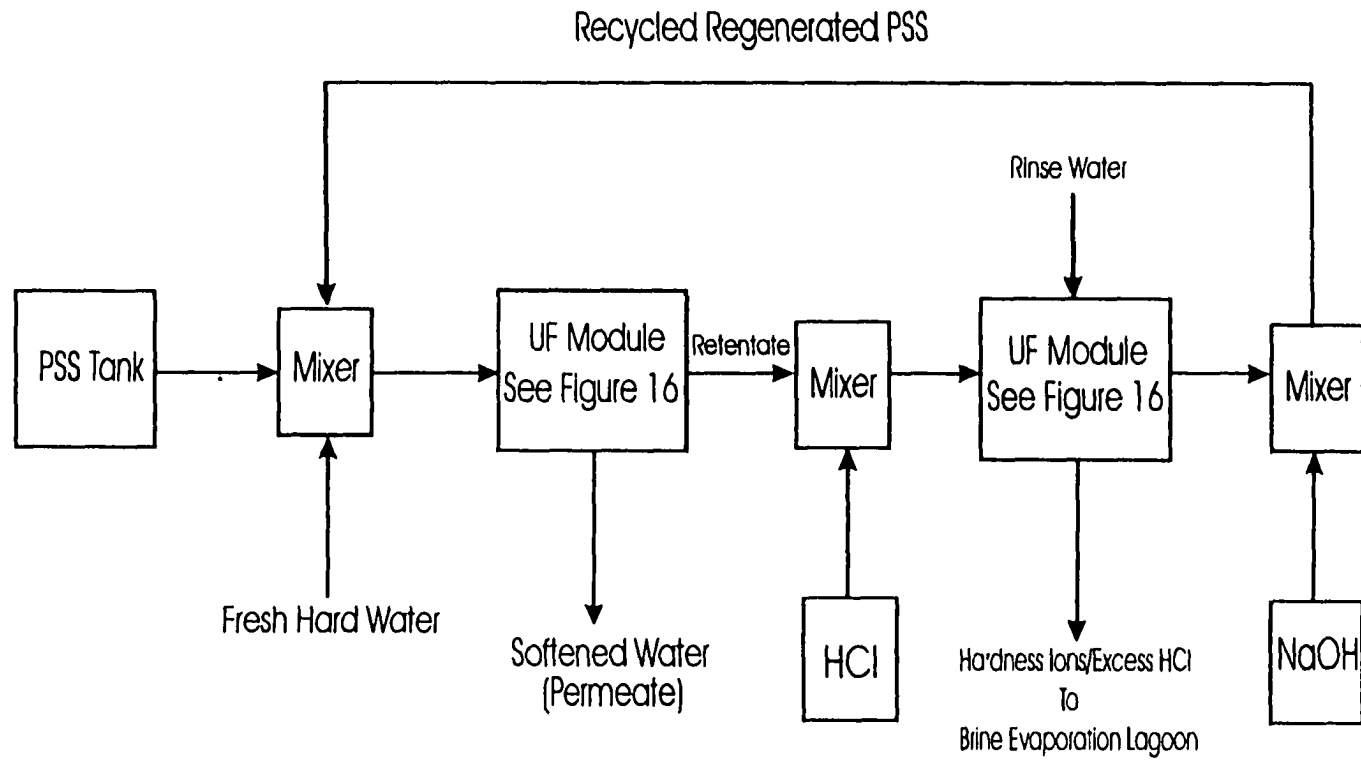


Figure 17: PEUF with PSS regeneration using HCl.

and excess HCl go through the membrane and are disposed of in a brine evaporation lagoon. The PSS in the retentate stream is mixed with sodium hydroxide in a static mixer to adjust its pH to about 5. The regenerated PSS stream is then mixed with fresh hard water feed and fresh PSS in a static mixer.

6.2.3 Na_2CO_3 addition for recovery of the PSS (PEUF/ Na_2CO_3). In this process, shown in Figure 18, water containing hardness ions is mixed with fresh and recycled PSS in a static mixer. The solution goes through an ultrafiltration module resulting in a softened water stream and a concentrated PSS/hardness ion stream. The retentate goes to a static mixer where it is mixed with excess sodium carbonate; sodium ions replace calcium and magnesium ions leading to precipitation of calcium carbonate and magnesium carbonate. The stream containing the precipitated ions goes through a clarifier where coagulants such as alum are added to the calcium carbonate/magnesium carbonate crystals to aid in settling of the precipitate. A very small fraction of the PSS also settles with the precipitate. The stream containing the regenerated PSS goes to a static mixer where it mixes with HCl to adjust its pH back to approximately 5. The regenerated PSS stream is then mixed with fresh hard water feed and fresh PSS in a static mixer. The fresh PSS added accounts for PSS lost through the membrane as well as PSS lost in the clarifier. The sludge from the clarifier is sent to a sludge dewatering lagoon.

6.3 Economic Analysis Procedure

A water softening cost analysis was performed for PEUF, ion exchange and lime softening for similar conditions. A cradle to grave scenario was considered to include treatment and/or disposal of waste streams from each process. The PEUF scale-up was based on experimental stirred cell results (14) which showed up to 99.7% rejection of hardness metal ions (calcium and/or magnesium) can be achieved in a single stage of PEUF. Increasing temperature causes negligible change in hardness rejection, but leads to an increase in flux. The effect of low concentrations of added salt results in a slight decrease in rejection of hardness ions. However, rejection decreases substantially as the salt concentration increases. It has also been shown (15) that fluxes and rejections in batch stirred cell and continuous spiral wound membrane are approximately the same.

The capital and operating costs were based on vendor quotes, plant design references and government reports. This study has relied heavily on information contained in Gumerman, et. al.(50) which compiled the cost of many different water treatment systems, including lime softening, ion exchange softening, mixing tanks for salt, acid and base, sludge disposal, brine evaporation pond, as well as ultrafiltration (without colloid) plant for flow rates ranging from 1000 gallons/day to 10^6 gallons/day.

Each system analyzed here has a breakdown of capital and operating cost. The capital cost includes manufactured equipment, excavation and site work, concrete, installation,

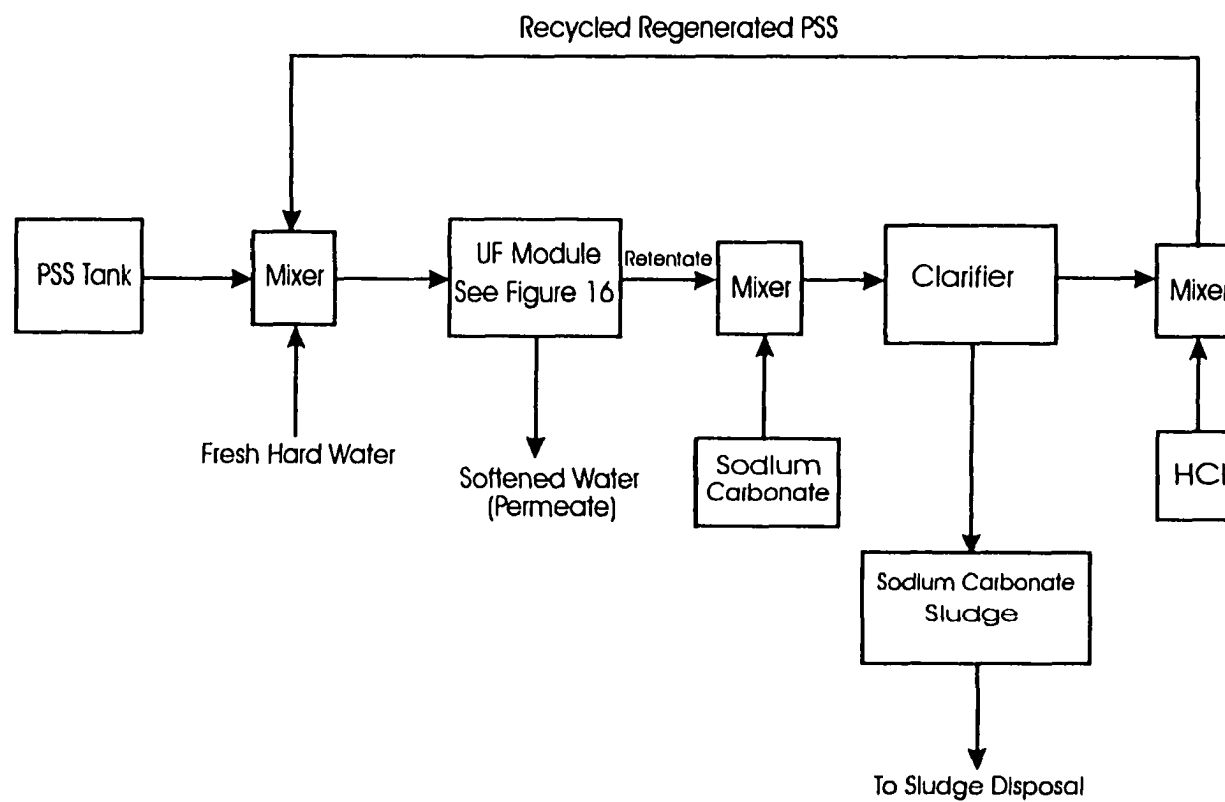


Figure 18: PEUF with PSS regeneration using sodium carbonate.

steel, pipes and valves, instrumentation, housing, and design contingencies. The fraction of the manufactured equipment in total capital cost for each system depends on the flowrate and therefore size of the unit. The operating costs include labor, maintenance, and energy costs. The maintenance cost accounts for replacement of parts (such as membrane, resin, pump seals, etc.) as needed for the process. Energy requirements include both process and buildings-related energy such as ventilation. In Gumerman et. al. (50), the labor and energy are reported as hours per year and kwh per year of operation, respectively. Therefore, labor and energy costs can be obtained by applying the current labor (\$21/hr) and energy (\$0.07/kwh) rates (51). The operating costs assume continuous operation 24 hours a day, 365 days a year. For the UF package, the maintenance cost includes membrane replacement every four years as well as membrane backwashing for 30 minutes every day. For the ion exchange package, resin replacement of 10% per year, accounting for the resin wear as well as daily regeneration of the resin, was included in the maintenance cost. The ion exchange resin capacity for the calculations were based on 20000 grains of hardness/ft³ of resin (52) where 1 grain equals 17.1 ppm. For both UF and ion exchange, the volume of water ($\$6.00 \times 10^{-5}$ per gallon)) (51) required for rinsing the colloidal solution or resin after brine or acid addition was 6% for the removal of 200 ppm hardness (as CaCO₃), 12% for 400 ppm hardness, and 18% for 600 ppm hardness. A surface loading rate of 1500 gallons per day per square foot was assumed for sizing of the clarifier in the scheme where PSS is recovered by adding sodium carbonate as well as for the lime softening (53). This is the rate at which the PSS stream flows over the clarifier in order to insure complete settling

of the suspended precipitate particles. Also, the volume of the sludge from the clarifier was assumed to be 2.5 times the volume and weight of the lime or sodium carbonate used in the precipitation processes (54). The capital and maintenance costs from Gumerman et.al. (50) were analyzed for 1993 costs by using the Marshall and Swift Index (966 for Sept 1993, 786 for 1983) of 1.229. The costs from Gumerman et.al. (50) did not include the depreciation and capital interest. Therefore, depreciation cost (assuming a 20 years plant life, straight line depreciation) and interest on capital (10% compounded yearly) were added to that operating cost. Straight line depreciation was assumed due to its simplicity.

Quotes were obtained from vendors for ultrafiltration units (based on \$750.00 for a 4"x40" spiral wound membrane), ion exchanger (based on \$80.00/ft³ of resin), and static mixers. The vendor quotes were closely comparable to estimates obtained from Gumerman et.al (50). A list of vendors from whom information was obtained for this study is included in Table 13. The chemical costs were obtained from both vendors and Chemical Marketing Reporter (55).

The cost for the UF units in Gumerman et.al. (50) were based on pure water. To determine the costs of PEUF modules, the effect of concentration polarization as a result of the presence of PSS on flow was taken into account by dividing the actual fresh hardwater feed flow rate (containing the PSS) by the relative flux to obtain the feed flowrate based on pure water. The feed flow rate based on pure water was then used to

size the PEUF unit and calculate the capital and operating costs. A best fit correlation for the capital cost of each system from Gumerman et.al. (50) was obtained. Other correlations included flux of the polyelectrolyte solution through the ultrafiltration modules, operation and maintenance costs, and percent of feed recovered. These correlations were implemented into a computer program (written in FORTRAN 77) for each colloid recovery scheme as shown in Appendix C. Each program was then used to determine the capital and operating costs for a given feed and product hardness concentration, product flow rate, and fraction of feed recovered. These four parameters define the overall PEUF process. The capital and operating costs for the optimum process were minimized with respect to the fraction of feed recovered. Fraction of feed recovered is defined as the ratio of softened water (permeate) flow rate divided by actual fresh hardwater feed flow rate (containing the PSS).

Table 13: List of Vendors Providing Cost Information

Product	Vendor	City, State
Static Mixers	Koch Engineering	Wichita, KS
Static Mixers	EMI Inc.	Clinton, CT
UF Module	Cuno Separations	Norwood, MA
UF Module/ Membranes	IonPure	Lowell, MA
UF Membranes	Continental Water Systems	Oklahoma City, OK
Ion Exchange Resins	Culligan Water Conditioners	Oklahoma City, OK
Ion Exchange Resins	Graver Chemical Company	Texarkana, TX
Lime Softening	Norman Water Treatment	Norman, OK
PSS Cost cat#:29-7070	National Starch & Chemical Company	Bridgewater, NJ
PMVEMA Cost CAS#:25153-40-6	GAF Chemical Company	Wayne, NJ

6.4 Results of Economic Analysis

The results show the effects of flow rate, hardness, and fraction of feed recovered on total cost. Total cost for different PSS recovery methods is also presented. The PEUF process is compared with lime softening, ion exchange, and a combination of ultrafiltration and ion exchange. Two different feed streams are analyzed for the case of PEUF versus ion exchange; one containing only hardness ions, and another with hardness ions as well as bacteria, viruses, and pyrogen. In the following analysis, hardness indicates carbonate (as CaCO_3) hardness. All the figures are based on September 1993 costs.

Figure 19 shows the effect of fraction of feed stream recovered on total cost for a 10^6 gallon/day feed stream containing 602.5 ppm hardness and a softened water stream of 2.5 ppm hardness using PEUF/NaCl. For this case, a minimum for total cost is achieved at 77.9% of the feed recovered corresponding to a total cost of \$3.51/1000 gallon of softened water. At low and high fraction of water recovered, the total cost increases dramatically. For high fraction of feed recovered, the high cost is due to decreased retentate volume, increased colloid concentration, decreased relative flux, and therefore, high capital cost. For low fraction of feed recovered, the small volume of product leads to a high cost of operation. It is important to note that the major factors contributing to the total cost of PEUF are capital and maintenance cost. As seen later in this report, a major part of the capital cost is due to the high cost of the PEUF module.

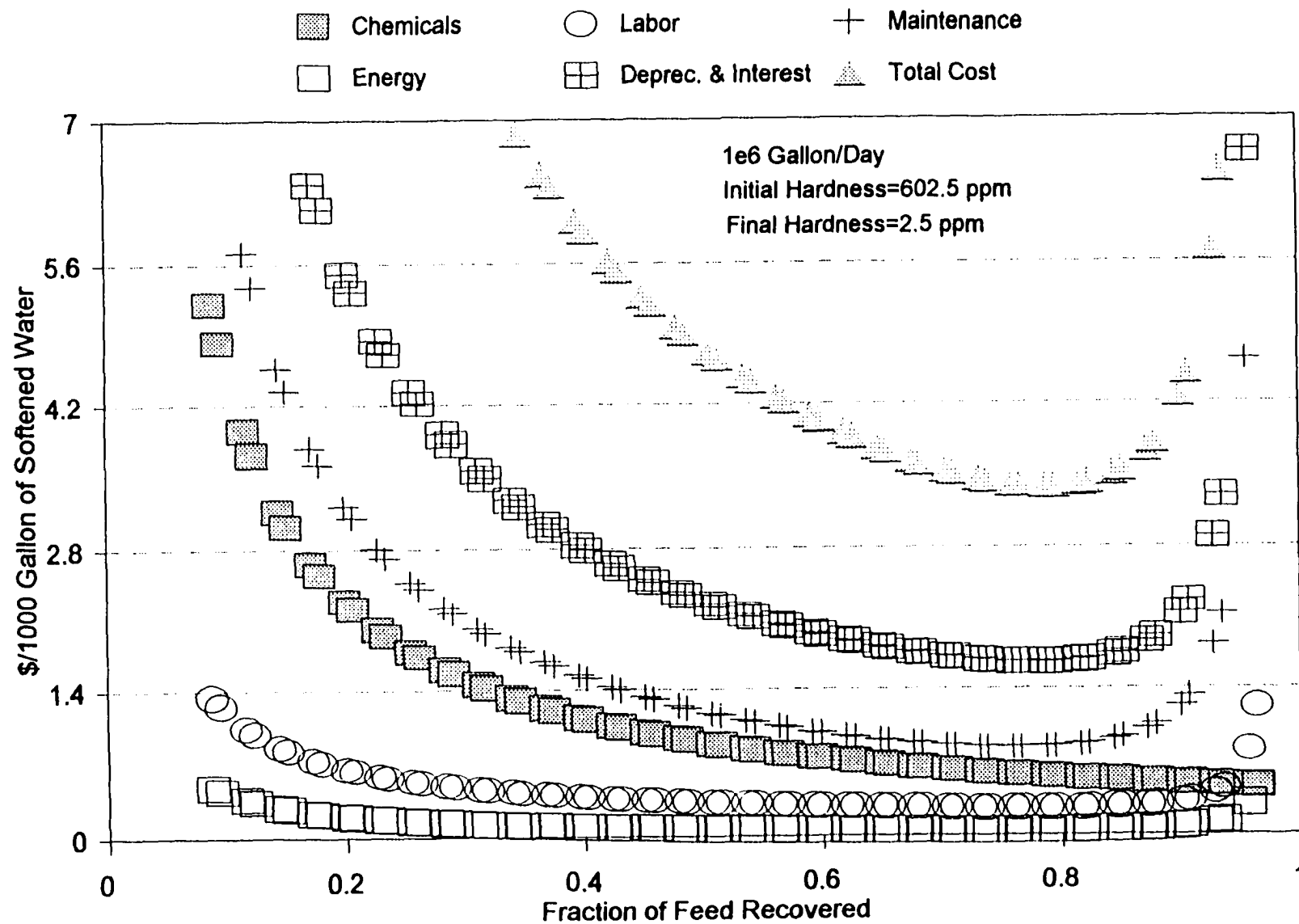


Figure 19: Effect of Fraction of Feed Recovered on Total Cost of PEUF

The costs shown for PEUF in the following figures show a minimum with respect to the fraction of feed recovered. Figure 20 shows the effect of hardness on the optimum fraction of feed recovered and total cost for a 10^6 gallon/day stream at a final hardness concentration of 5 ppm. As hardness concentration increases, the optimum fraction of feed recovered decreases, while the total cost of the process increases. An increase in the feed hardness concentration requires more PSS to achieve the hardness removal, therefore, reducing the relative flux. The lower relative flux leads to lower fraction of feed recovered and a higher operating cost due to higher capital cost. The cost for three PEUF processes with different PSS recovery methods were compared for a range of flow rates with feed and permeate hardness concentrations of 602.5 ppm and 2.5 ppm, respectively, as shown in Figure 21. The process requiring NaCl for the recovery of PSS was the least expensive scheme mainly due to lower chemical cost. The method requiring addition of sodium carbonate was by far the most expensive process with the cost of PSS as the major factor contributing to its high cost followed by the cost of maintenance. The higher cost for the HCl process was also due to the higher cost of chemicals, specifically HCl addition for reducing pH following the hardness removal step. The cost of chemicals includes PSS, NaCl, HCl, NaOH, Na_2CO_3 , alum and water (rinse) as applicable for each process. Figure 21 also shows the effect of flow rate on the PEUF process. As the flow rate increases, the total cost decreases, reflecting a larger volume of softened water. Due to the lower cost of PEUF with NaCl for PSS regeneration, it is used as the method of choice for cost comparisons with lime softening

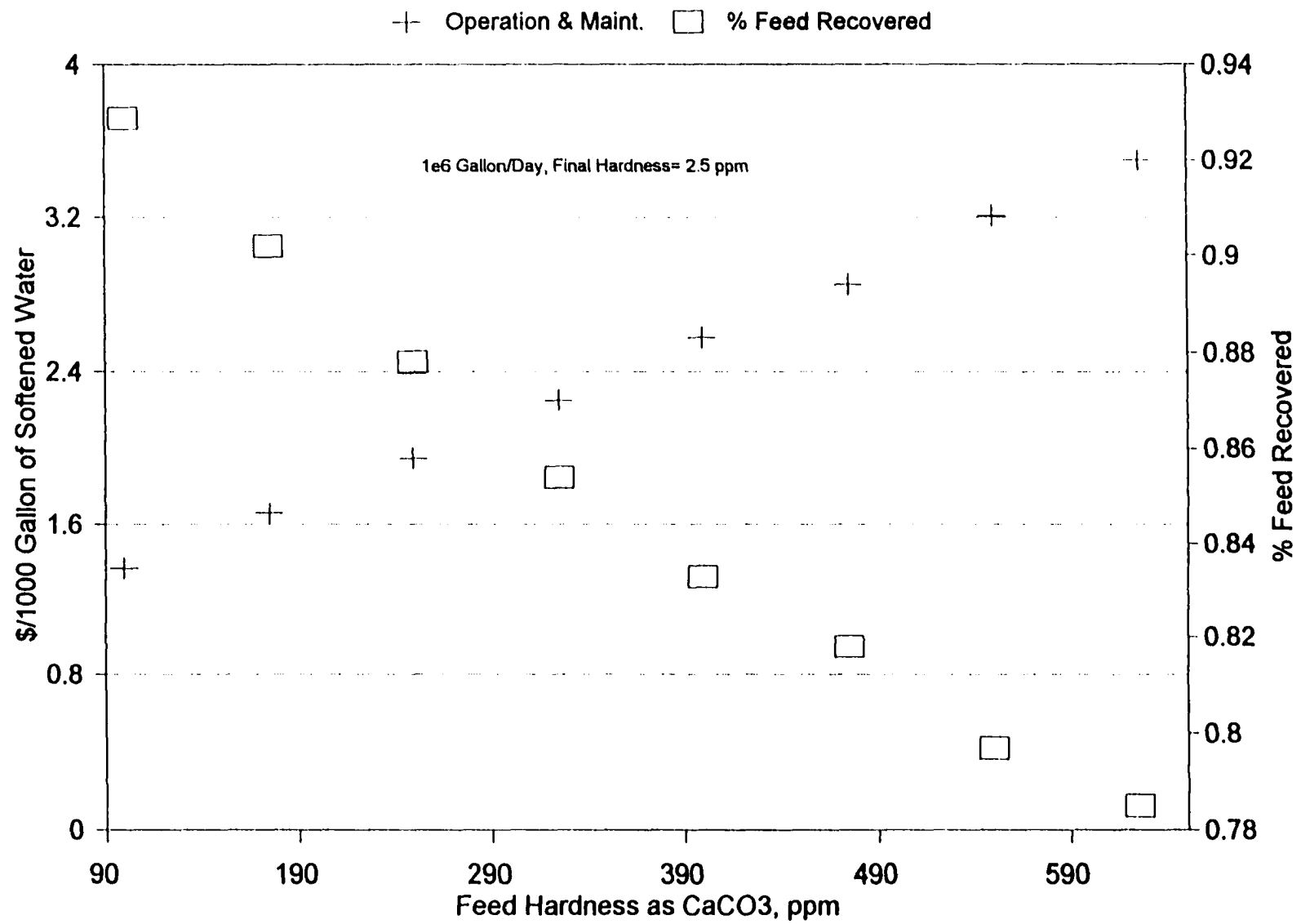


Figure 20: Effect of Hardness Level on PEUF Cost and % Feed Recovered

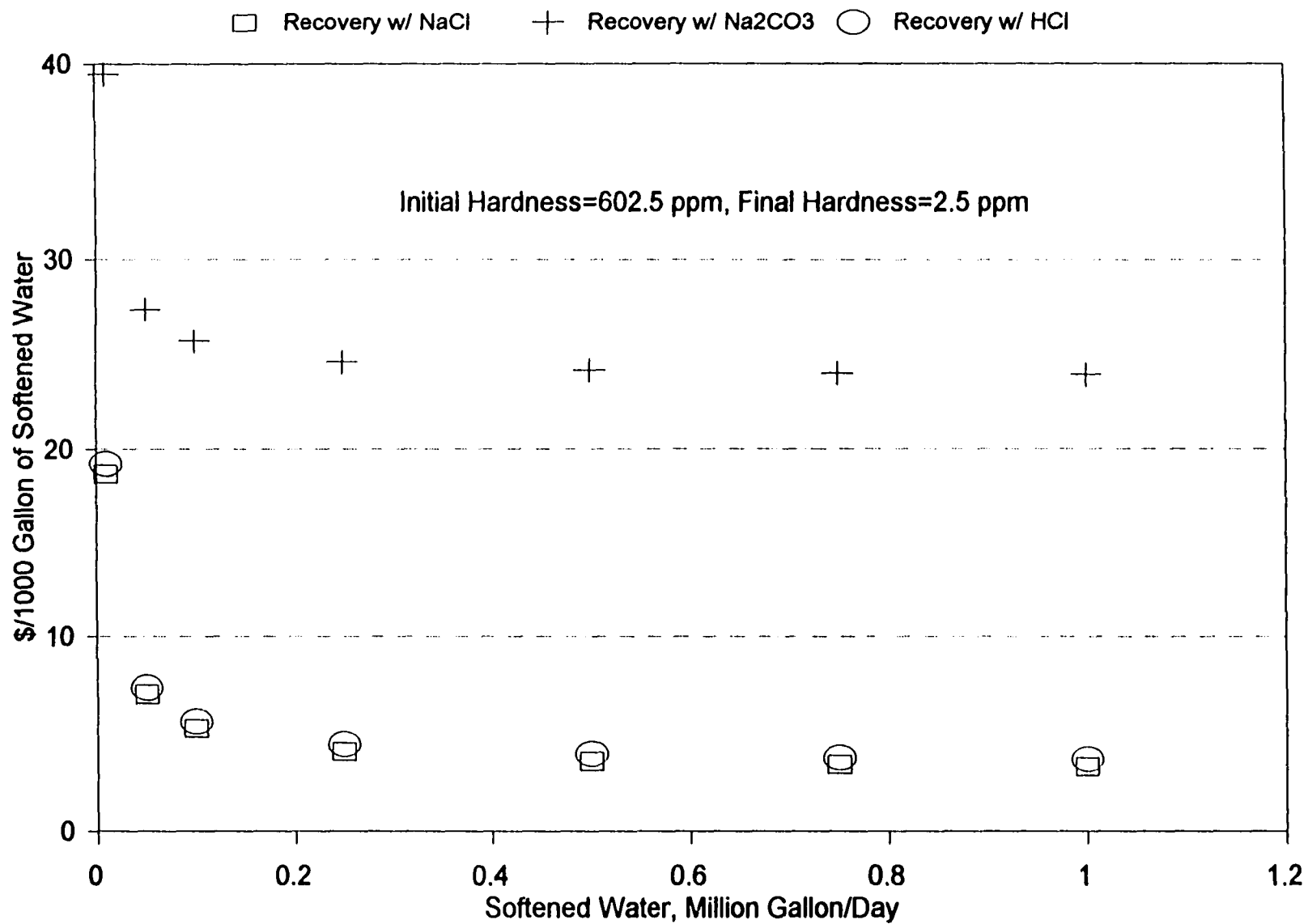


Figure 21: Comparison of Different PSS Recovery Methods

and ion exchange. Tables 14 and 15 show breakdown of operating and capital costs, respectively, for a 10^6 gallon/day stream for the three PEUF processes studied.

The effect of staging of the PEUF process is shown in Figure 22 for a range of flow rates. A single stage process is less expensive than a multiple stage process. Up to 99.7% rejection of hardness can be achieved in a single pass. Introduction of a second stage and therefore, reducing the level of rejection required at each stage, increases the relative flux at each stage by reducing the required PSS to hardness ratio. The higher relative flux at each stage reduces the operating cost of each stage. However, the additional capital cost of a second stage makes the process more expensive than a single stage process.

Figure 23 compares the PEUF/NaCl process with lime softening for a range of flow rates for reducing hardness concentration from 432.5 to 80 ppm. At high flow rates, major cost differences between PEUF and lime softening are chemical, capital, and maintenance costs. These differences diminish considerably at low flow rates making PEUF/NaCl more competitive with lime softening where for a 15.00×10^3 gallon/day process, PEUF/NaCl process costs are \$12.20/1000 gallon versus \$11.64/1000 gallon for lime softening. The breakdown of operating and capital costs for a 15.00×10^3 gallon/day stream for PEUF/NaCl versus lime softening are shown in Tables 16 and 17, respectively.

Table 14: Breakdown of Operating Cost For PEUF With Different PSS Recovery Methods: Treatment of 10^6 gallon/day Stream For Removal of 600 ppm of Carbonate Hardness And No Other Contaminants

	PEUF/NaCl \$/1000 gal	PEUF/HCl \$/1000 gal	PEUF/ Na_2CO_3 \$/1000 gal
Energy	0.059	0.063	0.072
Chemicals,total	0.580	0.993	18.618
PSS	0.003	0.003	12.680
Labor	0.270	0.223	0.334
Maintenance	0.893	0.906	4.313
Interest	1.139	1.155	1.270
Depreciation	0.569	0.578	0.635
Total	3.511	3.917	25.242

Table 15: Breakdown of Capital Cost For PEUF With Different PSS Recovery Methods: Treatment of 10^6 gallon/day Stream Containing 600 ppm of Carbonate Hardness And No Other Contaminants

	PEUF/NaCl \$/MGD	PEUF/HCl \$/MGD	PEUF/Na ₂ CO ₃ \$/MGD
Excavation/Sitework	0.923	0.919	0.458
UF Module Only	(1.575)*	(1.581)*	(1.827)*
Manufactured Equipment, All	1.622	1.647	2.004
Concrete	0.110	0.128	0.153
Installation	0.365	0.373	0.693
Pipe and Valves	0.060	0.065	0.087
Instrumentation	0.325	0.326	0.387
Housing	0.213	0.213	0.265
Design Contingencies	0.539	0.547	0.589
Total	4.157	4.217	4.635

* Numbers in parenthesis are included in "All Manufactured Equipment" cost. Therefore, they are not added separately into the total cost.

Table 16: Breakdown of Operating Cost For PEUF Versus Lime Softening: Treatment of a 15×10^3 gallon/day Stream For Decreasing Carbonate Hardness From 433 to 80 ppm.

	Lime Softening \$/1000 gal	PEUF/NaCl \$/1000 gal
Energy	0.211	0.174
Chemicals	0.088	0.302
PSS		0.001
Labor	5.687	4.518
Maintenance	0.719	0.823
Capital Interest	3.293	4.253
Depreciation	1.646	2.126
Total	11.644	12.197

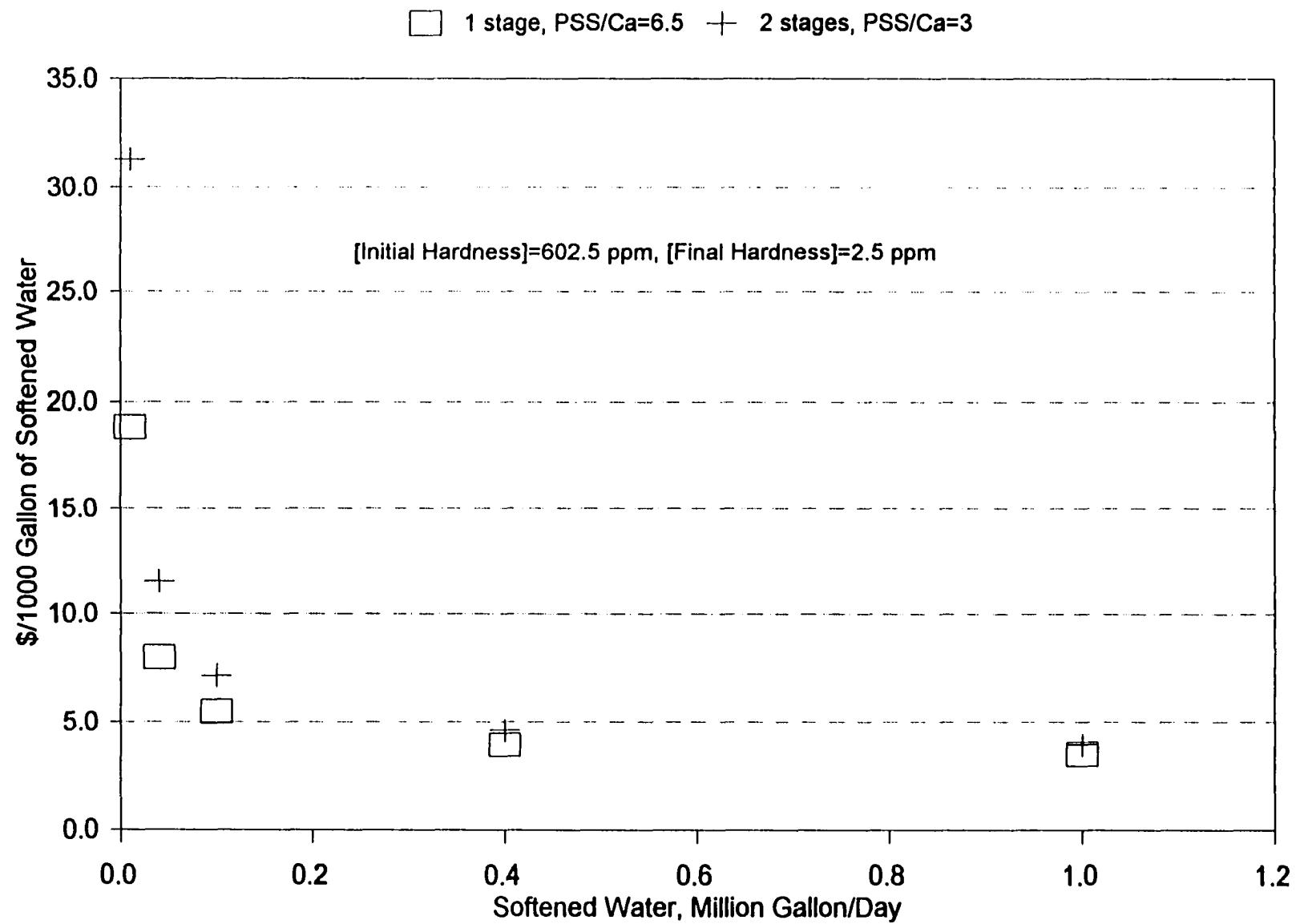


Figure 22: Effect of Staging on PEUF Cost

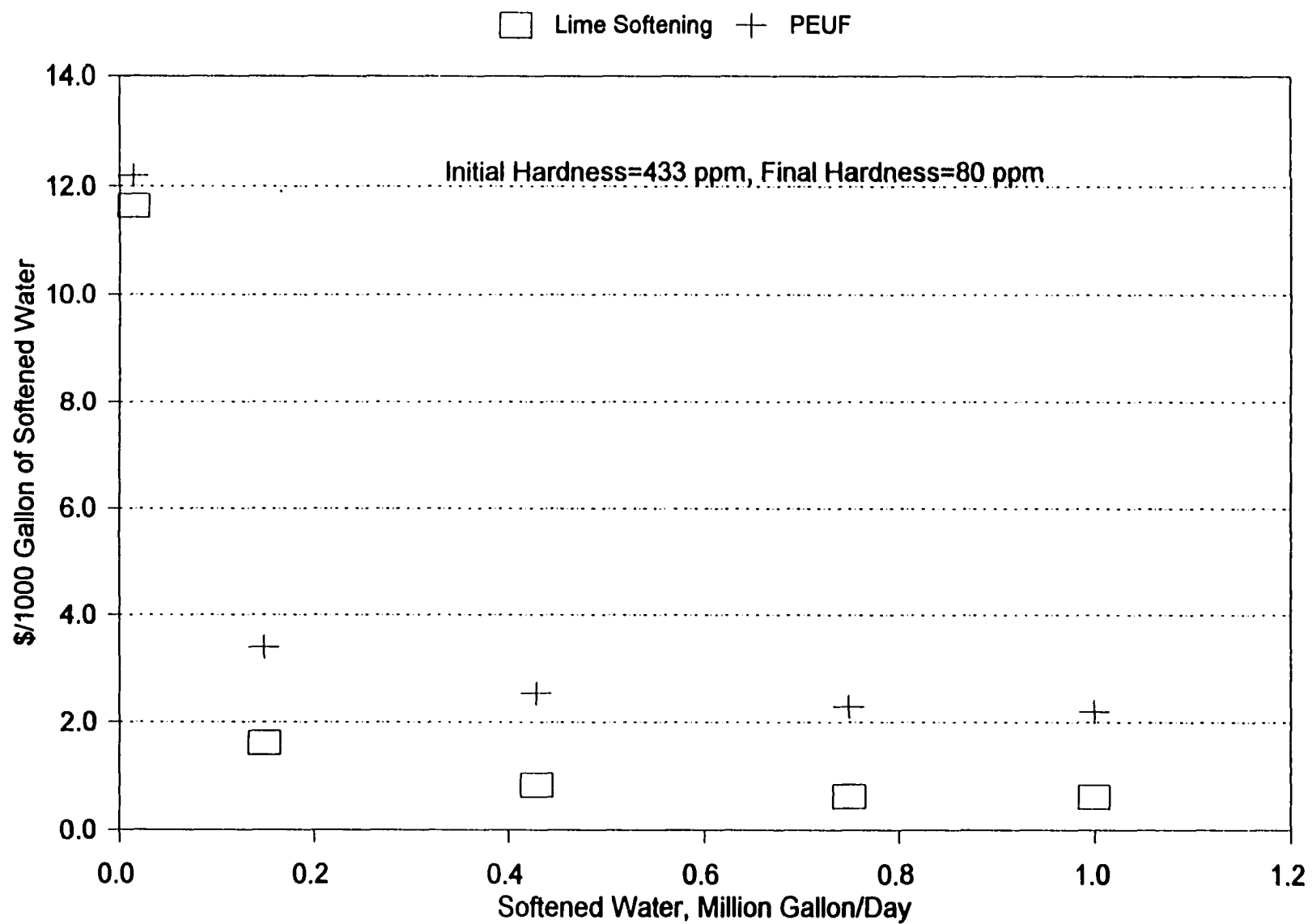


Figure 23: Total Cost of PEUF Versus Lime Softening

Table 17: Breakdown of Capital Cost For PEUF Versus Lime Softening: Treatment of a 15×10^3 gallon/day Stream For Decreasing Carbonate Hardness From 433 to 80 ppm.

	Lime Softening \$/MGD	PEUF/NaCl \$/MGD
Excavation/Sitework	0.009	0.044
UF Module Only		(0.061)*
Manufactured Equipment, All	0.069	0.085
Concrete	0.002	0.009
Installation	0.030	0.014
Pipe and Valves	0.011	0.004
Instrumentation	0.018	0.014
Housing	0.018	0.036
Design Contingencies	0.023	0.028
Total	0.180	0.233

* Numbers in parenthesis are included in "All Manufactured Equipment" cost. Therefore, they are not added separately into the total cost.

The PEUF/NaCl process is compared with ion exchange for removal of 200, 400, and 600 ppm of hardness metals in Figure 24. In each case, PEUF/NaCl is more expensive than ion exchange due to mainly higher capital, maintenance, and labor cost. For example, for removal of 600 ppm of hardness for a million gallon per day stream, PEUF costs \$3.51/1000 gallon versus \$1.04/1000 gallon for ion exchange.

In addition to removing the colloid and bound hardness ions, however, the ultrafiltration membrane of PEUF has potential to retain other contaminants such as virus, bacteria, and pyrogen from the feed stream (26,30) whereas the ion exchange process can only remove ionic species. This would be particularly applicable to a pharmaceutical industry where the water used must be free of most contaminants. Other industrial applications requiring ultrapure water include semiconductor manufacturing. Therefore, in a pharmaceutical or semiconductor industry, the water purification requires two stages, one to remove the organics and one to remove the hardness ions. To remove bacteria and viruses from a stream where an ion exchange resin is used for the removal of ions, a UF or an RO membrane must also be placed before the ion exchange resin. This will increase the capital and operation costs of the water treatment process. However, the PEUF process removes both the ions as well as the virus and bacteria simultaneously. Therefore, if the feed stream considered for treatment contains viruses, bacteria, and pyrogen as well as hardness ions, then the difference between PEUF and a combination of ultrafiltration units and ion exchange (IE/UF) narrows. Specifically, treatment costs

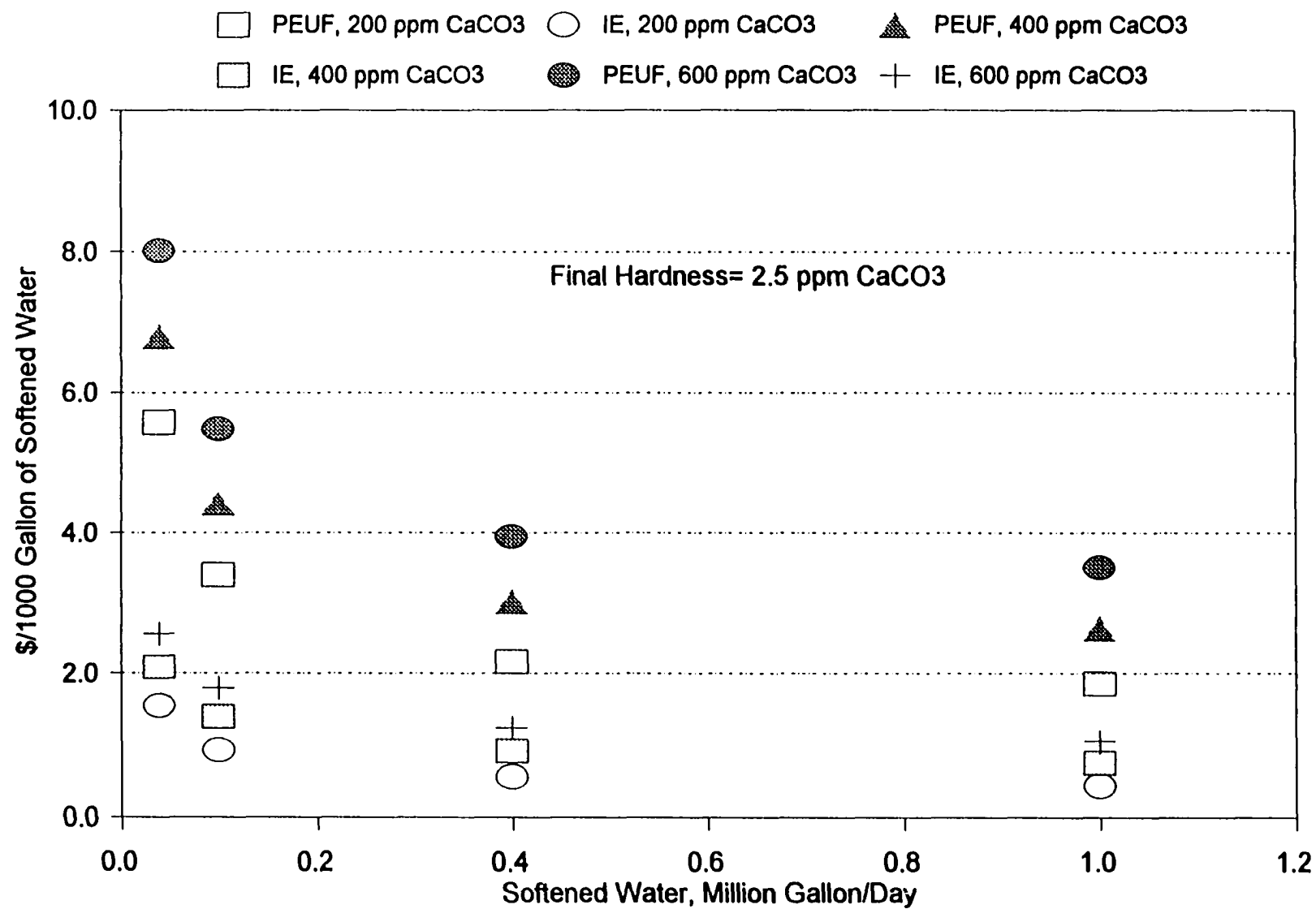


Figure 24: Total Cost of PEUF Versus Ion Exchange

\$3.51/1000 gallon of softened water using PEUF/NaCl versus \$1.80/1000 gallon for IE/UF. This effect is shown in Figure 25.

The PEUF/NaCl cost of \$3.51/1000 gallon is based on a relative flux of 0.585. This low relative flux is due to formation of concentration polarization. If, hypothetically, the relative flux could be increased to 0.99, then a smaller ultrafiltration unit would be required; hence, the PEUF cost can be reduced to \$1.92/1000 gallon making PEUF/NaCl closely competitive with the IE/UF process. Tables 18 and 19 show the breakdown of operating and capital cost for ion exchange, IE/UF, PEUF at an actual relative flux of 0.585 and PEUF at a hypothetical relative flux of 0.99. An increase in relative flux might be possible by considering another colloid or a combination of colloids instead of PSS. A recent study has shown that relative flux can be increased by using a mixture of polyelectrolyte/surfactant (16) instead of surfactant alone. Improvements in ultrafiltration membranes or turbulence enhancement might also contribute to an increase in relative flux.

The costs in Tables 14 to 19 indicate that a major factor contributing to the capital cost is the high cost of ultrafiltration modules, indicating the need for research to improve the flux in ultrafiltration to lower the ultrafiltration module capital cost and improve the economics of the PEUF processes.

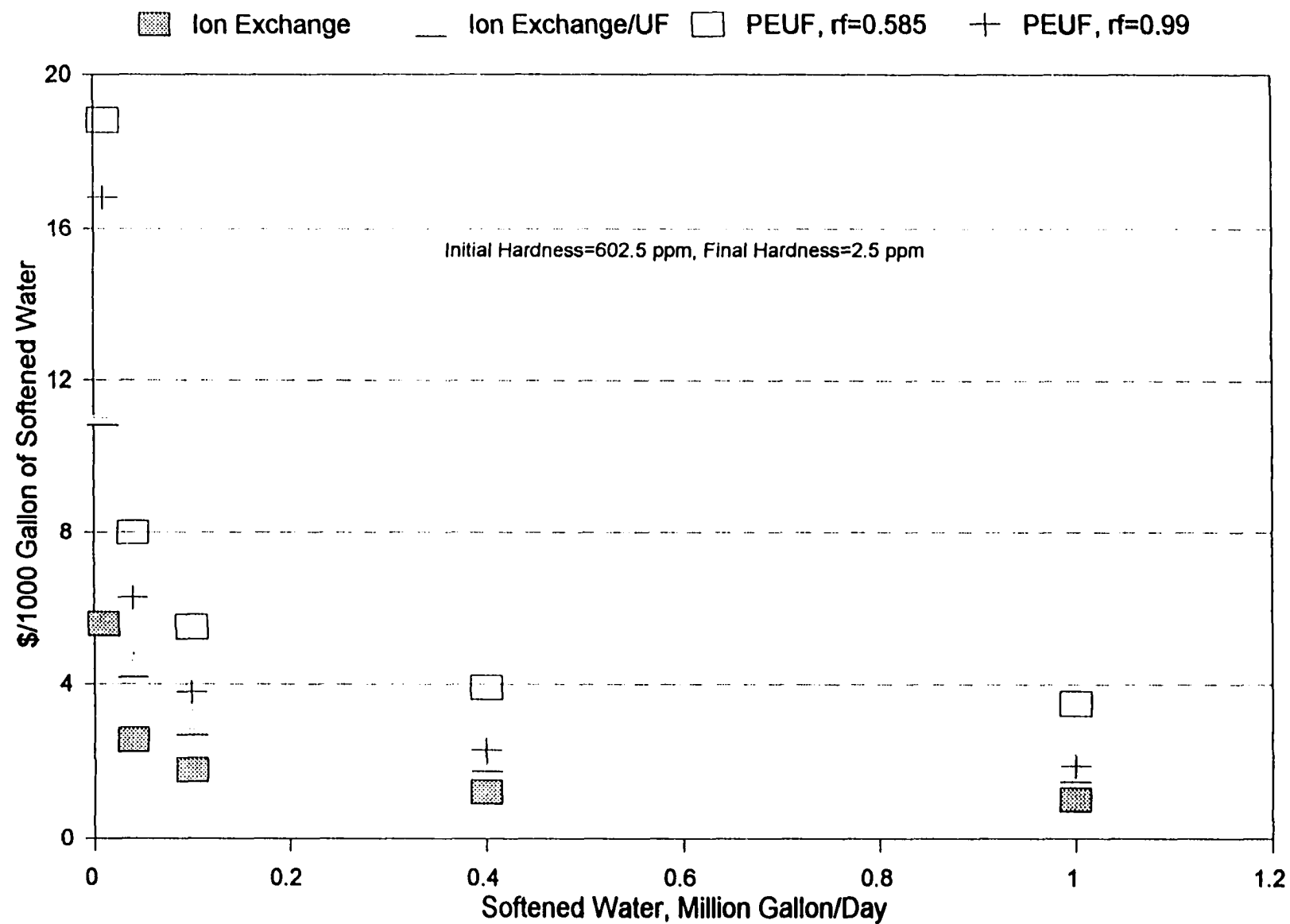


Figure 25: Comparison of PEUF (at $rf=0.585$ and 0.99) with Ion Exchange and Combination of Ion Exchange/Ultrafiltration

Table 18: Breakdown of Operating Cost: PEUF Versus UF/Ion Exchange Combination: Treatment of $4.38 \times 10^{-2} \text{ m}^3/\text{s}$ (10^6 gallon/day) Stream For Removal of 600 ppm of Carbonate Hardness As Well As Bacteria, Viruses, And Pyrogen

	Ion Exchange \$/1000 gal	Ion Exchange/UF \$/1000 gal	PEUF/NaCl RF=0.585 \$/1000 gal	PEUF/NaCl RF=0.99 \$/1000 gal
Energy	0.006	0.026	0.059	0.025
Chemicals	0.3157	0.316	0.580	0.449
PSS			0.003	0.001
Labor	0.002	0.065	0.270	0.183
Maintenance	0.070	0.356	0.893	0.352
Interest	0.415	0.690	1.139	0.608
Depreciation	0.207	0.345	0.569	0.304
Total	1.039	1.797	3.511	1.920

Table 19: Breakdown of Capital Cost for PEUF Versus UF/Ion Exchange Combination: Treatment of $4.38 \times 10^{-2} \text{ m}^3/\text{s}$ (10^6 gallon/day) Stream For Removal of 600 ppm of Carbonate Hardness As Well As Bacteria, Viruses, And Pyrogen

	Ion Exchange \$/MGD	Ion Exchange/UF \$/MGD	PEUF/NaCl RF=0.585 \$/MGD	PEUF/NaCl RF=0.99 \$/MGD
Excavation/ Sitework	0.749	0.767	0.923	0.758
UF Module Only		(0.524)*	(1.575)*	(0.654)*
Manufactured Equip., All	0.301	0.826	1.622	0.696
Concrete	0.023	0.059	0.110	0.046
Steel	0.027	0.027		
Installation	0.073	0.182	0.365	0.168
Pipe and Valves	0.040	0.048	0.060	0.041
Instrumentation	0.007	0.115	0.325	0.134
Housing	0.095	0.166	0.213	0.090
Design Contingencies	0.197	0.328	0.539	0.287
Total	1.513	2.518	4.157	2.219

* Numbers in parenthesis are included in "All Manufactured Equipment" cost. Therefore, they are not added separately into the total cost.

6.5 Conclusions

This study shows the feasibility of using PEUF to remove hardness ions from water. Several methods have been developed for the recovery of PSS following ultrafiltration with some leading to almost complete recovery of the PSS. The economically optimum percent feed recovery is dependent upon the level of hardness removed. Increasing hardness concentration causes a decrease in the percent of feed recovered and an increase in the cost of softened water. Having more than one stage increases the total cost due to higher capital cost. A comparison of PEUF for the removal of hardness ions with lime softening shows limited applicability of PEUF at low flow rates while its comparison with an ion exchange process shows a clear disadvantage for PEUF. However, a comparison of PEUF with a combination of ion exchange and ultrafiltration for the removal of hardness ions as well as viruses, bacteria, and pyrogen shows greater promise for PEUF. The results of this study show that concentration polarization due to the presence of PSS has a detrimental effect on flux and therefore on total cost. Further improvements in the PEUF process might be possible by considering combination of colloids as well as development of lower cost membranes or improved turbulence promoters providing lower resistance to flux. It should be noted that the PEUF process is a relatively new separation technique. The results of this study seem to indicate the potential of PEUF as a significant technology in water softening with some reasonable technological improvements.

The interested reader may be interested to know that this work has already been published (56).

Chapter 7: CONCLUSIONS

This work has investigated the application of a relatively novel separation process, polyelectrolyte-enhanced ultrafiltration (PEUF), for the removal of hardness ions from an aqueous stream. The following three areas have been addressed: 1. technical feasibility of PEUF for water softening, 2. regeneration of the polyelectrolyte for its subsequent use in the PEUF process, and, 3. a comprehensive economic analysis of the PEUF process for water softening and its comparison to conventionally used water softening processes, specifically, lime softening and ion exchange.

7.1 Technical Feasibility of PEUF for Water Softening

The technical feasibility results have shown that PEUF is highly effective in the removal of multivalent ions from aqueous streams. Using calcium and magnesium ions as the multivalent ions and poly(sodium styrene sulfonate) or poly(methyl vinyl ether maleic acid) as the polyelectrolyte, up to 99.7% rejection of the multivalent ions was possible. As the polyelectrolyte to metal ratio increases, the rejection of multivalent ions also increases. Furthermore, at a constant ratio of polyelectrolyte to total metal, simultaneous decrease in the PSS and metal concentration leads to lower metal concentration in the permeate and therefore higher rejection. In the presence of added salt, the rejection decreases due to the added ionic strength of the solution. However, at lower salt concentrations, the rejection is still remarkably high. Temperature effects

were negligible on rejection. However, as temperature increases, flux of the solution across the ultrafiltration membrane increases as well.

The modified ion-binding model has been utilized to test the effectiveness of the model to predict rejections in the PEUF process. The ion binding model provides an excellent prediction of metal ion concentrations in the permeate in the absence of added salt or in the presence of a low concentration of salt. The presence of high salt concentration, however, results in moderate to extreme deviations of the model predictions from observed data.

7.2 Polyelectrolyte Recovery

To optimize the PEUF process for water softening, studies were performed to recover as much of the polyelectrolyte as possible. The feasibility of recovery of both PSS and PMVEMA were shown in this study. However, due to difficulties with the use of PMVEMA, majority of the work emphasizes on the use of PSS. Of the recovery methods that were investigated, three offered the greatest promise. These were 1. addition of NaCl to exchange sodium ions with hardness ions, 2. addition of HCl to exchange hydrogen ions with the hardness ions, and 3. addition of Na_2CO_3 for precipitation of hardness ions as CaCO_3 or MgCO_3 . The purpose was to recover as much of the PSS as possible and to achieve maximum hardness rejection using the

regenerated PSS. An excess amount of NaCl, HCl, or Na₂CO₃ had to be added to the spent PSS solution to achieve its regeneration.

With NaCl and HCl addition, almost complete recovery of the PSS was possible whereas with Na₂CO₃ addition, only about 95% of the PSS was recovered. The PSS loss in the case of Na₂CO₃ addition may be due to the adsorption of PSS on the calcium carbonate and/or magnesium carbonate precipitate. The feasibility for recovery of PMVEMA was also shown in this study. The recovered PMVEMA was effective in the rejection of more than 99% of the hardness ions.

It is important to note that rejection of hardness ions using regenerated polyelectrolyte is generally slightly lower than when using fresh polyelectrolyte. However, the rejection using regenerated polyelectrolyte is considerably high (close to 99%).

7.3 Economic Feasibility of PEUF for Water Softening

The results from technical feasibility of PEUF for water softening and polyelectrolyte recovery were used to develop a model which would optimize the PEUF process. The parameters of the experimental runs were scaled up to determine cost requirements for commercial applications. The PEUF process was then compared with other conventional water softening methods, specifically, ion exchange and lime softening. A

cradle to grave scenario was developed to account for all costs associated with the three processes.

This study shows the feasibility of using PEUF to remove hardness ions from water for certain applications. The economically optimum percent feed recovery is dependent upon the level of hardness removed. Increasing hardness concentration causes a decrease in the percent of feed recovered and an increase in the cost of softened water. Having more than one stage increases the total cost due to higher capital cost. A comparison of PEUF for the removal of hardness ions with lime softening shows limited applicability of PEUF at low flow rates while its comparison with an ion exchange process shows a clear disadvantage for PEUF. However, a comparison of PEUF with a combination of ion exchange and ultrafiltration for the removal of hardness ions as well as viruses, bacteria, and pyrogen shows greater promise for PEUF.

While this study has focused on the application of PEUF for water softening, the results can easily be extended for the removal of heavy metal ions. Previous studies have demonstrated the effectiveness of PEUF for the removal of copper (9,12,17) and chromate (6,48).

7.4 Future Work

The results of this study have shown that the PEUF is generally feasible as a method for the removal of multivalent ions from aqueous streams. More importantly, this study defines bottlenecks to economic ultrafiltration of PEUF. The areas of research that could potentially improve the PEUF process include development of alternative ultrafiltration membranes, design of ultrafiltration module configuration, synthesis of custom-made polyelectrolytes, and/or the use of a mixture of polyelectrolytes.

This work has shown that concentration polarization due to the presence of PSS has a detrimental effect on flux and therefore on total cost. Further improvements in the PEUF process might be possible by considering combination of colloids as well as development of lower cost membranes or improved turbulence promoters providing lower resistance to flux. Improved turbulence could be achieved by either the choice of the polyelectrolyte or design of new membrane modules so to minimize concentration polarization. Additionally, synthesis of custom-made polyelectrolytes which would work best with a particular ultrafiltration membrane material might lead to improvements of the PEUF process.

It should be noted that the PEUF process is a relatively new separation technique. The results of this study seem to indicate the potential of PEUF as a significant technology in with some reasonable technological improvements. Given the tremendous use of

membranes for various applications, development and improvement of membranes is ongoing. Therefore, although the PEUF process is not economically feasible at this time, it may be worthwhile to reevaluate this process in a decade or two.

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APPENDIX A: List of Vendors

The following is a list of the vendors contacted for obtaining quotes for this economic study (quotes obtained in Sept. 93). The vendor quotes for static mixers were actually used for the cost analysis in this report. The other quotes were used mainly for comparison with the values obtained from the EPA report.

1. Static mixers: Koch Engineering Company, Inc., John Concanon, Wichita, KS 67220, (316) 832-8387.
2. Static mixers: EMI Inc., Dave Wharton, Clinton, CT, (800) 243-1188.
3. Ultrafiltration module: Cuno Separations, Graham Jones, Norwood, MA, (800) 367-6805.
4. UF membranes and module: IONPURE, Scott McKenzie, Lowell, MA, (800) 783-7873.
5. UF membranes: Continental Water Systems, Gary Arnold, Oklahoma City, OK, (405) 681-0759.
6. Ion exchange resins: Culligan Water Conditioning, Jan Latimer, OKC, OK, (405) 672-7821.
7. Ion exchange resin: Graver Chemical Company, Chris Bruce, Texarkana, TX, (903) 832-3369.
8. Lime softening: Norman water treatment, Brian Hapke, Norman, OK, (405) 321-2182

9. Cost of PSS (cat#: 29-7070): National Starch and Chemical Company, Christy Gies, Bridgewater, NJ, (800) 453-8480.

10. Cost of PMVEMA (Gantrez S-95) (CAS#: 25153-40-6): GAF Chemical Corporation, NJ, (800) 622-4423.

APPENDIX B: Cost Correlations Used in the Programs in Appendix C

Analysis programs. A FORTRAN 77 program is written for each of the PSS recovery schemes. With the product flow rate in gallons per day, feed and product hardness concentration as calcium ions in ppm, and percent of feed volume recovered, the program calculates the individual elements contributing to the total operation and capital cost taking into account the effect of concentration polarization as a result of the presence of PSS. A list of symbols for the programs is included at the beginning of the programs.

Mass balances. The average concentration of hardness ion, H , in the retentate was calculated by knowing its concentration in the permeate and feed as well as the permeate flow rate and percent of feed recovered. The feed flow rate was determined by:

$$flow_{feed} = \left(\frac{flow_{per}}{\% feed_{rec}} \right) \quad (B-1)$$

$$flow_{ret} = flow_{feed} - flow_{per} \quad (B-2)$$

$$[H]_{av,ret} = \frac{([H]_{feed} * flow_{feed}) - ([H]_{per} * flow_{per})}{\left(flow_{feed} - \left(\frac{flow_{per}}{2} \right) \right)} \quad (B-3)$$

Using this knowledge, the average rejection was determined by:

$$rej_{avg} = \left(1 - \left(\frac{[H]_{per}}{[H]_{av,ret}} \right) \right) * 100 \quad (B-4)$$

The average rejection was then used to determine the ratio of PSS to hardness ions needed to achieve the required separation. The PSS concentration was then determined from the feed hardness concentration and PSS to hardness ion ratio as:

$$[PSS]_{feed} = \left(\frac{[PSS]}{[H]} \right) * [H]_{feed} \quad (B-5)$$

The feed PSS concentration and permeate PSS concentration with the volume of the feed and permeate were then used to determine the retentate PSS concentration. The PSS retentate concentration was in turn used to determine the relative flux (rf) (flux of solution containing PSS/flux of pure water) using a correlation from a concentration polarization study of PSS (9). The correlation is as follows:

$$rf = 1.0152 * \exp(-3.1197 * [PSS]_{ret}) \quad (B-6)$$

The relative flux was used to size the ultrafiltration unit. Since the correlations for the ultrafiltration package obtained from the EPA report used in this study are based on pure water, flux of the stream containing the PSS also had to be stated in terms of pure water flux. Therefore, the PSS feed flux, $flow_{feed}$ was divided by the relative flux to obtain pure water feed flux, $flow_{pure}$. The pure water feed flux was then used to size the ultrafiltration unit.

Chemical costs. The moles of PSS and hardness were calculated from the feed, permeate and retentate concentrations. Based on the moles of PSS and hardness, and the optimum ratio of NaCl, HCl, or Na₂CO₃ to hardness, chemical cost of treatment for each process was determined.

Operation and Capital Costs. The costs obtained from the EPA report were based on an independent parameter for each package. These included membrane surface area and flow rate for the ultrafiltration package, resin volume for the ion exchange package, settling surface area for the clarifier, flow rate for lime softening package, chemical feed rate in lb per day for chemical tanks, effective storage volume for sludge disposal, and lagoon surface area for brine evaporation lagoons. The correlations were made such that some include the labor and energy cost whereas others have to multiplied by the labor and energy rate to obtain those costs.

APPENDIX C

Appendix C.1: Description of Fortran 77 Program For PEUF Process

Introduction

This appendix presents three Fortran 77 programs for the use of PEUF for water softening. Each program accounts for a particular method used for the recovery of the polyelectrolyte. A brief description of each program is provided at the beginning of each program.

c
c
c Evaluation of Polyelectrolyte-Enhanced Ultrafiltration for Water Softening
c
c The following is a description of symbols used in the subsequent
c programs. The final results of these programs report the hardness
c concentrations as ppm of calcium ion. To convert to hardness
c concentration as ppm of CaCO_3 , multiply the ppm of calcium ion hardness
c concentration by 2.5 [(MW of CaCO_3)/(MW of the calcium ion)].
c
c The polyelectrolyte used is sodium poly(styrene sulfonate) (PSS). The
c recovery of the PSS using NaCl , Na_2CO_3 , and, HCl is studied.
c
c ***** SYMBOL DESCRIPTION *****
c
c alugal= total cost of alum used in the process, \$/1000 gallon
c amixcp= capital cost of static mixer for Na_2CO_3 addition, \$
c apcdy= cost of alum and polymer per day (as coagulants to remove
c turbidity in clarifier), \$/day
c ashca= molar ratio of Na_2CO_3 to hardness metal ions to achieve maximum
c PSS recovery (based on experimental results)
c ashcos= cost of Na_2CO_3 , \$/ton
c ashgal= total cost of Na_2CO_3 used in the process, \$/1000 gallon
c ashtcp= capital cost of Na_2CO_3 tank, \$
c ashtoe= energy cost of Na_2CO_3 tank, \$/yr
c ashtol= labor cost of Na_2CO_3 tank, \$/yr
c ashtom= maintenance cost of Na_2CO_3 tank, \$/yr
c belcap= capital cost of brine evaporation lagoon, \$
c bell= labor cost of brine evaporation lagoon, \$/yr

- c belm= maintenance cost of brine evaporation lagoon, \$/yr
- c cafinl= hardness concentration in softened water, mol/L
- c cainit= hardness concentration in feed, mol/L
- c capgpd= total capital cost on a gallon per day basis, \$/gpd
- c capint= total cost of interest on capital, \$/yr
- c cappmf= hardness concentration of metal ions (ex: Ca^{2+}) in softened water, ppm
- c cappmi= hardness concentration of metal ions (ex: Ca^{2+}) in feed, ppm
- c careav= average (midpoint) hardness concentration in retentate, mol/L
- c caret= hardness concentration in retentate, mol/L
- c cashdy= cost of Na_2CO_3 per day
- c chl03g= total chemical cost per 1000 gal, \$/1000gal
- c chcldy= total cost of HCl per day
- c clarcp= capital cost of clarifier, \$
- c clarif= operation and maintenance cost of clarifier, \$/yr
- c cncldy= total cost of NaCl per day
- c cnohdy= total cost of NaOH per day
- c cwater= total cost of water per day
- c deprec= total depreciation cost (based on 20 year lifetime), \$/yr
- c energc= cost of electricity, \$/kwh
- c fafeed= actual (taking relative flux into account for equipment design)
- c feed flowrate of hard water, gallons/day
- c fmixcp= capital cost of static mixer at the feed, \$
- c frfeed= feed flowrate of hard water, gallons/day
- c firprod= softened water (permeate) flowrate, gallons/day
- c frret= retentate flowrate, gallons/day
- c hclash= molar ratio of HCl to Na_2CO_3 to reduce pH of recovered PSS
- c stream (based on experimental results)
- c hclca= molar ratio of HCl to hardness metal ions to achieve maximum
- c PSS recovery (based on experimental results)
- c hclcos= cost of HCl, \$/ton
- c hclgal= total cost of HCl used in process, \$/1000 gallon
- c hcltcp= capital cost of HCl tank, \$
- c hcltoe= energy cost of HCl tank, \$/yr
- c hcltol= labor cost of HCl tank, \$/yr
- c hcltom= maintenance cost of HCl tank, \$/yr
- c hmixcp= capital cost of static mixer for HCl addition, \$
- c intrat= interest rate, %/100
- c laborc= cost of labor, \$/hr
- c lashyr= lb of Na_2CO_3 per year

- c lbps= total lb of PSS required for process
- c lbpsa= lb of PSS added to replace the PSS lost in permeate per day
- c lhcdy= lb of HCl per day
- c lnldy= lb of NaCl per day
- c mashdy= moles of Na_2CO_3 per day
- c mhcdy= moles of HCl per day
- c mnldy= moles of NaCl per day
- c moleca= moles of hardness ions
- c molpss= moles of PSS
- c naclca= molar ratio of NaCl to hardness metal ions to achieve maximum PSS recovery (based on experimental results)
- c naohc= cost of NaOH, \$/lb
- c naohcl= molar ratio of NaOH to HCl to increase pH of recovered PSS stream (based on experimental results)
- c nclcos= cost of NaCl, \$/ton
- c nclgal= total cost of NaCl used in process, \$/1000 gal
- c ncltcp= capital cost of NaCl tank, \$
- c ncltoe= total energy cost of NaCl tank, \$/yr
- c ncltol= total labor cost of NaCl tank, \$/yr
- c ncltom= total maintenance cost of NaCl tank, \$/yr
- c nmixcp= capital cost of static mixer for NaCl or NaOH addition, \$
- c nohgal= total cost of NaOH used in process, \$/1000 gal
- c nohtcp= capital cost of NaOH tank, \$
- c nohtoe= total energy cost of NaOH tank, \$/yr
- c nohtol= total maintenance cost of NaOH tank, \$/yr
- c nohtom= total maintenance cost of NaOH tank, \$/yr
- c pdplos= total cost of PSS lost in the overall process per day, \$/day
- c pdpper= total cost of PSS lost in softened water, \$/day
- c pdpwas= total cost of PSS lost in PSS recovery step, \$/day
- c pfrecd= percent of relative feed recovered
- c prepss= % PSS lost in precipitation of hardness ions in the Na_2CO_3 scheme
- c pssca= molar ratio of PSS to hardness metal ions needed to achieve the desired rejection (based on experimental results)
- c psscos= cost of PSS, \$/lb
- c pssfcp= capital cost of PSS tank, \$
- c pssfed= operation and maintenance cost of PSS tank, \$/yr
- c pssgal= total cost of PSS lost in process, \$/1000 gallon
- c pssin= PSS concentration in feed, mol/L
- c pssper= PSS concentration in softened water (permeate), mol/L

- c pssret= PSS concentration in retentate, mol/L
- c ptplos= percent PSS loss in softened water (permeate)
- c rej= hardness rejection, %/100
- c rf= relative flux of softened water (relative to pure water)
- c sludge= volume of sludge disposed per year
- c slugca= capital cost of sludge disposal, \$
- c slugom= operation and maintenance cost of sludge disposal, \$/yr
- c t10kg= cost of operation and maintenance per 1000 gal, \$/1000 gal
- c tashyr= ton of Na_2CO_3 per year
- c tc103g= total interest and depreciation cost per 1000 gal, \$/1000 gal
- c tcap= total capital cost of the process, \$
- c tcapom=total interest and depreciation cost of capital, \$/yr
- c tchdy= total chemical cost per day (Water, PSS, NaCl, etc.), \$
- c tchyr= total chemical cost per year, \$
- c te103g= total energy cost per 1000 gal, \$/1000 gal
- c tenerg= total energy cost, \$/yr
- c thcldy= ton of HCl per day
- c tl103g= total labor cost per 1000 gal, \$/ 1000 gal
- c tlabor= total labor cost, \$/yr
- c tm103g= total maintenance cost per 1000 gal, \$/1000 gal
- c tmaint= total maintenance cost, \$/yr
- c tnclyr= ton of NaCl per year
- c tomcyr= total operation and maintenance cost, \$/year
- c tpssct= total PSS cost for the PSS in feed
- c ufprcp= capital cost of ultrafiltration unit for water softening, \$
- c ufprec= energy cost of ultrafiltration unit for water softening, \$/yr
- c ufprlc= labor cost of ultrafiltration unit for water softening, \$/yr
- c ufprmc= maintenance cost of ultrafiltration unit for water softening, \$/yr
- c ufprtc= total cost of ultrafiltration unit for water softener, \$/yr
- c uftrcp= capital cost of ultrafiltration unit for PSS rinse, \$
- c ufwrwc= energy cost of ultrafiltration unit for PSS rinse, \$/yr
- c ufwrwc= labor cost of ultrafiltration unit for PSS rinse, \$/yr
- c ufwrwc= maintenance cost of ultrafiltration unit for PSS rinse, \$/yr
- c ufwrwc= total cost of ultrafiltration unit for PSS rinse, \$/yr
- c waterc= cost of raw water, \$/gallon
- c watgal= cost of water used in PEUF, \$/1000 gallon

Appendix C.2: PEUF Using NaCl For Recovery of PSS

```
c
c ***** PEUF USING NaCl FOR RECOVERY OF PSS *****
c
c program nacl
c
c ***** PURPOSE OF PROGRAM *****
c
c Given the softened water flowrate in gallons per day, hardness in the
c feed and product in ppm, and % of feed recovered, this program
c calculates the capital and operational cost (labor, energy,
c maintenance, chemicals, capital) of the polyelectrolyte-enhanced
c ultrafiltration (PEUF) process for the removal of hardness metals from
c drinking water. The PSS recovery is achieved by adding NaCl.

real nclgal,watgal,pssgal
real tlabor, tmaint,tenerg,tcapom,ch103g,tc103g,te103g,tm103g,tl103g
real lncldy, retwas,frret,frfeed,frprod,psscscos,waterc
real ufrwec, ufrwlc, ufrwmc, ufprmc, ufprlc, ufprec, ufprtc,ufrwtc
real naclca,pssper,nclcos,laborc,energc,fafeed,cappmi
real cainit,cafinl,cappmf,rej,pssin,pssca,pssmax,rf,moleca,molpss
real tcap, capint, lbpss, caret, pssret, ptplos, tpssct, pdpper, pdpwas
real pssfed, lbpssa, intrat, nmixcp
intrat=0.10
psscscos=3.39
waterc=.00006
naclca=5
pssper=1e-6
nclcos=60.
laborc=21.
energc=.07
write(6,50)
50 format('feedprod',2x,'%rec',2x,'Cai',3x,'Caf',3x,'Chem/10e3g',3x,
* 'Labor',3x,'Maint',3x,'Energy',3x,'Int/Dep',
* 4x,'O&M,$/10KGal',4x,'Cap,$/gpd')
c do 10 i=3,6,1
c do 20 cappmi=40,240,20
c do 25 cappmf=2,10,8
```

```

c do 30 pfrecd=0.758,.998,0.003
c fprod=10**i
5 print*, 'Enter the the product flow in gallons per day.'
  read*, fprod
  print*, 'Enter percent recovery of feed desired.'
  read*, pfrecd
  print*, 'Enter initial hardness as Ca in ppm'
  read*, cappmi
  cainit=cappmi/40.08e3
  print*, 'Enter final hardness as Ca in ppm'
  read*, cappmf

c
c Mass Balances to determine PSS and hardness ion concentration in
c the Retentate. Determination of rejection based on feed and output
c concentrations.
c
  cainl=cappmf/40.08e3
  frfeed=fprod/pfrecd
  frret=fprod-fprod
  caret=((cainit*frfeed)-(cainl*fprod))/frret
  careav=((cainit*frfeed)-(cainl*fprod))/(frfeed-(fprod/2))
  rej=1-(cainl/careav)
c ** The following rejection values are based on experimental results ***
  if(rej.ge.0.995)pssca=6.5
  if((rej.ge.0.99).and.(rej.lt..995))pssca=6
  if((rej.ge.0.985).and.(rej.lt.0.99))pssca=5.5
  if((rej.ge.0.983).and.(rej.lt.0.985))pssca=5
  if((rej.ge.0.979).and.(rej.lt.0.983))pssca=4.5
  if((rej.ge.0.967).and.(rej.lt.0.979))pssca=4
  if((rej.ge.0.95).and.(rej.lt.0.967))pssca=3.5
  if((rej.ge.0.915).and.(rej.lt.0.95))pssca=3
  if((rej.ge.0.815).and.(rej.lt.0.915))pssca=2.5
  if((rej.ge.0.77).and.(rej.lt.0.815))pssca=2
  if((rej.ge.0.65).and.(rej.lt.0.77))pssca=1.5
  if((rej.ge.0.55).and.(rej.lt.0.65))pssca=1
  pssin=cainit*pssca
  pssret=((pssin*frfeed)-(pssper*fprod))/frret

c
c Determine relative flux of PSS/metal ions stream based on concentration
c polarization study of PSS.

```

```

c      rf=1.0152*exp(-3.11971*pssret)
      fafeed=frfeed/rf
c
c      Chemical Costs: Water, NaCl, PSS
c
c      moleca=frfeed*3.785*cainit
      molpss=pssca*moleca
      ptplos=pssper/pssret
      lbpss=.4546*molpss
      tpssct=lbpss*psscscos
      pdpper=ptplos*tpssct
      pdpwas=ptplos*(tpssct-pdpper)
      pdplos=pdpper+pdpwas
      lbpssa=pdplos/psscscos
      tnclyr=naclca*3.785*5e-4*58.45*365*frret*caret/453.59
      lncldy=tnclyr*2000/365
      cncldy=tnclyr*ncscos/365
      mncldy=caret*frret*naclca*3.785
      retwas=0.00075*cappmi*frfeed
      cwater=retwas*waterc
      tchdy=pdplos+cncldy+cwater
      tchyr=tchdy*365
c
c      **** Maintenance, Energy, and Labor Costs for Equipment ****
c
c      ***** UF module/Water Softener *****
c
      ufprmc=-99.79+0.1046*fafeed
      ufprec=367.01+0.0067*fafeed
      ufprlc=7458.5+0.0156*fafeed
c
c      ***** UF module/ PSS solution rinse *****
c
      ufrwmc=-99.79+0.1046*((frret+retwas)/rf)
      ufrwec=367.01+0.0067*((frret+retwas)/rf)
      ufrwlc=7458.5+0.0156*((frret+retwas)/rf)
      ufrwtc=ufrwmc+ufrwec+ufrwlc
      ufprtc=ufprmc+ufprec+ufprlc

```

c *****NaCl tank *****

ncltom=10**(1.213472+.35107*log10(lncldy))
ncltol=10**(2.010064+0.269009*log10(lncldy))*laborc
ncltoe=10**(1.717257+0.431192*log10(lncldy))*energc

c ***** Brine evaporation lagoon *****

belm=10**(.289481+.39184*log10(retwas*365))
bell=(10**(-.15083+.321404*log10(retwas*365)))*laborc

c ***** PSS feed tank *****

pssfed=1245.*exp(0.0119073*lbssa)

c

c ***** Capital Cost of Equipment *****

c

c ***** UF package *****

ufprcp=66966+.938125*fafeed
uftrcp=66966+.938125*((retwas+frret)/rf)

c *** Feed and NaCl Mixers: 1440 is to convert the flow from gpd to gpm ***

fnixcp=342.+1.68*((frret+frfeed)/1440)-1.71e-4*((frfeed+frret)/1440)**2
nmixcp=342.2+1.68*((frret)/1440)-0.000171*(frret/1440)**2

c ***** Brine Evaporation Lagoon: factor 2 is based on the assumption that

c half of the volume of the brine solution from the lagoon is evaporated

c throughout the year.

belcap=10**(0.939543+.667938*log10(365*retwas/2))

c ***** NaCl Tank *****

ncltcp=10**(2.8633+0.389366*log10(lncldy))

c ***** PSS feed tank *****

pssfcp=19012.

c ***** Total Capital Cost *****

```

tcap=ufprcp+ufrtc+fmixcp+nmixcp+belcap+ncltcp+pssfcp
capgpd=tcap/frprod
c
c ***** Operation Cost *****
c
deprec=tcap/20
capint=tcap*intrat
tlabor=ncltol+ufprlc+ufrwlc+bell
tmaint=ncltom+ufprmc+ufrwmc+belm+pssfed
tenerg=ncltoe+ufprec+ufrwec
tcapom=capint+deprec
c
c Costs of Chemical, labor, maintenance, energy, and capital per 1000
c gallons of product
c
ch103g=tchyr*1000/(365*frprod)
tl103g=tlabor*1000/(365*frprod)
tm103g=tmaint*1000/(365*frprod)
te103g=tenerg*1000/(365*frprod)
tc103g=tcapom*1000/(365*frprod)
one=tchyr+ufprtc+ufrwtc+ncltom+ncltol+ncltoe
two=belm+bell+pssfed+deprec+capint
tomcyr=one+two
t10kgl=tomcyr*1000/(365*frprod)
write(6,40)frprod,pfrecd,cappmi,rf,ch103g,tl103g,tm103g,te103g,
* tc103g,t10kgl,capgpd
40 format(f8.0,1x,f4.3,1x,f4.0,1x,f4.3,1x,f6.4,1x,f7.4,1x,f7.4,1x,f7.4,
* 1x,f7.4,1x,f7.3,1x,f7.3)
c
c Cost of PSS, NaCl and Water per 1000 gallons of product stream
c
pssgal=dpdpos*1000/frprod
nclgal=cncldy*1000/frprod
watgal=cwater*1000/frprod
c write(6,60)pssgal,nclgal,watgal
c60format('pssgal',f14.6,2x,'nclgal',f14.6,2x,'watgal',f14.6)
30 continue
25 continue
20 continue

```


10 continue
stop
end

Appendix C.3: PEUF Using Na₂CO₃ For Recovery of PSS

```
c
c ***** PEUF USING Na2CO3 FOR RECOVERY OF PSS *****
c
c
c program na2co3
c
c ***** PROGRAM PURPOSE *****
c
c Given the softened water flowrate in gallons per day, hardness in the
c feed and product in ppm, and % of feed recovered, this program
c calculates the capital and operational cost (labor, energy, maintenace,
c chemicals, capital) of the polyelectrolyte-enhanced ultrafiltration
c (PEUF) process for the removal of hardness metals from drinking water.
c The PSS recovery is achieved by adding Na2CO3.

real pssgal,ashgal,alugal,hclgal
real ufprmc,ufprlc,ufwmc,ufwlc,ufwec,ufwtc,ufprtc,tlabor
real tmaint,tenerg,tcapom,ch103g,tl103g,tm103g,te103g,tc103g
real lhcldy, lashdy,frret,frfeed,frprod,psscsc,waterc
real hclash,pssper,hclcos,laborc,energc,ashcos,fafeed,cappmi
real cainit,cafinl,cappmf,rej,pssin,pssca,pssmax,rf,moleca,molpss
real tcap,capint,lbpss,caret,pssret,ptplos,tpssct,pdpper,pdppre
real pssfed,lbpssa,intrat, ashtom,ashtol,ashtoe,amixcp,ashtcp
intrat=0.10
psscsc=3.39
waterc=.00006
ashca=5.228
pssper=1e-6
ashcos=98.
laborc=21.
energc=.07
hclash=3.271
hclcos=78.
prepss=0.05
write(6,50)
50 format('feedprod',2x,'%rec',2x,'Cai',3x,'Caf',3x,'Chem/10e3g',3x,
* 'Labor',3x,'Maint',3x,'Energy',3x,'Int/Dep',
```

```

* 4x,'O&M,$/10KGal',4x,'Cap,$/gpd')
c do 10 i=3,6,1
c do 20 cappmi=40,240,20
c do 25 cappmf=4,32,7
c do 30 pfrecd=0.758,.998,0.003
c frprod=10**i
5 print*, 'Enter the the product flow in gallons per day.'
  read*, frprod
  print*, 'Enter percent recovery of feed desired.'
  read*, pfrecd
  print*, 'Enter initial hardness as Ca in ppm'
  read*, cappmi
  cainit=cappmi/40.08e3
  print*, 'Enter final hardness as Ca in ppm'
  read*, cappmf

c
c Mass Balances to determine PSS and hardness ion concentration in
c the Retentate. Determination of rejection based on feed and output
c concentrations.
c
  cafinl=cappmf/40.08e3
  frfeed=frprod/pfrecd
  frret=frfeed-frprod
  caret=((cainit*frfeed)-(cafinl*frprod))/frret
  careav=((cainit*frfeed)-(cafinl*frprod))/(frfeed-(frprod/2))
  rej=1-(cafinl/careav)

c
c **The following rejection values are based on experimental results **
c
  if(rej.ge.0.995)pssca=6.5
  if((rej.ge.0.99).and.(rej.lt..995))pssca=6
  if((rej.ge.0.985).and.(rej.lt.0.99))pssca=5.5
  if((rej.ge.0.983).and.(rej.lt.0.985))pssca=5
  if((rej.ge.0.979).and.(rej.lt.0.983))pssca=4.5
  if((rej.ge.0.967).and.(rej.lt.0.979))pssca=4
  if((rej.ge.0.95).and.(rej.lt.0.967))pssca=3.5
  if((rej.ge.0.915).and.(rej.lt.0.95))pssca=3
  if((rej.ge.0.815).and.(rej.lt.0.915))pssca=2.5
  if((rej.ge.0.77).and.(rej.lt.0.815))pssca=2
  if((rej.ge.0.65).and.(rej.lt.0.77))pssca=1.5

```

```

iff((rej.ge.0.55).and.(rej.lt.0.65))pssca=1
pssin=cainit*pssca
pssret=((pssin*frfeed)-(pssper*frprod))/frret

```

c

c Determine relative flux of PSS/metal ions stream based on concentration
 c polarization study of PSS

c

```

rf=1.0152*exp(-3.11971*pssret)
fafeed=frfeed/rf

```

c

c Chemical Cost: PSS, Water, HCl, Na₂CO₃, alum

c

```

moleca=frfeed*3.785*cainit
molpss=pssca*moleca
pssret=((pssin*frfeed)-(pssper*frprod))/frret
ptplos=pssper/pssret
lbpss=.4546*molpss
tpssct=lbpss*psscscos
pdpper=ptplos*tpssct
pdppre=prepss*(tpssct-pdpper)
pdplos=pdpper+pdppre
lbpssa=pdplos/psscscos
tashyr=ashca*3.785*5e-4*286.14*365*frret*caret/453.59
lashdy=tashyr*2000/365
cashdy=tashyr*ashcos/365
mashdy=caret*frret*3.785*ashca
mhcldy=hclash*mashdy
lhcldy=mhcldy*36.5/453.59
chcldy=lhcldy*hclcos/2000
sludge=1197*2.5*tashyr/7.4805
apcdy=(0.00453046*frret-.198981)
tchdy=pdplos+cashdy+chcldy+apcdy
tchyr=tchdy*365

```

c

c **** Maintenance, Energy, and Labor Costs for Equipment ****

c

c **** UF module ****

```

ufprmc=-99.79+0.1046*fafeed
ufprec=367.01+0.0067*fafeed

```

ufprlc=7458.5+0.0156*fafeed
ufprt=ufprmc+ufprec+ufprlc

c **** HCl Tank *****

hcltom=10**(1.21494+0.549754*log10(lhcldy))
hcltol=10**(3.356396+.116736*log10(lhcldy))
hcltoe=10**(-.21935+.692864*log10(lhcldy))

c **** Na2CO3 Tank *****

ashtom=10**(1.1213472+0.35107*log10(lashdy))
ashtol=10**(2.010064+0.269009*log10(lashdy))*laborc
ashtoe=10**(1.717257+0.431192*log10(lashdy))*energyc

c **** PSS tank ****

pssfed=1012.614+0.962299*lbssa

c **** Clarifier: 1500 is the surface loading rate in gallons per day
c per square foot to give settling surface area needed.

clarif=10.5829*(fret/1500)+3342.05

c **** Sludge disposal *****

slugom=.194393*sludge+96.5963

c

c *** Capital Cost of Equipment ****

c

c **** UF module ***

ufprcp=66966+.938125*fafeed

c **** Mixers for feed, HCl, and Na2CO3 *****

fmixcp=342.+1.68*((fret+fifeed)/1440)-1.71e-4*((fifeed+fret)/1440)**2
hmixcp=342.2+1.68*((fret)/1440)-0.000171*(fret/1440)**2
amixcp=342.2+1.68*(fret/1440)-0.000171*(fret/1440)**2

c ***** HCl Tank *****

$$hcltcp = 10^{(2.954015 + .425884 \cdot \log_{10}(lhcldy))}$$

c ***** PSS tank ***

$$pssfc = 19012.$$

c ***** Na₂CO₃ Tank *****

$$ashtcp = 10^{(2.8633 + 0.389366 \cdot \log_{10}(lashdy))}$$

c ***** Sludge Disposal Lagoon: factor 2 is based on the assumption that
c half of the volume of the lagoon is evaporated throughout the year.

$$slugca = 2391.98 + 0.2856 \cdot (\text{sludge}/2)$$

c ***** Clarifier *****

$$clarcp = 75056 + 365 \cdot (\text{fret}/1500)$$

c ***** Total Capital Cost *****

$$\begin{aligned} tcap &= ufprcp + fmixcp + hmixcp + amixcp + hcltcp + ashtcp + pssfc + slugca + clarcp \\ capgpd &= tcap / \text{frprod} \end{aligned}$$

c

c ***** Operation Cost of Process *****

c

$$\begin{aligned} \text{deprec} &= tcap / 20 \\ \text{capint} &= tcap \cdot \text{intrat} \\ \text{tlabor} &= hcltol + ashtol + ufprlc + \text{clarif} \\ \text{tmaint} &= hcltom + ashtom + ufprmc + \text{slugom} + \text{pssfed} \\ \text{tenerg} &= hcltoe + ashtoe + ufprec \\ \text{tcapom} &= \text{deprec} + \text{capint} \end{aligned}$$

c

c Cost of Chemical, labor, maintenance, energy and capital per 1000
c gallons of product stream

c

$$\begin{aligned} \text{chl03g} &= \text{tchyr} \cdot 1000 / (365 \cdot \text{frprod}) \\ \text{tl03g} &= \text{tlabor} \cdot 1000 / (365 \cdot \text{frprod}) \end{aligned}$$

```

tel03g=tenerg*1000/(365*frprod)
tml03g=tmaint*1000/(365*frprod)
tc103g=tcapom*1000/(365*frprod)
one=tchyr+ufprom+hcltom+hcltol+hcltoe+slugom+clarif
two=ashtom+ashtol+ashtoe+pssfed+deprec+capint
tomcyr=one+two
t10kgl=tomcyr*1000/(365*frprod)
write(6,40)frprod,pfrecd,cappmi,rf,ch103g,t103g,tml03g,te103g,
* tc103g,t10kgl,capgpd
40 format(f8.0,1x,f4.3,1x,f4.0,1x,f4.3,1x,f7.3,1x,f7.4,1x,f7.4,1x,f7.4,
* 1x,f7.4,1x,f7.3,1x,f7.3)
c
c Cost of PSS, Na2CO3, HCl and alum per 1000 gallons of stream
c
pssgal=pdplos*1000/frprod
ashgal=cashdy*1000/frprod
hclgal=chcldy*1000/frprod
alugal=apcdy*1000/frprod
c write(6,60)pssgal,ashgal,hclgal,alugal
c60format('pssal=',f12.5,'ashl=',f12.5,'hclgal=',f12.5,'alugal',f12.5)
30 continue
25 continue
20 continue
10 continue
stop
end

```

Appendix C.4: PEUF Using HCl For Recovery of PSS

```
c
c ***** PEUF USING HCl FOR RECOVERY OF PSS *****
c
c
c program hcl
c
c ***** PURPOSE OF PROGRAM *****
c
c Given the softened water flowrate in gallons per day, hardness in the
c feed and product in ppm, and % of feed recovered, this program
c calculates the capital and operational cost (labor, energy,
c maintenace, chemicals, capital) of the polyelectrolyte-enhanced
c ultrafiltration (PEUF) process for the removal of hardness metals from
c drinking water. The PSS recovery is achieved by adding HCl.

real watgal,pssgal,nohgal,hclgal
real tlabor, tmaint,tenerg,tcapom,ch103g,tc103g,te103g,tl103g,tm103g
real ufrwec,ufrwmc,ufrwlc,ufprlc,ufprec,ufprmc,ufrwlc,ufprtc
real cnohdy,lhcldy, retwas,fret,frfeed,frprod,psscscos,waterc
real naohc,hclca,pssper,hclcos,laborc,energc,fafeed,cappmi
real cainit,cafinl,cappmf,rej,pssin,pssca,pssmax,rf,moleca,molpss
real tcap,capint,lbps, caret,pssret,ptplos,tpssct,pdpper,pdpwas
real pssfed,lbpsa,intrat, nmixcp,hmixcp,lnohdy,naohcl
intrat=0.10
psscscos=3.39
waterc=.00006
hclca=9
pssper=1e-6
hclcos=78.
naohc=0.15
naohcl=0.0463
laborc=21.
energc=.07
write(6,50)
50 format('feedprod',2x,'%rec',2x,'Cai',3x,'Caf',3x,'Chem/10e3g',3x,
* 'Labor',3x,'Maint',3x,'Energy',3x,'Int/Dep',
* 4x,'O&M,$/10KGal',4x,'Cap,$/gpd')
```



```

c  do 10 i=3,6,1
c  do 20 cappmi=40,240,20
c  do 25 cappmf=4,32,7
c  do 30 pfrecd=0.758,.998,0.003
c  frprod=10**i
5  print*, 'Enter the the product flow in gallons per day.'
   read*, frprod
   print*, 'Enter percent recovery of feed desired.'
   read*, pfrecd
   print*, 'Enter initial hardness as Ca in ppm'
   read*, cappmi
   cainit=cappmi/40.08e3
   print*, 'Enter final hardness as Ca in ppm'
   read*, cappmf

c
c  Mass Balances to determine PSS and hardness ion concentration in
c  the Retentate. Determination of rejection based on feed and output
c  concentrations.
c
   cafinl=cappmf/40.08e3
   frfeed=frprod/pfrecd
   frret=frfeed-frprod
   caret=((cainit*frfeed)-(cafinl*frprod))/frret
   careav=((cainit*frfeed)-(cafinl*frprod))/(frfeed-(frprod/2))
   rej=1-(cafinl/careav)

c  ** The following rejection values are based on experimental results***

if(rej.ge.0.995)pssca=6.5
if((rej.ge.0.99).and.(rej.lt..995))pssca=6
if((rej.ge.0.985).and.(rej.lt.0.99))pssca=5.5
if((rej.ge.0.983).and.(rej.lt.0.985))pssca=5
if((rej.ge.0.979).and.(rej.lt.0.983))pssca=4.5
if((rej.ge.0.967).and.(rej.lt.0.979))pssca=4
if((rej.ge.0.95).and.(rej.lt.0.967))pssca=3.5
if((rej.ge.0.915).and.(rej.lt.0.95))pssca=3
if((rej.ge.0.815).and.(rej.lt.0.915))pssca=2.5
if((rej.ge.0.77).and.(rej.lt.0.815))pssca=2
if((rej.ge.0.65).and.(rej.lt.0.77))pssca=1.5
if((rej.ge.0.55).and.(rej.lt.0.65))pssca=1

```

```

pssin=cainit*pssca
pssret=((pssin*frfeed)-(pssper*frprod))/frret
c
c Determine relative flux of PSS/metal ions stream based on concentration
c polarization study of PSS.
c
rf=1.0152*exp(-3.11971*pssret)
fafeed=frfeed/rf
c
c Chemical Cost: PSS, Water, HCl, Na2CO3, alum
c
moleca=frfeed*3.785*cainit
molpss=pssca*moleca
ptplos=pssper/pssret
lbpss=.4546*molpss
tpssct=lbpss*psscscos
pdpper=ptplos*tpssct
pdpwas=ptplos*(tpssct-pdpper)
pdplos=pdpper+pdpwas
lbpssa=pdplos/psscscos
thclyr=hclca*3.785*5e-4*36.5*365*frret*caret/453.59
lhcldy=thclyr*2000/365
chcldy=thclyr*hclcos/365
retwas=0.00075*cappmi*frfeed
cwater=retwas*waterc
mhcldy=caret*frret*hclca*3.785
lnohdy=mhcldy*40.0*naohcl/453.593
cnohdy=lnohdy*naohc
tchdy=pdplos+chcldy+cwater+cnohdy
tchyr=tchdy*365
c
c **** Maintenance, Energy, and Labor Costs for Equipment ****
c
c **** UF Module/ Water Softener ***
c
ufprmc=-99.79+0.1046*fafeed
ufprlc=7458.5+0.0156*fafeed
ufprec=367.01+0.0067*fafeed
c **** UF module/ PSS solution rinse ****

```

```

ufwmc=-99.79+0.1046*((fret+retwas)/rf)
ufwec=367.01+0.0067*((fret+retwas)/rf)
ufwlc=7458.5+0.0156*((fret+retwas)/rf)
ufwtc=ufwec+ufwlc+ufwmc
ufprtc=ufprec+ufprlc+ufprmc

```

c **** HCl Tank ****

```

hcltom=10**(1.21494+0.549754*log10(lhcdy))
hcltol=10**(3.356396+.116736*log10(lhcdy))
hcltoe=10**(-.21935+.692864*log10(lhcdy))

```

c *** NaOH Tank ****

```

nohtom=10**(1.673446+0.266131*log10(lnohdy))
nohtol=10**(3.4763+0.092831*log10(lnohdy))
nohtoe=10**(0.207808+0.902045*log10(lnohdy))

```

c **** Brine Evaporation Lagoon ****

```

belm=10**(.289481+.39184*log10(retwas*365))
bell=(10**(-.15083+.321404*log10(retwas*365)))*laborc

```

c *** PSS feed Tank ****

```

pssfed=1245.*exp(0.0119073*lbssa)

```

c

c *** Capital Cost of Equipment ****

c

c **** UF module ****

```

ufprcp=66966+.938125*fafeed
ufrtc=66966+.938125*((retwas+fret)/rf)

```

c **** Mixers for feed, HCl and NaOH

```

fmixcp=342.+1.68*((fret+frfeed)/1440)-1.71e-4*((frfeed+fret)/1440)**2
hmixcp=342.2+1.68*((fret+frfeed)/1440)-1.71e-4*(fret/1440)**2
nmixcp=342.2+1.68*((fret+frfeed)/1440)-1.71e-4*(fret/1440)**2

```

c **** NaOH Tank ****

$$\text{nohtcp} = 10^{**}(3.058588 + 0.43346 * \log_{10}(\text{lnohdy}))$$

c **** Brine Evaporation Lagoon: factor 2 is based on the assumption that

c half of the volume of the brine solution from the lagoon is evaporated
c throughout the year.

$$\text{belcap} = 10^{**}(0.939543 + .667938 * \log_{10}(365 * \text{retwas}/2))$$

c **** HCl Tank ****

$$\text{hcltcp} = 10^{**}(2.954015 + 0.425884 * \log_{10}(\text{lhcldy}))$$

c **** PSS feed Tank ****

$$\text{pssfc} = 19012.$$

c **** Total Capital Cost ****

$$\begin{aligned} \text{tcap} &= \text{ufprcp} + \text{ufrtcp} + \text{fmixcp} + \text{nmixcp} + \text{hmixcp} + \text{nohtcp} + \text{belcap} + \text{hcltcp} + \text{pssfc} \\ \text{capgd} &= \text{tcap} / \text{frprod} \end{aligned}$$

c

c ***** Operation Cost of Process *****

c

$$\begin{aligned} \text{deprec} &= \text{tcap} / 20 \\ \text{capint} &= \text{tcap} * \text{intrat} \\ \text{tlabor} &= \text{hcltol} + \text{nohtol} + \text{ufwlc} + \text{ufprlc} + \text{bell} \\ \text{tmaint} &= \text{ufprmc} + \text{ufwmc} + \text{belm} + \text{hcltom} + \text{nohtom} + \text{pssfed} \\ \text{tenerg} &= \text{ufprec} + \text{ufwec} + \text{hcltoe} + \text{nohtoe} \\ \text{tcapom} &= \text{deprec} + \text{capint} \end{aligned}$$

c

c Cost of chemical, labor, energy and maintenance per 1000 gallons of
c purified stream

c

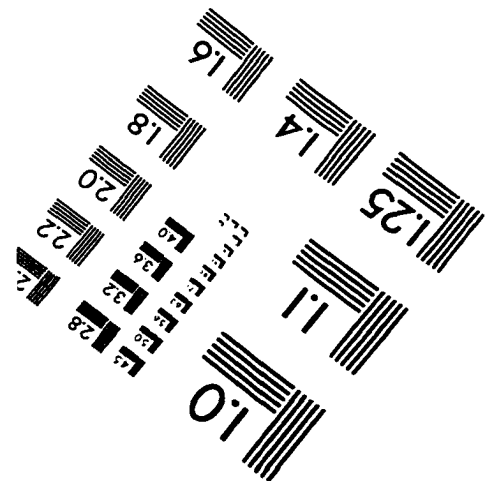
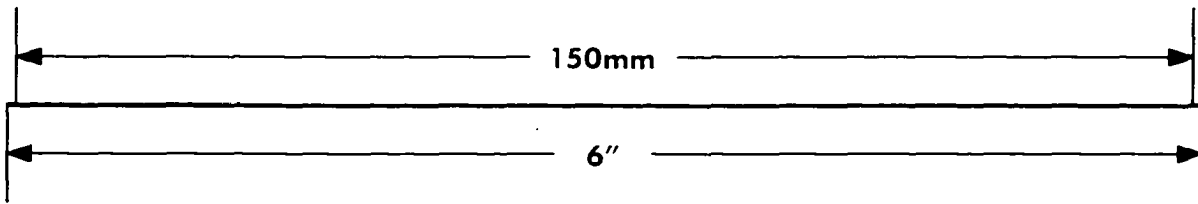
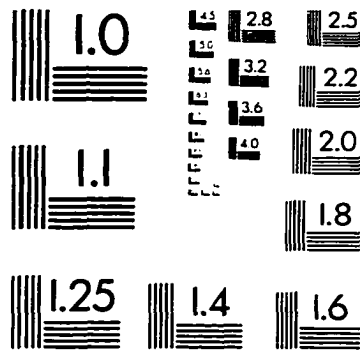
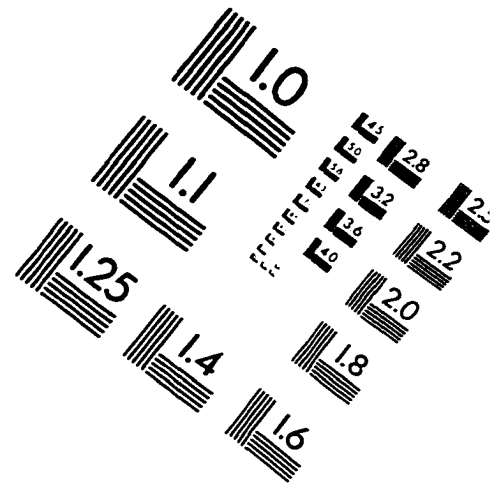
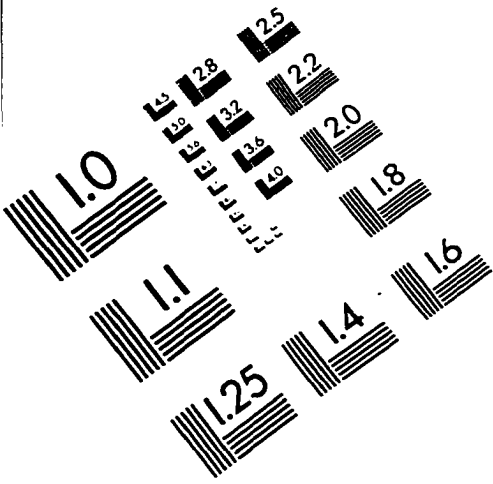
$$\begin{aligned} \text{chl03g} &= \text{tchyr} * 1000 / (365 * \text{frprod}) \\ \text{tl103g} &= \text{tlabor} * 1000 / (365 * \text{frprod}) \\ \text{tel03g} &= \text{tenerg} * 1000 / (365 * \text{frprod}) \\ \text{tm103g} &= \text{tmaint} * 1000 / (365 * \text{frprod}) \end{aligned}$$

```

one=tchyr+ufrwlc+ufrwmc+ufrwec+ufprmc+ufprlc+ufprec+hcltom+hcltol
two=hcltoe+belm+bell+pssfed+deprec+capint+nohtom+nohtoe+nohtol
tc103g=tcapom*1000/(365*frprod)
tomcyr=one+two
t10kgl=tomcyr*1000/(365*frprod)
write(6,40)frprod,pfrecd,cappmi,rf,ch103g,tl103g,tm103g,te103g,
* tc103g,t10kgl,capgpd
40 format(f8.0,1x,f4.3,1x,f4.0,1x,f4.3,1x,f6.4,1x,f7.4,1x,f7.4,1x,f7.4,
* 1x,f7.4,1x,f7.3,1x,f7.3)
c
c Cost of PSS, HCl, Water and NaOH per 1000 gallons of purified stream
c
pssgal=pdplos*1000/frprod
hclgal=chcldy*1000/frprod
watgal=cwater*1000/frprod
nohgal=cnohdy*1000/frprod
c write(6,60)pssgal,hclgal,watgal,nohgal
c60 format('pss',f14.5,'hcl',f14.5,'water',f14.5,'naoh',f14.5)
30 continue
25 continue
20 continue
10 continue
stop
end

```

IMAGE EVALUATION TEST TARGET (QA-3)



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