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REPLACEMENT OF CHEMICAL INTENSIVE WATER TREATMENT
PROCESSES WITH ENERGY SAVING MEMBRANE PROCESSES

Final Report

By
Michael C. Mickley
Steven W. Goering

November 1983

Work Performed Under Contract No. FC07-83ID12243

Coury and Associates, Inc.
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ABSTRACT

The project investigated the use of charged ultrafiltration membranes to treat hard water. More specifically, the work was undertaken to (1) make charged ultrafiltration membranes to demonstrate the technical feasibility of the chemical grafting approach; (2) evaluate the market potential for charged ultrafiltration membranes; and (3) evaluate the cost and energy savings for using charged ultrafiltration as compared to lime-based clarification and other treatment methods. The results suggest that chemical grafting is a relatively simple, reproducible and low-cost way to modify existing substrate materials to give them enhanced transport performance. Process studies lead to the identification of good market potential for membrane processes using charged ultrafiltration membranes. Capital and operating costs relative to lime-based clarification are favorable for low- and medium-sized treatment plants. Finally, substantial energy savings are apparent as compared to lime-based precipitation systems which incur substantial energy consumption in the lime production and transportation steps.

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I. INTRODUCTION

In the last decade, while equipment capital costs have doubled, energy costs have increased by a factor of 5 to 10. There is a need for energy efficient separation processes and this need has increased because of increasing resource constraints and environmental regulations. Membrane systems, in general, do not require the formation of a new phase and consequently they are less energy intensive than traditional separation methods such as distillation. In this same timeframe, improvements in membrane technology have been made which have resulted in the use of membrane processes for a wide variety of applications. Some of these improvements have been in the area of membrane materials. Early membranes were made primarily out of cellulose esters which provided a useful hydrophilic membrane for limited ranges of operating conditions. More recently, hydrophobic membranes possessing superior physical strength and chemical resistance have been successfully made and applied. Improved performance has been attained by making the hydrophobic material more hydrophilic--by achieving a balance between the superior strength and resistance nature of the hydrophobic material and the superior mass transport and antifouling nature of hydrophilic membranes. The most hydrophilic surfaces are charged and it might be argued that whereas previous generations of membranes were neutral, the new generation is charged.

The current project investigates the making of charged membranes by a particular approach--that of chemical grafting--for the specific application of treating hard water. Such a membrane has the potential to:

- be relatively easily made;
- be cost-effective;
- be mechanically and chemically stable;
- achieve increased flux and allow operation at lower pressures;
- achieve increased rejection of electrolytes having a degree of selectivity for multivalent ions;
- have reduced fouling.
- result in a membrane process highly competitive with lime clarification and other alternative means of treating hard water.

While there have been several efforts at making charged membranes, and indeed there are charged membranes commercially available, most of these efforts have been with tight reverse osmosis (RO) membranes or with large pore-sized microfiltration (MF) membranes. The target membrane in this work would be considered on the borderline between RO and ultrafiltration (UF) membranes. It might be considered a loose RO or a tight UF membrane.

The technology applications include situations where complete or near-complete demineralization is not required. These include:

- Softening (municipal and industrial water use);
- Acid mine waters;
- Industrial cooling tower/sidestream softening;
- Municipal sewage treatment;
- Metal processing wastes;
- Brackish-water treatment.

An important consideration in this work is the cost and energy savings possible relative to the use of alternative treatment methods, primarily the lime-based clarification process. A comparison of alternative processes represents part of the effort to determine the technical and economical feasibility of and the market for the charged membrane-based process.

Section II of the report presents the project objectives and the approach used to accomplish these objectives. Section III contains background material in three areas: (1) the lime/soda ash clarification process and the alternative processes of ion exchange, reverse osmosis, and electrodialysis; (2) charged membranes; and (3) chemical grafting. Section IV discusses the research work carried out, namely the making and testing of charged membranes. The results of the research and discussion of the results comprise Section V. Process concerns and charged ultrafiltration membrane economic feasibility, including comparison with the lime/soda ash softening and RO processes are discussed in Section VI. Section VII contains the conclusions and recommendations based on the project work.

Acknowledgment is made here to Diana Menapace for the dependable, conscientious laboratory work; to Dr. Alfred Pollak for many helpful discussions; and to Dr. Mohan Sanduja and Polymer Research Corporation of America for the chemical grafting work.

II. OBJECTIVES AND APPROACH

The specific project objectives are to:

1. Demonstrate the technical feasibility of making charged membranes by the chemical grafting approach--membranes having enhanced properties for demineralization applications and specifically for softening. Although the performance during this phase need not be optimum, the desired performance is:

Greater than 60% rejection of divalent ions;

Flux at operating pressures of less than 100 psi that is two to three times greater than the flux of RO membranes, which is 10 to 30 gallons per day per square foot.

2. Identify and evaluate the market potential for charged ultrafiltration membranes as applied to water softening processes.
3. Identify and document the energy savings for utilizing charged ultrafiltration membranes as compared to lime-based clarification and RO separation methods.

The approach taken to meet the first objective involved:

1. Identifying and obtaining existing substrate materials.
2. Using water-based inorganic initiation and catalyst systems due to cost and probability of success.
3. Going through several iterations of modifying the membranes, characterizing the membranes, and analyzing results.
4. After several iterations, focusing on the best result obtained to improve membrane performance by exercising the several grafting variables.
5. Characterizing the resultant membrane on a flow cell using both single- and multi-salt solutions and specifically a hard water solution.

The approach to accomplish objectives 2 and 3 included discussions with members of the membrane community as part of an information-gathering effort and analysis and the comparison of process considerations.

III. BACKGROUND: WATER SOFTENING, CHARGED MEMBRANES AND GRAFTING.

A. THE WATER SOFTENING REQUIREMENT AND PROCESS ALTERNATIVES

1. Background and Scope of Softening Applications

The term "hardness" in water treatment applications refers to the concentration of calcium and magnesium compounds in water. Other divalent ions such as strontium, ferrous ion, and manganese may contribute to hardness to a lesser degree. Calcium and magnesium bicarbonates are designated as "carbonate hardness," and calcium and magnesium sulfates (or chlorides or nitrates), are said to be "non-carbonate hardness." Water "softening" is the treatment process to achieve the removal of these species. The anions with which these divalent cations are associated are principally the bicarbonate and sulfate ions. High concentrations of calcium and magnesium ions are of concern and require treatment and control for three reasons. First, hardness interferes with and decreases normal soap and detergent activity levels, thereby necessitating significantly higher detergent addition levels as compared to "soft" water. This concern is particularly applicable to municipal applications. Second, calcium carbonate and magnesium hydroxide scale deposition in process equipment, pipes, and on heat transfer equipment in industrial process systems, such as in cooling systems and steam boiler systems, can cause major operating problems and substantially impact overall system operation. High concentrations of Ca and Mg salts also may impact other process considerations in specific industrial processes aside from the power steam generation categories; for example, it inhibits certain specific steps in the textile dying process.

Finally, although not solely hardness focused, significant brackish-water resources containing high concentrations of not only hardness, but sulfates, chlorides, sodium, and color and taste impacting constituents such as iron, could be used for potable water supply. These resources are found to be present across a wide geographical spectrum from Florida and along eastern U.S. coastal regions to through the West and Southwest. These brackish-water levels typically range from 1,500 to 7,000 mg/l total dissolved solids; adequate treatment is required to meet Federal drinking water standards for potable use, and this will be inclusive of hardness removal.

To summarize, the water softening process application for Mg and Ca ion removal is one of the very most widespread of process applications traversing practically every major industrial category (steel, power, petroleum-petrochemical, etc.) where high quality water and/or water reuse is required. These industrial treatment applications can range from small systems where only boiler feed-water is required to large systems of multimillion gallons per day capacities for large industrial cooling systems. Likewise, municipal applications are widespread over large ranges of system capacities.

2. Alternative Processes

a) Introduction

Water treatment approaches for each of the many different feed qualities and product uses will of course vary. Figure 1 presents a generalized spectrum of water quality as related to water origin and use, where quality is depicted by the salinity, or dissolved salt content of the water. In order to increase the quality of sea water or brackish waters, so that they are suitable for domestic or industrial uses, four general processes are typically used. They are demineralization by ion exchange, by membrane processes, by precipitation treatment, and by evaporative separation. Figure 1 also illustrates the general range of feedwater salinity applicable to the charged ultrafiltration process, when these waters also contain significant quantities of hardness compounds.

Membrane separation processes and, in particular, the charged ultrafiltration membrane process and competing lime/soda precipitation processes, will be the principal focus of our discussion of process alternatives. Evaporative-distillation separation is applicable to high TDS sea waters or concentrated wastewater brines and as a rule would not be an active alternate for softening lower range TDS waters. Ion exchange, on the other hand, is clearly a strong application where softening and demineralization to very high product purities are required; for example, ultra high purity process waters in the electronics industry and for high purity-high pressure boiler water in steam generation systems. It is a continuous, low-pressure process and can be highly selective in its removal of specific ions, both anions and cations. The ion exchange resin bed becomes saturated after extended periods of operation, thus requiring periodic regeneration of the bed. The intervals at which this is required vary directly with feed concentrations. Regeneration and the processing and disposal of regeneration wastes are major process considerations and normally limit ion exchange application within upper bounds of 300 to 500 mg/l TDS. Recent studies²⁸ have, in fact, indicated that ion exchange should best be utilized only as a polishing step behind a reverse osmosis pretreatment for TDS levels generally above 130 mg/l.

b) Membrane Processes

Three different membrane processes are currently used extensively for water softening and brackish-water treatment or pretreatment: (1) reverse osmosis (RO); (2) ultrafiltration (UF); and (3) electrodialysis (ED). The current work focuses on the development of charged ultrafiltration membranes which will preferentially remove divalent cations such as Ca and Mg at low pressures and high flux. This section discusses the process characteristics of each of these membrane processes and highlights the potential application range of the new charged ultrafiltration approach.

FIGURE 1
THE WATER SALINITY SPECTRUM

--Reverse Osmosis is the process by which fluids are transported through a semipermeable membrane against the normal osmotic pressure gradient. Figure 2 schematically illustrates the flow principles of RO; the driving force for the separation is pressure; RO systems operate on wide ranges of feed-water qualities and include ion exchange pretreatment applications on low TDS waters and large Mid-East seawater desalting units.

RO is especially applicable to removal of Ca and Mg salts, chloride salts, and bacteria and virus. Significant RO pretreatment may be required, including pH adjustment and suspended solids removals. Flux is comparatively low, in the range of 10 to 30 gallons per day per square foot, even at high pressure/high energy operating conditions (200 to 1200 psi). To achieve high RO water recoveries, multiple units in series or tapered arrangements are required. Also, RO systems exhibit calcium sulfate and silica scaling tendencies when these species are present at high concentrations in the brine reject stream. In summary, RO has established a commercial market for domestic and industrial water and wastewater treatment applications. Low pressure RO (250 psi) is used for softening and TDS removal for potable water in municipalities, and for process water purification and wastewater treatment.

--Ultrafiltration is a membrane process similar to RO in being driven by pressure, using membranes of similar materials, and operating in the same mode as far as the feed, permeate, and rejection streams are arranged. It uses more porous membranes and operates under lower pressure than RO, and successfully removes colloidal materials and high molecular weight solutes and particulates. Like RO, it is unable to remove dissolved organic salts.

To summarize, UF operates at low pressure (20 to 100 psi), and with a relatively high flux typically greater than 40 gallons per day per square foot; it is less susceptible to organic fouling and is designed for mechanical and chemical cleaning. UF usually exhibits an organic molecular weight cutoff. Typical applications include removals of proteins, soluble and suspended oils, pretreatment particulate removal, bacteria and virus removal, and removals of polymers and clays.

--Charged ultrafiltration membranes, which are the primary focus of the current work, would retain the low pressure-high flux attributes of UF, and they would also have the capability of removing divalent and trivalent cations and anions, such as Ca^{++} , Mg^{++} , $\text{SO}_4^{=}$, and $\text{PO}_4^{=}$. Heavy metals such as Cu^{++} , Zn^{++} , Hg^{++} , Pb^{++} , and Fe^{++} , non-ionic silica, and silica complexes might also have enhanced rejections relative to a neutral UF membrane. Rejections of target species are lower for charged UF as compared to RO, so charged UF could be used for other services such as water softening,

FIGURE 2
SCHEMATIC DIAGRAM OF REVERSE OSMOSIS AND ULTRAFILTRATION SEPARATION PROCESSES

acid mine waters, wastewater treatment prior to reuse or discharge, metal processing wastes, and brackish-water treatment. Charged UF applications are lower bounded by product purity requirements and upper bounded on the high side by the shielding effect of high ionic strength-high TDS solutions against the membrane charges. Figure 1 illustrates this feedwater quality range.

--Electrodialysis separation, unlike RO and ultrafiltration, which are pressure driven, is induced by an electrical potential gradient. Cation- and anion-selective membranes are alternately placed across the current path. The electrically attracted cations are allowed to pass through the cation membranes and the anions through the anion membranes, thus increasing and decreasing ionic concentrations in alternating spaces between membranes. Reject streams, containing high concentrations of ions, and product streams, containing low concentrations of ions, can then be separated. Figure 3 shows the typical flow schematic for ED systems. ED operates on systems in the 5,000 mg/l range and greater and will concentrate these to levels of 250,000 mg/l. Colloidal, particulates, and high molecular weight solutes are not removed. Membranes may be flushed with acid, detergents, air and/or other chemicals to inhibit fouling or to clean membranes. Typical applications include NaCl production from seawater, desalting brackish waters, desalting whey, sweetening citrus juices, specialized chemical recoveries, and cooling tower effluent reduction.

3. Lime/Soda Ash Softening

Lime or lime/soda ash precipitation is the most widely used and most generally applicable precipitation-softening process. Lime softening is the reduction of hardness by the application of lime to precipitate CaCO_3 , $\text{Mg}(\text{OH})_2$, or both. The lime addition adjusts the water conditions (pH) such that the least soluble salts, CaCO_3 and $\text{Mg}(\text{OH})_2$, will form. The addition of lime reduces the amount of calcium bicarbonate through precipitation of calcium carbonate. In the pH range of natural waters (5 to 9), most of the dissolved CO_2 is in the bicarbonate form (HCO_3^-). Addition of alkali to raise the pH to about 10.5 converts the bicarbonate to carbonate, which reacts to calcium ions to form CaCO_3 . The addition of lime can also remove magnesium alkalinity. Its addition forms magnesium hydroxide and calcium carbonate. The basic reactions are as follows:

FIGURE 3
SCHEMATIC DIAGRAM OF ELECTRODIALYSIS SEPARATION PROCESS

These reactions indicate that double the amount of lime required to remove calcium alkalinity is needed to remove magnesium alkalinity. In either instance, dissolved carbon dioxide reacts with lime to form insoluble calcium carbonate as follows:

Lime/soda softening, as compared solely to lime softening, is applied to waters containing noncarbonate hardness when the total hardness exceeds the total alkalinity. To counter this condition and allow removal of additional hardness, an artificial source of alkalinity is added in the form of soda ash (Na_2CO_3). The basic reactions are:

Lime/soda softening is most often applied to process waters. When water is to be used for high-purity uses such as boiler makeup, ion exchange softeners are often used in combination with lime softening pretreatment. The lime/soda softening operating requirements are straightforward and of minimal complexity. Figure 4 shows a schematic flow diagram for the process. Required equipment includes a clarifier-softener vessel with sludge recycle capabilities, storage and feed equipment for lime, soda ash, and any coagulant or polymer, and a waste sludge treatment/disposal system. Using the proper chemical additives, primarily lime, soda ash, and sulfuric acid, the following concentrations can be achieved for most waters: calcium--35 ppm as CaCO_3 ; magnesium--10 ppm as CaCO_3 ; bicarbonate alkalinity--0 ppm as CaCO_3 ; silica--varies, depending on starting concentration, water temperature and interfering ions.

FIGURE 4. SCHEMATIC FLOW OF LIME/SODA ASH PRECIPITATION SOFTENING

B. PREVIOUS WORK WITH CHARGED MEMBRANES

The term "charged membranes" applies to any membrane which possesses charged groups capable of influencing membrane performance. Based on intended function, charged membranes may be divided into ion-exchange membranes and other membranes. Ion-exchange membranes are generally isotropic and are used in electrodialysis where convective flow is unwanted. The membranes are highly crosslinked though the charged groups themselves may not be chemically attached to the polymer matrix. The charge density is high and commonly charges are located throughout the membrane. Much of the knowledge about the effects of fixed charges on solute transport comes from the ion exchange and electrodialysis experience.²¹ Our current interest and the following discussion concerns membranes not made for ion exchange use but for convective flow use. These membranes usually possess a charge density an order of magnitude below that of ion exchange membranes.

The uniqueness of charged membranes results from the interaction of charged groups with ionic species in solution and with water. These interactions can lead to making the membranes antifouling, to increasing the flux through the membrane and to enhancing rejections of electrolytes.

Most fouling problems are caused by materials such as clays, proteins, and oily particles which are hydrophobic in nature. They tend also to have a negative charge at pH less than 8. An obvious way to avoid hydrophobic interaction is to make a membrane that is hydrophilic. This can be done by incorporating charged groups into the membrane. If these groups are negative, the charges will also repel the charged portions of the fouling species. The charged surface thus helps maintain stable water fluxes over extended periods which can reduce membrane plant operating costs by extending membrane service life and reducing the need for cleaning chemicals. There has been much work in this area for all types of membranes (RO, UF, MF) and it represents the most successful example of making and using charged membranes. Specifically, the sulfonation of polysulfone has achieved the most success to date. The charges in making the membrane more hydrophilic, make the water-membrane interactions more favorable. The charges on a membrane can also cause orientation of the water dipole. Both effects result in increased fluxes through membranes.

Fixed charges on membranes will repel ions of like charge (the co-ion). Due to the requirement of electroneutrality the counter-ion is in effect rejected. The efficiency of this ion exclusion increases with:

- a) decreasing solute concentration. As the concentration of the solute electrolyte, and specifically the counter-ion, in the feed stream approaches the fixed charge capacity of the membrane, the membrane begins to lose its selectivity and it becomes more permeable to the

co-ion. This is sometimes referred to as charge neutralization or shielding. In the situation of very high counter-ion concentration, the membrane charges are ineffective and the membrane behaves as an uncharged membrane.

- b) increasing charge density (of wet swollen membrane);
- c) counter-ions of low valence and co-ions of high valence; i.e., for a negatively charged membrane the order of rejection should be $\text{Na}_2\text{SO}_4 > \text{NaCl} > \text{CaCl}_2$. This order would be reversed for a positively charged membrane. Counter-ions of higher valence more easily neutralize the fixed charges. In some cases of high enough concentration of trivalent counter-ions, charge reversal can take place--such as Lanthium (+3) changing a negatively charged membrane into an effective positively charged one.⁵ Higher valency co-ions are more strongly repelled by fixed charges than are monovalent co-ions.

Historically, the consideration of utilizing charges on membranes has come from several fronts. Early studies involved the use of ion exchange membranes for RO.³⁰ Systems containing membrane-impermeable polyelectrolytes were found to have increased rejections of simple electrolytes for membranes normally having no such rejection capability.^{7,31} This led to the study of "dynamic membranes" for reverse osmosis.³⁴ Early study of membrane fouling revealed that the most serious fouling problems were due to hydrophobic materials such as clays, protein, and other organics. Further, these materials tend to have negative charges. An obvious way to avoid hydrophobic interaction is to have a hydrophilic membrane surface and the most hydrophilic surfaces are charged surfaces.¹⁷ This situation of negatively charged particle fouling surfaces is essentially the same problem present in making biocompatible materials. The interaction of biological materials at interfaces received much attention in the same 25-year timeframe of the development of membranes. NIH funded many studies to develop non-blood clotting surfaces for use in extracorporeal and later in implantable biomaterials--the former including dialysis membranes.²² In particular, the anticlotting substance, heparin, contains sulfonate groups and several efforts were funded to incorporate heparin-like groups onto biomaterials.

In parallel with these and other efforts, advances in membrane technology have naturally led to the use of charges on membranes. Early membranes were almost exclusively made of fairly hydrophilic cellulose esters which have limits on their chemical and mechanical stability.¹¹ In addition, most of these membranes undergo degradation upon drying.¹¹ Later, hydrophobic materials such as polysulfone, which offers high temperature resistance, wide pH range and stability toward oxidizing agents³⁹ found their way into extensive use. These membranes, being hydrophobic, typically have low fluxes and need to be stored wet or must be manufactured with wetting agents and, in either case, cannot usually undergo drying.¹¹ More recently, membranes have been made which

combine the superior flux and general antifouling nature of hydrophilic materials with the superior strength and resistance nature of the hydrophobic materials. As the most hydrophilic materials possess charges, many newer membranes are charged membranes. Membranes may be made which can be dried without damage.

Several different approaches have been used to incorporate charges on the membranes to upgrade their hydrophobic nature. Some involve chemical treatment of the membrane matrix to produce charged groups such as in the sulfonation of polysulfone. Others blend a charged polymer, or one that can be modified to have a charge, with an uncharged polymer prior to casting of the membrane. Others involve swelling of the membrane matrix with subsequent entrapment of charged polymers. Still others involve grafting, or the formation of covalent bonds between the charged species and either the polymer prior to casting or the existing membrane matrix.

Several membrane companies are experimenting with charged membranes and some have such membranes commercially available. The methods used to put charges in the membranes include all those mentioned. These membranes are mostly thin film composite RO membranes and large pore-sized microfiltration membranes. The works most closely related to the present project in terms of application of charged UF membranes include Bhattacharyya's several laboratory studies using a Millipore experimental membrane.⁴ The behavior of di- and trivalent ions with charged membranes is well demonstrated in these studies. Membranes of much higher flux, yet of good rejection, have been reported by the Israel Desalination Engineering Company and discussed by Sachs.³³ The particular application was for processing sewage pond effluent. The work shows highly favorable comparisons with the lime reactor clarifier and with RO systems for this application.

Romicon has a positively charged membrane which was developed specifically for cathodic paint application.⁹ The membrane has good fluxes (28 gfd) at very low pressure (15 psi). Although positively charged membranes may encounter significant fouling from natural waters or other waters containing negatively charged foulants that are not removed by a pretreatment step, they can be quite attractive for specialized applications. Examples are the cathodic paint applications mentioned above, and RO systems where significant pretreatment is used.

There are several other charged membranes of recent note not discussed here, including those made by Puropore, Filmtec, Albany International and Nitto for RO and RO/UF purposes, and Cuno and Pall for MF purposes. The interest, development and use of charged membranes by these companies and others appears to be growing, and whereas the previous generation of membranes might be characterized as being uncharged, the new generation may be considered to be charged.

C. PREVIOUS MEMBRANE GRAFTING WORK AND CHEMICAL GRAFTING

Grafting in the present terms means attaching monomer molecules to a substrate or polymer molecules, and the subsequent polymerization of the monomers, thus building side chains onto the backbone of the existing substrate or polymer molecule. The grafting reaction between the substrate and unsaturated monomer is initiated by formation of a free radical on the substrate surface. The reaction then proceeds as a classical free radical addition polymerization reaction.

A good comprehensive review of grafting as pertaining to RO membranes is given in the 1977 reference 36. There are three general ways to initiate the grafting reaction. The initiation may be done chemically, photochemically, or with ionizing radiation. Although the capital equipment need is considerably less with the chemical and photochemical approach, most work on membranes has used the ionizing radiation approach. Potential advantages of this approach include good yields at relatively low temperature, the constant rate of production of radicals with time as opposed to chemical grafting, the generation of radicals deep in the polymeric structure independent of swelling conditions, and the absence of catalyst residues. The chemical approach, on the other hand, has the advantage of simplicity. The chemical approach has not received much attention--at least in terms of published literature. Any of the grafting approaches may be used either to graft onto the raw polymer prior to casting the modified polymer into a membrane or to graft onto an existing film or substrate material. To obtain charges, the grafted species may itself be ionic or it may be nonionic, followed by suitable chemical modification to render it ionic as in the manufacturing of ion exchange membranes.

Referring back to the discussion of making a hydrophobic substrate hydrophilic, it is preferable to have the ionic group as a pendant group which does not impart hydrophilicity to the structurally important hydrophobic backbone.¹¹ Grafting approaches assure this. From published studies,^{25,27} it has been found that the rejection of electrolytes in tight membranes initially increases as the amount of charged groups on the wet membrane increases, since the charge density is also being increased. However, as the number of charged groups continues to increase, the amount of water attracted by the charges also increases and the membrane will swell. A point is reached when the additional swelling caused by added charges is proportionally greater than the relative number of new charges, such that the charge density actually decreases. At this point, the rejection will begin to decrease. Flux continues to increase as the membrane water content increases. A similar effect has been found in the sulfonation of polysulfone where above a certain amount of sulfonation the swelling pressure becomes excessive and the membrane solubilizes.²⁷ The goal then is high performance that does not swell the membrane.

The most extensive membrane chemical grafting work was done for the Office of Saline Water by Polymer Research Corporation of America.²³ In this work, many different hydrophilic monomers were grafted onto both cellulose acetate polymers and onto cellulose acetate membranes. The polymers were then cast into membranes. The best results in terms of rejection and flux were obtained from the grafting of charges directly onto the formed membrane. The grafting approach taken in the current work is similar to that of reference 23.

Figure 5 schematically represents the steps taking place in chemical grafting onto a substrate. The chemical reaction step is followed by a heat-curing step. The grafting chemical reaction may be represented by

where SUB represents the substrate and * represents a radical. A vinyl monomer molecule then reacts with the activated substrate:

where X represents the functional group containing the charge. A second molecule of monomer then attaches itself to the first:

Additional side-chain propagation may take place to some extent, depending on the grafting materials, concentrations and conditions. The side-chain or pendant group is strongly attached by a covalent bond to the backbone substrate material. Typically, the bond cannot be broken by ordinary acids, bases or solvents. Water soluble polymers when bonded to the substrate will not leach out. It is important that the initiator activates a substrate molecule without activating monomer molecules. The formation of homopolymers in the solution uses up monomers that could otherwise be attached to the membrane.

The grafting can be done at atmospheric pressure and temperatures less than water boiling temperature and less than the limits of substrate degradation.

FIGURE 5. GRAFTING REACTION STEPS

IV. RESEARCH WORK CARRIED OUT

A. INTRODUCTION

This section discusses the research performed in the making and testing of membranes. The investigation and development of process feasibility estimates, which is research of a different kind, is discussed in Section VI.

The grafting work was done in two phases, not by design but by what the results dictated. In the first phase, two substrate materials of large pore size, industrial cellophane of 75 Angstroms and unmodified polysulfone of 175 Angstroms were used. From practical considerations of solute size and the range of charge effects, the charged membrane should be in the range of 10 to 30 Angstroms--this is supported by the successful attempts at making similar charged membranes^{6,9,33} by different means. We found that significant decreases in the pore size required massive crosslinking of the grafted species. The apparent result was that a gel film formed which collapsed upon testing. Membranes were made that had extremely low fluxes such that it became impractical to measure rejections. Later, several substrate materials were found that were nominally of 10 to 15 Angstroms in pore size. The discussion and results presented are from this second phase effort. The actual chemical grafting was performed by Polymer Research Corporation of America. The grafting process variables, the materials and chemicals used, and the procedures followed are discussed in detail in Section IV-B.

The testing of the membranes included both batch and flow cell determinations of flux and rejection. Discussion of the test equipment, procedures and conditions are discussed in Section IV-C.

B. GRAFTING WORK

This subsection contains detailed information about the chemical grafting work performed and complements the general discussion of subsection III-C. Shown in Figure 6 are the grafting operation steps that were followed during the time when many different kinds and combinations of chemicals and different substrate materials were being tried. The pre- and post-drying was necessary to determine the add-on weight. The variables of the grafting process are given in Table 1. The treatment bath contains a minimum of four chemicals: the monomer, solvent, initiator and catalyst. More than one monomer, solvent, catalyst or initiator may be used. Both inorganic and organic chemicals may be used and have achieved success in grafting work. The chemicals used in this study were water-based inorganic chemicals chosen for cost and nontoxicity reasons. The variables include the identity and the concentration of all chemicals, together defining a "formulation", and the temperature and times of each of the drying, treatment and curing steps. Formulations that provided an add-on weight underwent cycles of soaking and drying to indicate whether or not the add-on was "permanent." In later

FIGURE 6
GRAFTING PROCESS FOR EXPERIMENTS

TABLE 1. VARIABLES IN GRAFTING PROCESS

DRYING:	Temperature (120 to 160°F)	
	Time (15 to 50 minutes)	
TREATMENT:	Monomer(s)	} Identity concentration
	Solvent(s)	
	Initiator	
	Catalyst	
	Temperature (120 to 160°F)	
	Time (5 to 50 minutes)	
CURING:	Temperature (120 to 160°F)	
	Time (15 to 50 minutes)	

work, where efforts focused on the more successful formulations, the sequence of processing steps was simplified to eliminate the drying and weighing steps. As mentioned in the results section, the drying of the substrates had a significant effect and the elimination of the initial drying step was done to avoid changes in the substrate prior to grafting. The grafting process steps were conducted at atmospheric pressure and in temperature ranges of 120°F to 160°F. The times of the drying, treatment and curing steps ranged from 5 to 50 minutes.

Table 2 lists the solvents and initiator used as well as the various monomer agents and membrane substrate materials. The monomers included charged monomers of both signs and uncharged acrylamide monomers. The solvents studied included water and isopropyl alcohol, both individually and in various ratios of the two solvents. The catalysts were varied between the concentration of 0.5 and 1.5 weight percent and the initiators between the concentrations of 10 and 50 ppm.

Filmtec Polysulfone and an industrial cellophane were used in the initial phase of work discussed in the Introduction. The second phase work was restricted to Osmonics substrates. The nominal pore sizes for the Polysulfone and VF₂, which is a polyvinylidene fluoride membrane, is 15 Angstroms. The cellulose acetate pore size is nominally 11 Angstroms. The membranes were received from Osmonics stored in a 5-weight percent solution of formaldehyde. Sheets of membranes, 7 inches square, were cut from rolls of membrane of approximately 36 inches width. All subsequent grafting and testing was done on either the sheets or portions cut from the sheets. After membrane strips were cut, some sheets were tested to determine flux and rejection to establish control values. Other sheets were sent to PRCA for modification by grafting. Two-inch squares were cut from the larger sheets and used to identify which formulations gave "permanent" add-on weight. Formulations successful in this sense were then used to modify entire membrane sheets. The modified sheets were sent to us for testing. Sheets were sent in zip-lock plastic bags containing enough distilled water to keep the membranes wet. Very early in the work, formaldehyde was added to the water. Later, after suspicions of interaction of the formaldehyde with the modified membranes, this practice was discontinued. Eventually, 0.02-weight percent sodium azide solution was used as a preservative in all shipments and storage.

TABLE 2. MATERIALS USED IN GRAFTING STUDIES

SUBSTRATES

Polysulfone (Filmtec)
Cellophane

Polysulfone (Osmonics)
VF₂ (Osmonics)
CA (Osmonics)

MONOMERS

Polyethylenamine Epomin P-1000
2-Acrylamido 2-Methylpropanesulfonic Acid (AMPS)
Quaternary Ammonium Prepolymer LV-261
Vinyl Acetate Ethylene Prepolymer AIRFLEX-110
Sodium Vinyl Sulfonate
N-Methylene bisacrylamide
Dimethylaminoethylmethacrylate (DMAEMA)
Ethylene Glycol Dimethacrylate (EGDMA)
N-Methylol Acrylamide

SOLVENTS

IPA
H₂O

CATALYSTS

Proprietary

INITIATOR

Silver Perchlorate

C. MEMBRANE TESTING

Figure 7 shows the two testing systems used in characterizing the membranes according to their flux and rejection. The batch-stirred cell is an Amicon model 8050 which has a reservoir capacity of approximately 60 ml and tests 43 mm diameter membranes. All runs were made at 70 psi with the cell pressurized by nitrogen gas. The feed batch solution is concentrated with time as permeation takes place. A magnetic stirrer is used to drive a mounted stirring bar in the cell to lessen the influence of concentration polarization. The range of flux values encountered was quite large. In some cases the entire 60 ml batch feed could be pushed through the membrane in 20 seconds. In other cases it would take many hours. Typically, the first ml of filtrate was discarded and the next 5 to 10 taken as the permeate sample. The data on flux and rejection were not taken at steady-state conditions as was evident by the changing flux and rejection values during the early minutes of the testing. The flux would usually decrease with time and the rejection increase, likely due to compaction of the membrane. Even though the data were taken in this "batch" manner, the data were reproducible and useful for relative comparisons. The absolute values of flux and rejection were not, however, representative of steady-state values.

During the "screening" portion of the membrane testing, when treated membranes were being characterized to identify promising formulations, only this type of batch cell data were taken. The membranes were characterized by water flux, Na_2SO_4 flux and rejection, and CaCl_2 flux and rejection.

In later testing after the more promising formulations had been identified and subsequent work was restricted to these formulations, all data were taken on an Amicon TC1R flow cell. The flow cell permits efficient usage of the membrane by minimizing concentration polarization through high velocity flow across the membrane surface. Further, steady-state data could be easily achieved using full recycle of the concentrate and permeate streams back to the feed tank. The cell uses 150 mm diameter membranes. The test cell has a spiral flow path and the effective flow channel has dimensions of 14.3 mm width, 0.8 mm height and 90 cm length. The cross-sectional area for flow is 0.114 cm^2 and the effective surface area for permeation is 134 cm^2 . All runs were made at high velocity to minimize concentration polarization. Actual velocities used ranged from 150 to 400 cm/sec although tests showed that flux and rejections were unchanged for velocities much lower than these. Two feed tanks were used in an alternative manner during the testing. One tank was dedicated to water and the other to salt solutions. For a given membrane, the initial run was made with distilled water or a 0.02 weight percent solution of sodium azide. The run was typically one hour long during which time the flux and the conductivity-based rejection of species present reached steady-state values. The next run with a salt solution was usually made immediately following the water run. The

BATCH STIRRED CELL

FIGURE 7
MEMBRANE TEST SYSTEMS

solution contained either a single-salt such as either Na_2SO_4 , CaCl_2 , CaSO_4 or a synthetic hard water. Steady-state operation, as reflected by flux and rejection values, was always reached within one hour. A water run to rinse the membrane was made after each salt run. This run lasted at least 15 minutes. The water runs provided checks on the integrity and stability of the membranes.

The salt solutions were typically at a concentration of 5 milliequivalents/liter for all solutions used. Analysis of electrolyte concentrations was done by conductivity measurements, using a Beckman conductivity Bridge Model RC 16B2. Flux rates were determined by measuring volumetric flows using a graduated cylinder and a stopwatch. The feed solution was pumped by a model 220-646 high-pressure/high-flow magnetic gear pump made by Micropump. The pump output was separated into two flow streams--one going to the test cell and the other bypassing the test cell and going directly back to the feed tank. Each stream had a flow control valve and the flow and pressure to the test cell could be changed by adjusting the valve settings. The test cell concentrate flow stream also had a flow control valve to provide back pressure to the cell. By adjustment of all three valves, a wide range of cell flows and pressures could be obtained. The flow cell was run with inlet and exit pressures of 80 psig and 60 psi, respectively, giving an average pressure of 70 psi. Feed solutions of between 7 and 11 liters were kept in polypropylene tanks. A stainless steel cooling coil was placed in the tanks during runs to maintain temperatures to within $\pm 0.5^\circ\text{C}$ of a value in the range of 20 to 22°C . Tap water was used as the cooling fluid.

V. RESULTS OBTAINED AND DISCUSSION

A. BATCH-CELL TEST RESULTS

Tables 3-A, B, and C list the batch-cell test results for the three substrates tested. Initial entries are from the characterization of the membranes prior to modification by grafting. For the larger pore polysulfone and vinylidene fluoride-like membranes, considerable variation was found from samples taken within a single 7-inch square sheet and between sheets. The variability is likely due to both the small area of the membrane sample and also to the data not being taken at steady-state conditions. Other entries are listed for each substrate by formulation number. The monomers used in the formulation are listed by abbreviation. The key to the abbreviation is at the end of the table. The first entry is formulation 92. Approximately 70 formulations were tried with the large-pore polysulfone and cellophane substrates used in early grafting studies. Data from these tests are not presented in the report. Not all formulations gave grafting results with "permanent" add-on weight. Only those with such add-on weight were sent to us for testing. In the first 68 formulations, perhaps 4 were sent. Formulations from 70 to 118 correspond to the second set of substrates, the Osmonics polysulfone, polyvinylidene fluoride-like and cellulose-acetate membranes. The absence of table entries below formulation 92 reflects simply that none of these formulations was successful in giving "permanent" add-on weight. Appendix A contains information about all formulations tried.

In all cases, two different 47-mm diameter membranes were cut from the 7-inch square sheet of modified membrane and soaked in distilled water for 20 minutes. Each membrane was tested with both sodium sulfate and calcium chloride. One circle was tested with sodium sulfate first and the other with calcium chloride first. In nearly all instances the second run for each electrolyte gave a lower rejection than the first run. The effect was more dramatic where the rejections were low. The membranes were not rinsed well between runs and if rejections are assumed to follow charge density, then the results suggest a shielding effect where residual counterions from the first run masked some of the charges in the second run. The entries in Table 3 are composite values for the two runs.

Table 4 shows a summary of data for each of the substrates. It includes ranges of flux and rejection values found for the unmodified or virgin substrate, the modified substrate and for blanks. Blanks here are defined as substrates which were exposed only to the drying steps of the grafting process. As can be seen, the drying of membranes had pronounced effects on the three membrane substrates. These effects were accentuated in the true blank case where the substrate was also exposed to the solvent bath. For the polysulfone (PS) and the vinylidene fluoride-like (VF₂) membranes, the flux decreased and the rejection remained the

TABLE 3-A. BATCH TEST CELL RESULTS FOR POLYSULFONE SUBSTRATE

Formulation Number	Monomer(s) Used	Water Flux*	Na ₂ SO ₄		CaCl ₂	
			Flux	Rejection	Flux	Rejection
Virgin	--	1.4 to 14.6	0.76 to 15.4	0.0 to 0.15	1.6 to 4.2	0
92	EPOMIN, DMAEA	0.16	0.16	0.19	0.20	0.44
92A	EPOMIN, DMAEA	0.21	0.19	0.25	0.30	0.12
93		2.0	2.0	0.12	2.6	0.08
101	AMPS, NMBISA	1.0	0.80	0.53	0.70	0.14
103	SVS, NMBISA	1.25	0.87	0.78	1.75	0.13
104	SVS, NMBISA	4.10	4.73	0.14	5.79	0.02
106	AMPS, NMBISA	1.84	1.94	0.45	1.99	0.01
107	SVS, NMBISA	0.75	0.57	0.48	1.29	0.03
107A	SVS, NMBISA	2.91	3.50	0.36	4.22	0.01
115	SVS, NMA	1.46	0.75	0.15	1.00	0.05
115A	SVS, NMA	0.31	0.27	0.54	0.49	0.07
117	SVS, NMBISA	2.78	2.88	0.07	3.68	0.03
118	SVS, NMA	1.44	1.66	0.64	2.00	0.07

* Flux is in g/min for test cell; 1 g/min = 35.0 gfd

TABLE 3-B. BATCH TEST CELL RESULTS FOR VF SUBSTRATE

Formulation Number	Monomer(s) Used	Water Flux*	Na ₂ SO ₄		CaCl ₂	
			Flux	Rejection	Flux	Rejection
Virgin	--	43.0 to 89.0	37.0 to 86.0	0.02 to 0.06	39.0 to 96.0	0 to 0.04
92	EPOMIN, DMAEA	78.4	70.5	0.05	--	--
92A	EPOMIN, DMAEA	88.8	87.0	0.04	--	--
93		63.9	65.1	0.03	--	--
101	AMPS, NMBISA	83.8	69.0	0.05	77.4	0.03
103	SVS, NMBISA	35.7	34.0	0.14	39.0	0.08
104	SVS, NMBISA	78.9	80.0	0.07	64.5	0.02
106	AMPS, NMBISA	29.5	20.7	0.06	28.1	0.04
107A	SVS, NMBISA	28.8	16.0	0.05	25.4	0.01
111		77.2	31.3	0.06	46.4	0.03
112		40.4	48.7	0.05	64.2	0.03
114		34.8	11.9	0.08	21.0	0.06
115A	SVS, NMA	24.1	19.3	0.04	26.7	0.10
116	SVS, NMBISA	40.9	12.2	0.25	20.4	0.07
117	SVS, NMBISA	29.8	12.4	0.13	27.0	0.01
118	SVS, NMA	26.8	22.1	0.07	45.7	0.02

* Flux in in g/min for test cell; 1 g/min = 35.0 gfd

TABLE 3-C. BATCH TEST CELL RESULTS FOR CELLULOSE ACETATE SUBSTRATE

Formulation Number	Monomer(s) Used	Water Flux*	Na ₂ SO ₄		CaCl ₂	
			Flux	Rejection	Flux	Rejection
Virgin	--	0.50 to 0.58	0.35 to 0.56	0.89 to 0.92	0.39 to 0.41	0.57 to 0.62
92	EPOMIN, DMAEA	41.0	13.4	0.05	--	--
92A	EPOMIN, DMAEA	3.6	2.07	0.15	--	--
93		37.2	29.4	0.00	--	--
101	AMPS, NMBISA	0.20	0.13	0.50	0.20	0.10
106	AMPS, NMBISA	0.28	0.26	0.55	0.29	0.15
107A	SVS, NMBISA	0.07	0.05	0.61	0.05	0.48
115	SVS, NMA	0.35	0.13	0.73	0.15	0.59
115A	SVS, NMA	0.05	0.04	0.77	0.07	0.68
117	SVS, NMBISA	0.20	0.18	0.54	0.17	0.17
118	SVS, NMA	0.18	0.19	0.79	0.18	0.33

* Flux is in g/min for test cell; 1 g/min = 35 gfd

MONOMER KEY

EPOMIN = Polyethylenamine Epomin P-1000
 DMAEA = Dimethylaminoethylacrylate-Mon-Arc EA-1
 AMPS = 2-Acrylamido-2 methylpropanesulfonic Acid
 NMBISA = N-Methylenebisacrylamide
 QAP = Quaternary Ammonium Prepolymer LV-261
 SVS = Sodium Vinyl Sulfonate
 NMA = N-Methylolacrylamide

TABLE 4. SUMMARY OF BATCH TEST CELL RESULTS

MEM-BRANE	FORM	FLOW*	Na ₂ SO ₄ REJECTION	CaCl ₂ REJECTION	WEIGHT LOSS***
PS	Virgin	2 to 16	2 to 15%	0	--
	SS Virgin +	5.0 to 6.5	21 to 36	--	--
	Dried**	.3 to 2.5	0 to 32	2 to 3	--
	True Blank	.3 to 1.0	0 to 11	2 to 10	6%
	Treated	.1 to 5.0	3 to 78	2 to 44	--
VF	Virgin	40 to 80	2 to 9	0 to 4	--
	SS Virgin	5.8	--	--	--
	Blank	3 to 8	7 to 18	0 to 14	--
	True Blank	.2 to .6	7	0 to 17	.6%
	Treated	20 to 90	2 to 25	0 to 10	--
CA	Virgin	.3 to .6	89 to 95	57 to 62	--
	SS Virgin	0.42	--	--	--
	Blank	.1 to 1.0	17 to 68	10 to 60	--
	True Blank	3.5 to 13.4	4 to 10	2 to 6	1%
	Treated	.05 to 18.0	0 to 79	0 to 68	--

* Initial nonsteady state g/min for batch cell: 1 g/min = 35 gfd

** Dried exposed to heat effects only; blank exposed to both heat and solvent effects.

*** Relative to virgin membrane

+ Steady-state values obtained from flow cell and converted to batch cell area basis.

same or perhaps increased slightly. In the case of cellulose acetate (CA), the opposite effect happened--the flux increased while the rejection decreased. The weight loss encountered by the true blanks ranged from a high of 6 percent for PS to .6 percent for VF. These results are not totally unexpected. The hydrophobic membranes such as PS and VF are usually shipped wet and sometimes are manufactured with a plasticizer or wetting agent. After drying, these membranes can be difficult to wet. CA, on the other hand, is well-known to undergo irreversible morphological changes upon drying. The treated membranes appear not to show the effects that the blanks show. The treated membranes either did not undergo the same changes--as if the grafted species prevented such changes--or the changes were compensated for by a more substantial effect due to the grafted species.

B. FLOW-CELL TEST RESULTS

Because of high rejections, remaining work focused on formulations 103 and 118, and the polysulfone substrate. Both formulations use the sodium vinyl sulfonate monomer. Table 5 lists the flow-cell test results for various modifications of these two formulations. The values for both flux and rejection are steady-state values. Also listed are corresponding values for the virgin and blank membranes and the values for runs made to indicate the reproducibility of the grafting procedure. Formulation 120 achieved the highest sodium sulfate rejection, at 88 percent. Its value was checked after several weeks, which included several runs with other salt solutions. The sodium sulfate flux and rejection were unchanged.

Table 5 also contains the results of runs made with calcium chloride, calcium sulfate and synthetic hard water solutions. The rejections of these salts were considerably less than that of sodium sulfate.

The reproducibility of the grafting procedure is reflected in two different membranes made with formulation 125 and several made with a slight modification of formulation 120. Figure 8 shows the sodium sulfate flux plotted against the rejection for the virgin membrane, several formulations, and the two sets of membranes made for reproducibility checks. To demonstrate the behavior of some membranes, water or salts were added incrementally to see the effect on rejection. All results were consistent with those expected of charged membranes. The time to reach steady-state was much longer with the virgin membranes than with the treated membranes, including the blanks. Steady-state for the virgin membranes required as much as one hour, while only 10 minutes or less were required for the treated membranes.

C. DISCUSSION

The first important question to be answered in the grafting work was whether or not weight was being added to the membrane. In several early instances the add-on weight leached out of the treated membrane. In later formulations the add-on weight appeared permanent in that it did

TABLE 5. FLOW CELL RESULTS WITH POLYSULFONE MEMBRANE/SODIUM VINYL SULFONATE MONOMER
(All Salt Solution at 5.0 mequiv/Liter)

FORMULATION NUMBER	MONOMER USED	WATER FLUX+	Na ₂ SO ₄		CaCl ₂ OR CaSO ₄ ***		HARD WATER	
			FLUX	REJECTION	FLUX	REJECTION	FLUX	REJECTION
Virgin	None	50.0	--	--	--	--	--	--
Virgin	None	55.0	49.0	25.0	--	--	--	--
Virgin	None	--	60.0	35.0	--	--	--	--
Virgin	None	--	70.0	21.1	--	--	--	--
Blank	None							
Blank	None							
#119	SVS*	38.0	28.0	63.0	--	--	--	--
#120	SVS*	8.8	8.0	88.0	12.0	6.5	11.5	17.0
					10.4	27.0**	10.7	21.0
#121	SVS*	16.0	15.0	58.0	--	--	--	--
#122	SVS**	23.0	22.0	79.3	21.0	5.0	17.0	13.5
#123	SVS**	9.5	9.3	69.3	10.5	1.5	8.0	15.0
#124	SVS**	42.0	42.0	36.0	--	--	--	--
#125	SVS*	5.3	5.3	85.5	--	--	5.9	21.2
#125	SVS*	5.0	5.2	85.0	--	--	--	--
#120-E	SVS*	5.0	5.4	74.0	9.5	15.0***	9.7	11.0
Diluted with water; added 1 part new water to 2					9.5	18.0***		
Added NaCl at 1.5 mM					8.0	15.0***		
#120-D		5.0	5.0	71.5	--	--	--	--
#120-B		4.0	4.0	67.0	--	--	--	--
#120-A		4.0	4.0	69.2	--	--	--	--

+ -- 1 Unit = 3.5 gfd

* -- With N-Methylolacrylamide

** -- With N-Methylenebisacrylamide

FIGURE 8. FLOW CELL RESULTS; POLYSULFONE

not decrease with additional cycles of soaking and drying. Later, the stability of the membrane performance over time and with usage also suggested the add-on weight was "permanent." The "permanent" add-on weight could happen because covalent bonds are formed between the monomers and the substrate, or because an insoluble polymer is formed inside the pores of the substrate. This might happen where soluble monomers enter the pores and become heavily crosslinked as they polymerize. To avoid this second, unwanted situation we did not use strong crosslinking agents in the formulations. In view of this, the add-on weight is likely covalently attached to the substrate.

The next question to be answered was whether or not the add-on weight possessed charges; i.e., was the increased rejection because of the closing of the pores or because of the presence of charges (or both)? All monomers used, whether they contained charged groups or not, were hydrophilic. Thus the increased hydrophilicity of the membrane, as judged by visual and tactile changes in the membrane surface and by water uptake, could not indicate whether charges were present. The relative rejection of various salts, however, was consistent with Donnan exclusion behavior associated with the presence of charges. This was evident in negatively charged membranes by the higher rejection of sodium sulfate than of calcium chloride. In the positively charged membranes, calcium chloride rejection was higher than that of sodium sulfate.

The next important remaining question concerned the charge density. There are several indications that the charge density attained is low. In charged membranes following Donnan exclusion behavior, the rejection of salts increases with charge density of the coion and decreases with charge density of the counterion. For a negatively charged membrane, this means rejection of sulfate salts will be greater than rejection of chloride salts, and the rejection of a calcium salt will be less than that of the corresponding sodium salt. This is the behavior that was just described for the grafted membranes. The differences, however, in rejection values depends on the concentration of salts relative to that of the fixed charges. Where there is an excess of fixed charges, the differences in rejection should be small, for the presence of any of the salts has little effect on the total effective charge density. Where the electrolyte concentration is closer to the fixed charge concentration, differences in electrolytes become magnified and rejections reflect this. Even though the electrolyte concentrations used in the present work are fairly low, being about 5 milliequivalents/liter, the difference between the sodium sulfate and calcium chloride rejections is quite large. This strongly indicates that the charge density on the modified membranes is low.

The likelihood of a low charge density is also suggested by the formulations used. Formulations with only a charged monomer and no acrylamide present did not give permanent add-on weight. Acrylamide, a non-charged but hydrophilic monomer, was required to obtain add-on weight. Even though the charged monomers were present in excess of the acrylamide monomer, there is no guarantee that the ratio of monomers

in the polymerized chain is the same. The chain may be a predominantly uncharged monomer. Low charge density could occur by these circumstances.

The general performance level measured for the various chemical formulations appeared to be near optimum based on considerations of flux, rejection and pressure drop, and it is believed that the performance could not be greatly improved for any of the chemical systems made up of a specific combination of monomer, catalyst and inhibitor. In the course of the grafting and testing, grafting conditions were varied and the best set of conditions were those shown in Table 6. The initiator used was not varied and herein lies the most likely explanation for the low charge density. The initiator creates free radical reaction sites on the substrate surface and a more efficient initiator creates more sites. The more sites at which the grafting reaction takes place, the higher the surface charge density will be. The inorganic initiator used was chosen because it is water-based and thus relatively inexpensive and because it has produced good results in similar applications. Upon concluding that the initiator was a main factor for the low charge density, we no longer had the resources left to try other inorganic and organic initiators. We have, however, personal communications concerning recent experimental work that suggest that initiators other than the one used might produce substantially improved results. We expect that the need for acrylamides could be dispensed with or a second charged monomer could be used in their place. Without the acrylamide present, the grafted and polymerized chain would contain only charged monomer groups. Both the elimination of uncharged monomers and the creation of more bonding sites would lead to higher charge densities.

The reproducibility of the grafting procedure appears quite good. It also appears to be significantly better than the variability of the untreated virgin substrate. We expect reproducibility to be improved in a continuous as opposed to batch process and to be entirely adequate for ultrafiltration membranes.

In broad review, the grafting of membranes, like the making of membranes retains a character of art and experience. Our experience, as well as that of others that we have learned of through private discussions and published literature, suggests that it is very difficult to predict results based solely on theory. Many formulations did not result in "permanent" add-on weight due to peculiarities of their interaction with the substrate material at the grafting temperature and process timing tried. A subset of the formulations tried did result in "permanent" add-on weight and these membranes were then tested to determine flux and rejections of single salt solutions at a standard set of conditions. A portion of these membranes gave attractive flux and rejections sufficient for further investigation. At this point some optimization of grafting conditions took place. Generalization as to what formulations with what substrates work are difficult to make. It appears that each material must be considered by itself as there are unique interactions between the original substrate, the grafted polymer with its ionic group, and the ions and water present in the solution to be treated. Flux and rejection seemingly can independently go up or down, likely depending on the effect of the graft on membrane swelling, on membrane plugging and on water structure.

TABLE 6. OPTIMUM CONDITIONS FOR FORMULATIONS TRIED

CHARGED MONOMER:	Sodium Vinyl Sulfonate
UNCHARGED MONOMER:	N-Methylolacrylamide or N-Methylenebisacrylamide
MONOMER RATIO (by weight):	4:1 for N-Methylolacrylamide 16:1 for N-Methylenebisacrylamide
SOLVENTS:	50:50 Water and Isopropyl Alcohol
TREATMENT TIME:	10 minutes
TREATMENT TEMPERATURE:	140°F
CURING TIME:	30 to 35 minutes
CURING TEMPERATURE:	160°F

The current results, utilizing the water-based inorganic initiator and catalyst system, have proven the grafting concept and carried the work in the right direction. Membranes with stable properties, and of good reproducibility, were made. The charge density is lower than desirable; however, the believed cause for this and a probable solution to this has been identified.

VI. PROCESS ANALYSIS

A. INTRODUCTION

The purpose of Section VI is to focus in greater detail on the process considerations of the charged ultrafiltration membrane operation. The key factors affecting the technical and economic feasibility of the CUF are highlighted and potential energy savings are detailed as compared to reverse osmosis systems and lime precipitation systems, which are judged to be the process's principle market competition.

B. TECHNICAL PROCESS REVIEW

The process considerations critical to the technical feasibility of the CUF membrane process are principally performance related. For example, purely from a technical perspective, can the CUF approach remove the species targeted for removal simultaneously with water recoveries high enough such that process performance requirements can be achieved. For each application, the required separations will vary. For example, the rejections required for brackish-water softening for potable water use in southeast coastal regions will differ in nature from those required for operations on metal processing wastes where the concentrate represents a valuable product that can be recovered and recycled, and where the permeate probably must meet legal discharge requirements. In certain cases, the CUF process in combination with other pretreatment or post-treatment processing may meet the required performance level. In such cases, the feasibility issues become economic and operational rather than purely technical or performance oriented.

The basis for performance for the charged ultrafiltration process is the grafting of negative (or positive) charges onto a chosen substrate such that the original UF separation characteristics are substantively enhanced for certain target species. In the current work, negative charges were grafted onto a proven polysulfone substrate; the negative charges on the substrate then repel negative charged anions in the feed stream, such as the SO_4^{--} ion (or nitrate, chloride, etc.). The laws of electroneutrality then govern and cations are carried away with the repelled anions. Softening, i.e., Ca and Mg removal, are the specific applications considered in this study. For that case, Ca^{++} and Mg^{++} ions are rejected with the repelled anions. As discussed in Section III-B, the rejection of anions and cations is dependent on their charge density and concentration level and, more specifically, on their ability to be repelled by, or to shield, charges on the membrane. Higher charge density anions will be more effectively repelled by, and higher charge density cations will more effectively shield, the negative charges on the membrane. The pore size of the CUF is comparatively large relative to an RO pore size and the selective rejection of these multivalent ions is thus related to this pore size, as well as the effective charge density of the negative charges on the membrane, the ionic strength of the feedwater and the composition of the feedwater.

The significance of the above is twofold. First, the CUF process will not achieve high separations of singly charged ionic species such as NaCl salts, and its application for processes requiring high levels of overall TDS removal is not appropriate. Second, the rejection performance of the CUF membrane is a function of the unshielded charges on the membrane. When very high ionic strength feedwaters are processed, the positive ions in these solutions can shield the negative charges such that rejection can be markedly decreased. The salt concentrations at which significant shielding tends to occur, such that rejection falls to a range of 50% to 75% of its value in dilute salt solutions, is 3000 to 10,000 mg/l TDS.^{9,33} The actual salt concentration at which significant shielding occurs depends on the several factors just mentioned. As the concentrate stream moves horizontally across the membrane surface it becomes further concentrated. Referencing Figure 9, as the feedwater enters the membrane cartridge, the ionic strength is essentially that of the feedwater. The product permeate migrates through the membrane, experiencing selective removal of ions during its pass. The reject stream moves horizontally along the membrane surface toward the exit point of the cartridge, with it becoming more and more concentrated in ionic strength with each step along the path. This represents a higher ionic strength feed to the remaining membrane surface area and the resulting shielding effect of the charges on the CUF result in lower rejection levels of the anions present and consequently of the Ca^{++} and Mg^{++} ions associated with the anions.

FIGURE 9
FLOW SCHEMATIC FOR A MEMBRANE SEPARATION STEP

It is also clear that the shielding effect, for a specified feed stream nearing the recommended feed stream concentration upper bound, will also be dependent on the required water recovery. For high water recovery levels, the reject becomes more concentrated and the shielding effect increases. This effect then decreases the actual average rejection rates of the module as a whole.

The significance of the above discussion is that if feedwaters are of a higher than recommended ionic strength, high water recoveries must be balanced against high performance rejection objectives since high water recoveries may initiate shielding to the point of significantly affecting performance. The above discussion lays the basis for identifying commercial market potentials for the CUF process. It will likely be applicable to low-medium range TDS feedwater concentrations, of the order of 300 to 3,000 mg/l. Values as high as 5,000 mg/l may be appropriate depending on the individual chemical constituents and the product purity and water recovery requirements. Furthermore, it is more applicable to feed streams where high removals of monovalent inorganics are not required. The CUF system, like most UF systems, requires minimal pretreatment as compared to RO and the charges present can further contribute to the system being less susceptible to fouling.

At this juncture, it is also instructive to discuss two other process considerations which both affect the performance criteria of the process and very directly affect the economic viability of the CUF application. These two factors are flux and the accompanying pressure-driving force necessary to accomplish that flux.

The flux, defined as the flow of permeate through the membrane per unit area per time, directly determines the membrane surface area required for processing a given feed stream and hence defines the capital cost basis for the installation.

The key objective of the CUF approach is to obtain favorable flux within the framework of a low pressure driving force. Typical RO operates at pressures of 400 psi and as high as 800 to 1200 psi. This requires special feedwater pumps which are capital intensive, and it incurs high energy-based operating costs. Low pressure RO normally operates in the range of 200 to 250 psi, representing significant energy savings over higher operating pressures. This is accomplished at the expense of lower rejections (usually) but with similar flux. The CUF approach, however, goes a step beyond by decreasing operating pressures to the range of 20 to 100 psi while maintaining and likely increasing flux levels.

Flux is most often expressed as $\text{gal/ft}^2\text{-day}$ or GFD. A second useful measure of flux and its pressure driving force is expressed as flux per psi driving force. This is sometimes referred to as the membrane constant or the membrane permeability. Typical high pressure RO values are $0.05 \text{ gal/ft}^2\text{-day-psi}$; low pressure and loose RO systems may double that to $0.1 \text{ gal/ft}^2\text{-day-psi}$. CUF membranes can operate in the range of $2 \text{ gal/ft}^2\text{-day-psi}$, which represents a 20-fold increase in flux per

unit driving force. The net result is that for applications where partial, selective softening and TDS removal is required, the CUF separation process holds the significant potential for demonstrating its applicability to meet performance requirements at much lower energy consumption levels and with significantly lesser capital intensive equipment.

C. GRAFTING PROCESS CONSIDERATIONS

Prior to commercialization, the CUF membrane development must demonstrate a membrane production process capable of providing a chemically grafted membrane with high charge densities (to insure high performance) at reasonable and competitive costs. This will be based on availabilities of competitive costing substrates which can be treated (chemically grafted) inexpensively. The current study work indicates this can be done; already commercial substrates can be utilized (polysulfone in this testing) and treatment costs are estimated to run less than \$0.25 per ft² of membrane surface area, and most likely in the range of 2 to 10 cents per ft². This compares to typical commercial membrane costs of \$2.00 to \$8.00 per ft². Thus, one can conclude that the grafting step will not significantly increment the final product cost. In addition to low cost, the grafting process must produce a new membrane with good reproducibility characteristics--that is, the new membrane production process must be able to produce a uniform and consistent quality of membrane which can be demonstrated to consistently meet all performance criteria. The current work--even though not entirely representative of the expected production process--shows that the grafting process has an excellent potential for good reproducibility. The grafting processing step is a relatively simple one and in full-scale production represents the continuous pulling of the membrane materials through a chemical bath. Thus, the process is expected to become even more soundly reproducible once full-scale manufacturing is achieved.

Finally, the new membrane must prove to be mechanically sound and able to operate and maintain its new grafted characteristics within reasonable pH limitations (pH 4 to pH 9) and with reasonable resistance to chemical attack and subsequent degradation. Preliminary results of testing in these areas are promising.

D. ECONOMIC REVIEW

The economic feasibility and the commercialization potential of the proposed CUF process is dependent on two principal factors. First, the CUF separation must be competitive in initial capital costs. Too high a capital cost, even when combined with low operating costs, decreases the commercial attractiveness of a treatment approach. Second, the long-term operating costs of the system, projected over the life of the system, in combination with the amortization of the capital debt, must compete with the total cost of alternative processes. In developing such comparisons it is essential that the economic comparison is one of apples against apples, i.e., the process must perform essentially the

same service for the same advantage. Also, the costs must reflect essentially the same battery limits. For example, pretreatment and sludge disposal requirements must be considered consistently.

For purposes of our review here, our economic comparison of the competing processes will focus on preliminary analyses of capital costs and their principal components, and operating costs and their principal components. These costs are based on various telephone and written communications with suppliers and consultants, and supported by U.S. Environmental Protection Agency documented data. The analysis will consider both size and feedwater quality as integral to the review, and costs will be categorized according to the respective treatment requirements. For partial softening applications, low-pressure RO, charged ultrafiltration, and lime clarification are the three processes originally viewed as competing for the defined "softening-TDS removal" market utilized as the basis of the comparison. The softening application considered is one where very high (~90%) removals of TDS are not required but where removals of Ca^{++} and Mg^{++} hardness are of ~70%. Water recovery for the CUF case is defined at 75%, and product water is assumed for potable use. Each process has inherent advantages which may or may not be important for a specific treatment requirement and plant site. A few of these are mentioned here. For instance, membrane processes are inherently modular in nature. This means that if membrane processes have a cost advantage over alternative treatment processes it is usually for lower and medium-sized plants where the economy of scale applying to nonmodular processes is less significant. Membrane processes usually require less space than do capital equipment intensive processes such as lime/soda ash clarification. This space requirement may be very important in Florida but much less significant in Wyoming. The lime/soda ash process produces a sludge that must be disposed of, whereas the CUF concentrate-reject stream is not a sludge. The concentrate may be disposed of in a variety of ways depending on local requirements. These could range from constructive irrigation use to dewatering and the formation of a sludge for disposal. For these and other reasons, the analysis of costs of treatment waste streams is a difficult one to consistently consider. For purposes of our discussions here it is assumed that lime clarification precipitation sludges will equal costs surrounding disposal or reuse of the reject-concentrate stream. The overall validity of this assumption is, of course, application dependent. In a similar sense, no economic penalty is herein assigned to the CUF process for the lower water recoveries than achieved in the normal lime-softening process.

As referenced earlier, the competing processes for the defined application are low-pressure RO, the charged CUF and lime/soda ash precipitation. The following review quantitatively considers only the latter two. The reasons are twofold. First, the program focus was the replacement of chemical/energy intensive water treatment systems with

energy saving membrane systems; lime/soda ash softening is perhaps the most prominent of these. Second, for the defined service, the proposed CUF membrane system enjoys clear economic advantages against the RO system. This can be concluded as follows. The capital cost economics of RO versus CUF will favor CUF. CUF will require less pretreatment in the form of pH control, suspended solids removal, and protection against organic fouling. It generally is more easily cleaned and is, in fact, designed for such. Also, the flux of CUF systems is projected to be higher than its RO counterpart, and would thus require less surface area. With comparable unit area membrane costs, the CUF membrane costs would be less. In RO systems, which give relatively high rejections, only a portion of the feedstream may be treated and later mixed with the untreated portion to give a product water of intermediate quality. Where organics or color may be present such that their removal is required, this blending scheme cannot be used. The entire feed must be treated and if a high rejection membrane is used, costly overtreatment results. For this situation, a lower rejecting, low-pressure RO system is a better choice and a CUF membrane better yet.

CUF also enjoys distinct operating cost advantages, principally due to its low pressure operation of 25 to 75 psi as compared to 200 to 250 psi for the RO. The energy savings thus achieved are substantial. Finally, a significant, long-term operating expense of membrane systems is membrane replacement. These are judged as comparable for the two systems. Based on the above, the new CUF system once commercialized would enjoy a favored economic position, hence providing the basis for its comparison to lime softening in the following discussions.

The principal economic considerations of the two competing processes are presented in Table 7. CUF capital costs are estimated at \$.25 to \$.45/gallon per day of capacity for systems greater than 100,000 gpd. Operating costs for the CUF system are expected to average in the range of \$.25 to \$.30 per 1000 gallons of treated water for the same size or larger systems. Debt amortization is not included in these numbers. CUF operating costs are generally more independent of feedwater quality than lime precipitation softening.

For lime softening, capital costs for a 1.0-million gallon per day system are estimated at \$.30 per gallon per day of capacity.^{18,19,20} Costs will rise substantially per unit product water for smaller plants and conversely decrease for larger plants. Operating costs for lime systems will be heavily dependent on feedwater quality as related to the carbonate and noncarbonate hardness of the feedwater, since the chemical addition cost is the largest and most significant operating cost of that type of system.

It is useful, therefore, to bracket the operating cost as a function of the hardness removal. In Section E, energy savings likewise will be

TABLE 7

SYSTEM COST COMPONENTS*
CHARGED ULTRAFILTRATION AND LIME PRECIPITATION PROCESSES

CHARGED ULTRAFILTRATION

CAPITAL COSTS

Feedwater Pumps
Membrane System Cost
Miscellaneous Piping
Buildings Housing System
Controls and Instrumentation

Pretreatment -- None**
Reject Stream Disposal
Assumed Equal To That Of
Competing Alternative

OPERATING COSTS

Pumping - Electric Power
CUF Membrane Replacement
Labor

LIME/SODA ASH PRECIPITATION

Chemical Receiving and Feeding
System (Storage and Slakers)
Contactor/Precipitator/Clarifier
Buildings and Land
Controls and Instrumentation
Piping and Pumps, As Required
Acid Feed System
Sludge Handling and Disposal
Assumed Equal To That Of
Competing Alternative

Pumping, Electric Power As Required
Chemicals--Lime and/or Soda Ash
Sulfuric Acid
Labor

* Other significant factors affecting economics of both systems include system capacity (economy of scale) and feedwater composition

** Can be feedwater chemistry dependent.

similarly bracketed. For the operating cost figures presented below, costs are presented for feedwater qualities of 125 mg/l to 400 mg/l of calcium and magnesium carbonate hardness. For the 125 mg/l case, 0.9 pounds of 90% CaO-lime per 1000 gallons of feedwater are required; for the upper bound of our analysis of 400 mg/l hardness, the lime demand is 2.5 pounds of 90% CaO per 1000 gallons of treated water. This translates into operating costs of \$.25 per 1000 gallons for a one-million gallon per day plant, and suggests the lime clarification economy of scale may start to dominate at about this plant capacity. As noted earlier, these costs are exclusive of estimated sludge dewatering and ultimate disposal costs, which can be very significant and which would substantially increment the above figures.

These cost data confirm other communications regarding the capital and operating costs of these competing processes. Quinn³² suggests UF can compete favorably with lime systems at capacities less than 0.4 million gallons per day depending on the specific applications. Basic Technologies, Inc., which markets low-pressure RO systems, states that their systems are competitive in some instances with lime for capacities up to 2.5 mgd.¹⁶

E. ENERGY SAVINGS REVIEW

A principal focus of the current work effort was to establish the basis for energy savings through the use of low-pressure, 25 to 75 psi, charged ultrafiltration membrane separation as compared to lime precipitation processes. To accomplish a meaningful comparison, the principal energy demands of each process have been documented; the process energy requirement for the CUF separation is principally the electric energy to run the feedwater pumps to pump fluid across the membrane surface at the required operating pressures. For CUF systems, energy requirements are 1.02 kW hours per 1000 gallons of product water.¹⁹ The energy requirements for lime-based systems are somewhat more complex and include energy costs to run pumps, sludge rakes, and chemical feed equipment. Much more extensive, however, is the energy required for lime production and transportation of the lime to the site of use. These latter two energy demands are significant and are discussed below.

The energy consumed to produce lime occurs in the high temperature calcining process where limestone is converted to quicklime. Stated chemically, this reaction is:

The theoretical heat required for high-quality quicklime production is 2.77 million Btu/ton of CaO. Actual energy used is much higher; typical U.S. plants vary widely in thermal efficiency, with energy usage ranging from 4.5 to 12 million Btu/ton. A good average figure is 6.0 million Btu/ton of high-quality quicklime and 600 KW hours of electricity/ton.

Sodium carbonate, or soda ash, is most normally produced by mining and processing the naturally occurring deposits of trona in the Western

United States. In the mining process, trona (sodium sesquicarbonate, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) is brought to the surface in solid form, crushed and ground, and dissolved in water. The solution is clarified, thickened, filtered and sent to vacuum evaporator-crystallizers from which part of the soda ash is recovered in solid form. The remaining solution is cooled to precipitate additional soda ash and bicarbonate. These solids are then calcined to yield soda ash. The principal energy consumption occurs in the evaporation steps and amounts to 6.5 million Btu per ton of product and 200 kW hours of electricity per ton of soda ash. The energy required for the transportation of consumed water treatment chemicals is not included in the above figures. The following discussion illustrates a method that may be used to estimate transportation energy requirements.

Consumable materials are normally transported by railroad and/or truck. A 25-ton diesel truck, averaging 4 mpg and using fuel with a heat value of 142,500 Btu/gal, requires 1,425 Btu/ton-mile. An energy study for the Ford Foundation gives 670 Btu/ton-mile for railroad transportation of freight. Lime and some of the other consumables are usually delivered to or near the point of use by railroad. A railroad transportation distance of 1500 miles plus 50 miles round trip by truck gives a total energy requirement for transportation of about 1,150,000 Btu/ton. This amount of energy for transportation is about 19.2% of the total energy required for the production of lime; this figure could be even greater if rail delivery is not possible. For a completely rigorous energy analysis, the required energy for sludge dewatering and ultimate disposal should also be included. For the preliminary analysis presented here, the sludge handling and disposal requirements are assumed equal to the disposal requirements of the reject-concentrate of the CUF process.

Based on the production and transportation energy requirements of 7.15 million Btu/ton of lime as presented, energy consumption converted to equivalent energy expressed as kW hours for low hardness water would be 1.35 kW hours/1000 gallons; for the high hardness waters, the energy requirement is 3.50 kW hours/1000 gallons. Thus, the CUF process enjoys a net savings of 2.48 kW hours/1000 gallons. For a 1 million gallon per day plant, this represents an annual energy savings of 0.90 megawatts. On a national scale, this represents significant potential for savings. In 1983, U.S. lime production was 14.1 million tons; approximately 20% of that total was used for water treatment and pollution control applications.¹³ Because of the substantial variation of raw water and wastewater feed qualities to lime precipitation plants, it is difficult to quantify the exact potential for national energy savings. This analysis indicates it is very substantial, however.

Additional energy savings related to reduced soda ash consumption could also be realized due to that part of its total annual production rate of 8.3 million tons per year that is used for water treatment.

F. SUMMARY--PROCESS CONSIDERATIONS

Once commercialized, the charged ultrafiltration process offers significant process advantages over both the low-pressure reverse osmosis and the lime precipitation water treatment methods. The CUF process is a competitive process for low- to medium-range TDS feedwaters (300 to 3,000 mg/l) which require moderate removals (70%) of divalent and trivalent anions and cations, and where high removals of monovalent inorganics are not required. Bacteria and virus, suspended solids, and high molecular weight organics are also effectively removed via ultrafiltration application. In addition, charged ultrafiltration is characterized by:

- Low pressure/high flux operation
- Moderate capital cost
- moderate to low space requirements
- 65%-75% removal of Ca^{++} and Mg^{++} hardness
- Significant overall TDS removals
- Modular construction, eliminating necessity for overdesign to meet anticipated growth
- Moderate to low operating costs
- Low chemical addition requirements
- On-off operation minimizing time-consuming startups and operator attention
- Minimized sludge disposal requirements
- Favorable antifouling characteristics
- Ease of chemical cleaning.

VII. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The project work recently concluded provides a firm, positive basis for ultimately commercializing the process. Present chemical grafting results are consistent, reproducible, stable and explainable, and ways to improve the performance results are identified. The grafting approach to making charged membranes is simple and of low projected cost. The application of charged membranes to water softening is both technically and economically sound. Restrictions on use of such membranes are identified. The potential for both the chemical grafting approach and for charged membrane application go far beyond the specific softening application studied here.

Specific conclusions are:

1. Chemically grafted membranes were successfully produced that possessed charges and were stable with time.
2. High Na_2SO_4 rejections (88%) were obtained through the use of the newly grafted charged membranes.
3. Lower calcium salt rejection levels are attributable to lower than desired charge density. The choice of the initiator is the most likely factor significantly impacting the charge density.
4. The grafting studies have produced a membrane with stable and covalently bonded added-on materials.
5. The CUF membranes possessed charged groups; performance characteristics of the membranes were consistent with Donnan exclusion principles.
6. In more recent literature and experience, other initiators have achieved considerable success, even in cases where the current initiator has not worked to expected levels. Use of these initiators should improve the performance results significantly.
7. The use of rejection and flux performance is necessary to identify promising membranes for further study; however, surface charge density and surface analysis methods would be extremely useful and perhaps necessary tools to use in more completely understanding and interpreting grafting process results.
8. Chemical grafting onto substrate material to make membranes is a simple process mechanically and one of low cost.
9. Even at a stage of manual, small sample operation, reproducibility of results is good. Reproducibility should increase with more controlled automated operation.

10. Membrane making remains somewhat of an art and its success is characterized by knowledge and experience combined with sound fundamentally based engineering approaches. The current level of understanding and theory do not provide complete predictability as to what substrate, monomer and other chemicals will always lead to successful grafting.
11. The primary performance limitation is the shielding or neutralization of the fixed charges that takes place at high concentrations of counterions.
12. Charged ultrafiltration processes currently are economically favored as compared to lime-based precipitation systems for small- to moderately-sized plants with capacities up to 0.5 mgd and possibly as high as 2.5 mgd, depending on the specific site and process application.
13. CUF capital costs are estimated at \$.25 to \$.45 per gallon of plant capacity per day for plant sizes of 100,000 gpd and above. Operating costs are estimated at \$.25 to \$.30 per 1000 gallons of product water.
14. In many applications where RO-type product water is not needed, UF processes currently compete favorably with RO processes. The charged UF process, which provide rejections intermediate between the RO and UF membranes and do so at less pressure than either the RO or UF, should compete favorably with both RO and UF in these applications.
15. The energy savings associated with the use of charged UF membrane processes applied to hard water as compared to use of lime-based clarification are very substantial and the widespread application of CUF would save large quantities of energy currently consumed in water treatment chemicals production.
16. Estimated energy savings for a 1-mgd plant for softening applications range as high as 0.90 megawatt hours annually.

B. RECOMMENDATIONS

The charged ultrafiltration process shows strong potentials for commercialization and its continuing development should be pursued. The following recommendations for additional work phases are aimed at making a viable charged ultrafiltration membrane for use in treating hard water and in other important industrial and commercial applications. These efforts build on the positive technical and economic feasibility estimates developed in the current work.

The specific recommendations are:

1. Alternative initiators should be studied with the same polysulfone substrate, with the goal of improving surface charge density.
2. Surface analysis methods and charge density determinations should be used as tools to understand and direct the development of high-performance charged membranes.
3. Chemical and mechanical stability of the charged membranes should be further confirmed.
4. Larger pore-sized polysulfone should be investigated to determine the optimal substrate pore size.
5. Potentials for grafting onto less expensive substrate materials, such as polypropylenes, should be investigated.
6. The technical performance of the CUF membrane for softening applications should be demonstrated in field applications.

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APPENDIX A

Composition of Graft Coating
Formulations

Formulation #70

Parts By Weight

AMPS	4.00
N-Methylolacrylamide (48%)	4.00
Water	90.00
Hydrogen Peroxide (30%)	0.50

Formulation #72

Parts By Weight

AMPS	6.00
N-Methylolacrylamide (48%)	8.00
IPA	63.50
Water	40.50
Elvamide 80 63 (10% water/butanol 10/90)	3.00

Formulation #80

Parts By Weight

Sodium Vinyl Sulfonate	2.00
N-Methylenebisacrylamide	2.50
IPA	50.00
Water	47.00
Silver Perchlorate (0.1%)	0.01

Formulation #81

	<u>Parts By Weight</u>
Diallyldimethyl Ammonium Chloride	10.00
Water	45.00
IPA	43.50
	1.50
	0.50
Sipomer Q-6-75	1.50
Silver Perchlorate (0.1%)	0.01

Formulation #83

	<u>Parts By Weight</u>
Methacrylamidopropyl trimethyl	
Ammonium Chloride	3.50
N-Methylolacrylamide	1.50
	2.00
	0.50
Water	42.50
Silver Perchlorate (0.1%)	0.01

Formulation #85

	<u>Parts By Weight</u>
AMPS	0.50
HEMA	2.00
N-Methylolacrylamide	2.00
Water	40.00
IPA	50.00
	4.00

Formulation #85 Cont'd

	<u>Parts By Weight</u>
	0.50
Dimethylamino ethylacrylate	0.25
Silver Perchlorate (0.1%)	0.02

Formulation #86

	<u>Parts By Weight</u>
Monomer Sipomer Q-6-75	4.00
Dimethylamino Ethylacrylate	1.00
AMPS	0.50
	2.00
	0.20
Water	93.00
Silver Perchlorate (0.1%)	0.01

Formulation #90

	<u>Parts By Weight</u>
Monomer Sipomer Q-6-75	4.00
Dimethylamino Ethyl Acrylate	1.00
Acrylic-Vinylidene Copolymer Polidene 33-004	2.00
	2.00
Water	91.00

Formulation #92

	<u>Parts by Weight</u>
Polyethylenamine Epomin P-1000 (30%)	4.0
Dimethylaminoethylacrylate-Mon-Arc EA-1	1.0
Isopropanol	35.0
	0.2
	0.1

Formulation #92A

	<u>Parts by Weight</u>
Polyethylenamine EPomin P-1000 30%	2.0
Dimethylaminoethylacrylate Mon-Arc EA-1	1.0
Isopropanol	35.0
	0.2
	0.1

Formulation #101

	<u>Parts by Weight</u>
2-Acrylamido 2-methylpropanesulfonic Acid(AMPS)	8.00
N-Methylenbisacrylamide	2.00
	0.50
	0.10
Water	200.0
Silver perchlorate (0.1% solution)	0.10

Formulation #101A

	<u>Parts by Weight</u>
2-Acrylamido-2 methylpropanesulfonic Acid (AMPS)	8.00
N-Methylenbisarylamide	2.00
	0.5
	0.10
Water	100.00
Isopropanol	100.00
Silver Perchlorate (0.1% solution)	0.08

Formulation #102

	<u>Parts by Weight</u>
Quaternary ammonium prepolymer LV-261	5.00
Vinyl acetate ethylene prepolymer AIRFLEX-110	2.00
Water	95.00
Silver perchlorate (0.1% solution)	0.10

Formulation #103

	<u>Parts by Weight</u>
Sodium vinyl sulfonate (SVS-25% solution)	16.00
N-Methylene bisacrylamide	1.00
Water	48.00
Isopropanol	48.00
	5.0
	1.00
Silver perchlorate (0.1% solution)	0.10

Formulation #104

	<u>Parts by Weight</u>
Sodium vinyl sulfonate (SVS-25% in water)	16.00
N-methylenebisacrylamide	1.00
Water	96.00
Isopropanol	96.00
	5.00
	1.00
Silver perchlorate (0.1% solution)	0.08

Formulation #105

	<u>Parts by Weight</u>
Sodium vinyl sulfonate (SVS)	16.00
N-methylenebisacrylamide	2.00
Water	96.00
Isopropanol	96.00
	5.00
	1.00
Silver perchlorate (0.1% solution)	0.08

Formulation #106

	<u>Parts by Weight</u>
2-Acrylamido-2-methylpropanesulfonic Acid (AMPS)	4.00
N-Methylenebisacrylamide	2.00
Dimethylaminoethylmethacrylate (DMAEMA)	0.50
	5.00
	1.00

Formulation #106

	<u>Parts by Weight</u>
Water	69.5
Isopropanol	27.0
Silver perchlorate (0.1% solution)	0.10

Formulation #107

	<u>Parts by Weight</u>
Sodium vinyl sulfonate (SVS-25% in water)	25.00
N-methylenbisacrylamide	1.50
Ethylen glycol dimethacrylate (EGDMA)	0.50
Isopropanol	27.00
Water	65.0
	0.50
	1.00
Silver perchlorate (0.1% solution)	0.07

Formulation #107A

	<u>Parts by Weight</u>
Sodium vinyl sulfonate (SVS-25% solution)	20.0
N-methylenebisacrylamide	1.2
Dimethylaminoethylmethacrylate (DMAEMA)	0.5
Isopropanol	25.0
Water	60.0
	0.5
	1.0
Silver perchlorate (0.1% solution)	0.1

<u>Formulation #115</u>	<u>Parts By Weight</u>
Sodium Vinyl Sulfonate (25% Solution)	32.0
N-Methylol Acrylamide (48%)	4.0
Water	40.0
Isopropanol	25.0
	0.1
Silver Perchlorate (0.1% Solution)	0.1

Pretreatment: 50 VF Subjected to etching in 2% chlorosulfonic acid, OPS in methylene chloride for 3-4 minutes prior to treatment with monomer solution.

<u>Formulation #116</u>	<u>Parts By Weight</u>
Sodium Vinyl Sulfonate (25% Solution)	80.00
N-Methylene Bisacrylamide	5.00
Water	240.00
Isopropanol (IPA)	240.00
	1.00
	3.00
Silver Perchlorate (0.1% Solution)	0.35

Comments:

Samples of 50VF were preactivated by treating with 7% chlorosulfonic acid in methylene chloride for 10 minutes. Rinsed and washed with IPA/H₂O mixture of 50/50 and finally with deionized water, dried and then treated with formulation #116 for 10 minutes at 140°F. Curing time :30 minutes at 140°F.

<u>Formulation #117</u>	<u>Parts By Weight</u>
Sodium Vinyl Sulfonate (25% Solution)	100.00
N-Methylene Bisacrylamide	6.25
Water	170.00
IPA	340.00
	1.20
	4.00
Silver Perchlorate Solution (0.1%)	0.45

Comments:

50 VF preactivated with 7% chlorosulfonic acid for 10 minutes - rinsed and washed with IPA/H₂O - 50/50 and finally with deionized water. Treated with formulation #117 for 10 minutes at 140°F.

<u>Formulation #118</u>	<u>Parts By Weight</u>
Sodium Vinyl Sulfonate (25% Solution)	20.00
N-Methylolacrylamide (48% in Water)	2.50
IPA	45.00
Water	45.00
	0.15
	1.00
Silver Perchlorate (0.1%)	0.15

Comments:

50 CA-treated with formulation for 5 minutes at 120°F

OPS-preactivated with formulation for 10 minutes at 140°F.

OVF-preactivated with 7% chlorosulfonic acid for 10 minutes at 140°F prior to treatment with formulation for 10 minutes at 140°F.

<u>Formulation #119</u>	<u>Parts By Weight</u>
Sodium Vinyl Sulfonate (25%)	24.00
N-Methylolacrylamide	3.00
IPA	45.00
Water	45.00
	0.20
	1.50
Silver Perchlorate (0.1%)	0.10

<u>Formulation #120</u>	<u>Parts By Weight</u>
Sodium Vinyl Sulfonate (25%)	20.00
N-Methylolacrylamide	5.00
IPA	45.00
H ₂ O	45.00
	0.20
	1.50
Silver Perchlorate (0.1%)	0.10

Method of Treatment:

1. Washed/OPS with deionized water- thoroughly
2. Immersed in the formulation, which was preheated to 140°F for 10 minutes. Take it out
3. Subjected to cure in the oven at 160°F for 30-35 minutes.

<u>Formulation #121</u>	<u>Parts By Weight</u>
Sodium Vinyl Sulfonate (25%)	24.00
N-Methylolacrylamide	2.00
IPA	45.00

Formulation #121 Cont'd.Parts By Weight

Water

45.00

0.20

1.50

Silver Perchlorate (0.1%)

0.10

Formulation #122Parts By Weight

Sodium Vinyl Sulfonate (25%)

20.00

N-Methylenebisacrylamide

1.25

Water

45.00

IPA

45.00

0.25

0.025

Silver Perchlorate (0.1%)

0.10

Comments:

Method of treatment of OPS membranes with formulation #122 was the same as used in case of #120.

Formulation #123Parts By Weight

Sodium Vinyl Sulfonate (25%)

16.00

N-Methylenebisacrylamide

2.00

Water

45.00

IPA

45.00

0.25

0.025

Formulation #124Parts By Weight

Sodium Vinyl Sulfonate (25%)

24.00

N-Methylene Bisacrylamide

1.25

Water

45.00

IPA

45.00

0.25

0.025