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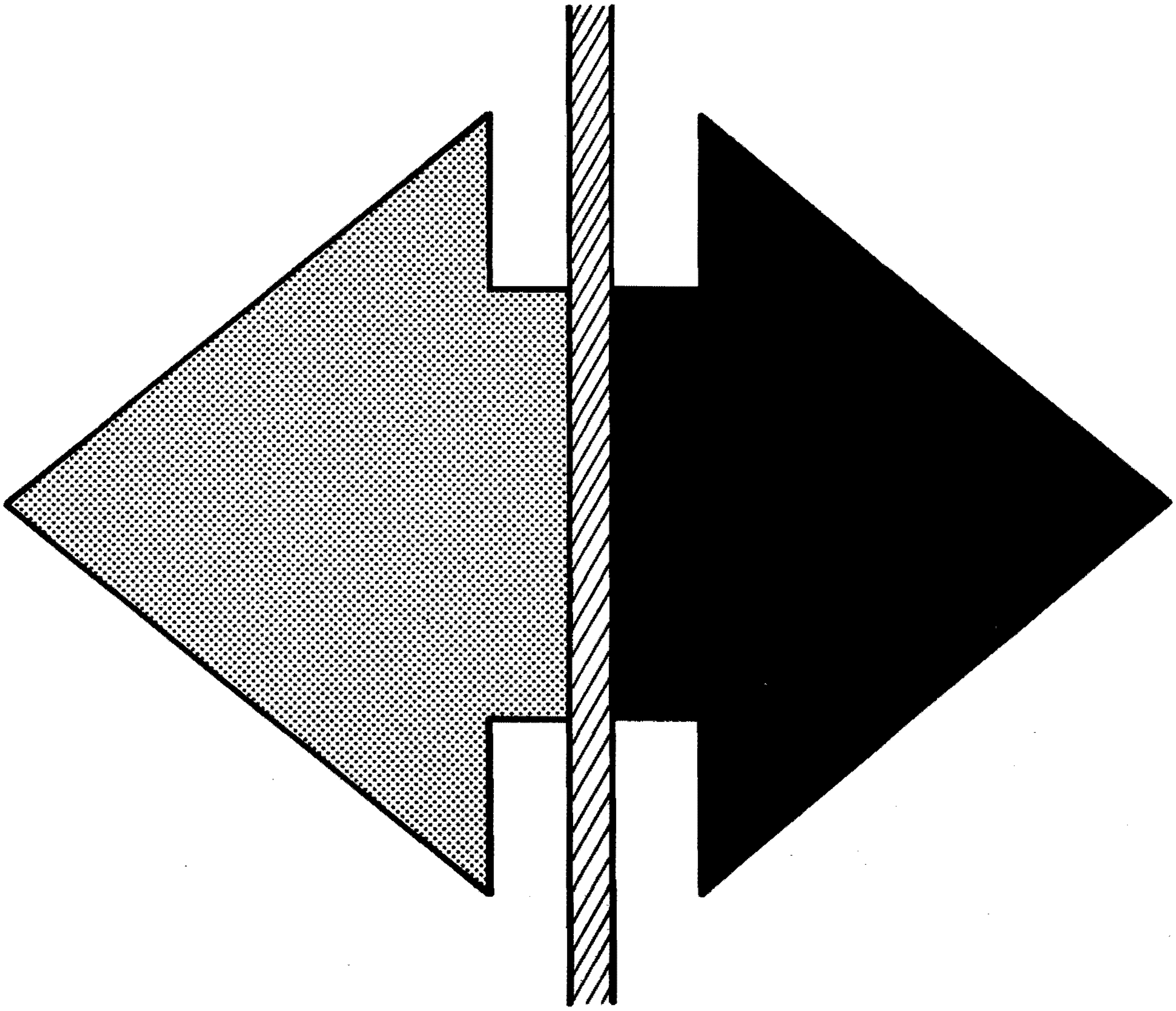

Utah Water Research Laboratory
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December 1982

WATER QUALITY SERIES
UWRL/Q-82/05

REVERSE OSMOSIS IN THE TREATMENT OF DRINKING WATER

by

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ABSTRACT

An extensive review of the literature was conducted and results were evaluated for the use of the reverse osmosis process in the treatment of drinking water supplies. All aspects of reverse osmosis technology, including pretreatment requirements; membrane type and configuration; membrane cleaning and maintenance; and reverse osmosis removal of organics, inorganics, and microbial contaminants were incorporated into the literature evaluation.

A survey (Appendix E) of existing full scale reverse osmosis installations was also carried out and results of the survey are discussed.

In light of data presented in the literature and results of the survey conducted, the following recommendations were made to prevent catastrophic membrane fouling occurrences and costly plant shutdowns in the future.

1) Conduct a comprehensive raw water quality evaluation.

2) Maintain continuous feed and product water quality monitoring.

3) Incororate process automation and system upset warning provisions in future installations.

4) Provide greatly improved training for reverse osmosis installation operators.

The reverse osmosis system is particularly well suited for the treatment of water supplies which contain a number of contaminants that would otherwise require a combination of treatment processes for their removal, due to the ability of the reverse osmosis process to remove salts, organics, and a number of microbial contaminants. Effective pretreatment and routine backwashing, membrane cleaning, and disinfeccion must be carried out; however, if adequate system operation is to be assured.

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CHAPTER I

INTRODUCTION

Fundamental Considerations

General Principles

Osmosis is defined as the spontaneous movement of a solvent through a semipermeable membrane from a less concentrated to a more concentrated solution. The ideal semipermeable membrane impedes solute movement but allows solvent flow. Solvent will pass through the membrane in both directions; however, it will pass more rapidly in the direction of the more concentrated solution until a hydrostatic pressure develops that produces equilibrium conditions of equal flow of solvent in both directions across the membrane, Figure 1. This hydrostatic pressure, Δh, is defined as the osmotic pressure, π, and is related to the solution's vapor pressure and temperature as shown in Equation 1.

$$\pi = \frac{RT}{V_A} \ln \frac{P_A^o}{P_A} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

π = osmotic pressure, atmosphere

R = 0.0882 l-atm/mole °K

T = °K

V_A = l/mole of solvent

P_A^o = vapor pressure of solvent in dilute solution

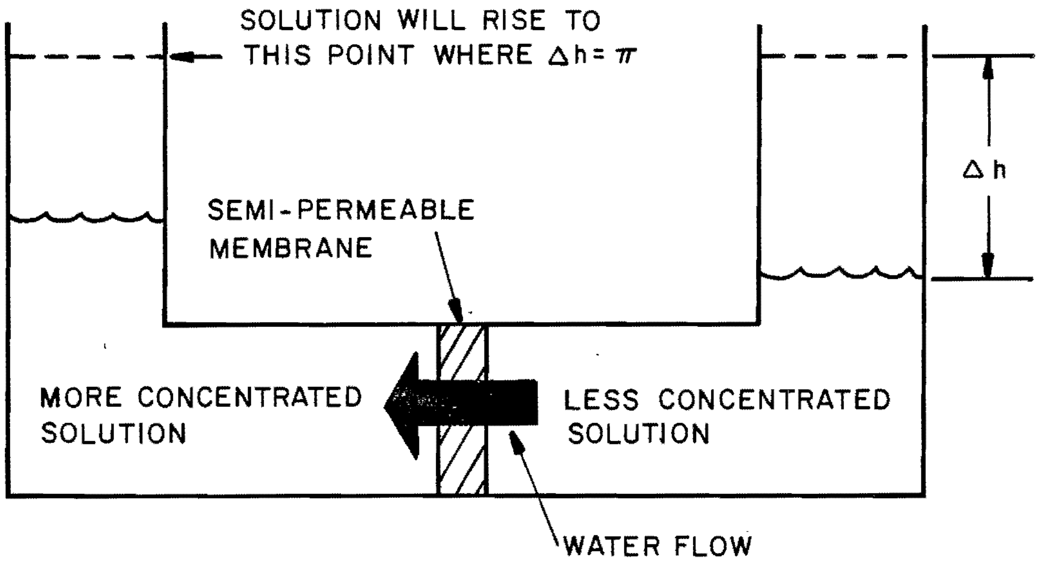


Figure 1. Simple osmosis.

P_A = vapor pressure of solvent in concentrated solution

Raoult's law relates the vapor pressure of a dilute solution to the concentration of particles in the solution. From this relationship, Equation 1 can be used to express the osmotic pressure in terms of the solute molar concentration as:

$$\pi = CRT \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

C = solute concentration, gm/mole

Equation 2 is valid only for dilute solutions where Raoult's law remains true.

The osmotic pressure of a solution increases with solution concentration as shown in Equation 2 and a rule of thumb based on sodium chloride is a 0.01 psi osmotic pressure increase for each mg/l increase in solution concentration (Culp et al. 1978). High molecular weight organics produce much lower increases shown by sucrose producing a 0.001 psi increase for each mg/l increase in solution concentration (Culp et al. 1978).

The spontaneous movement of solute to the more concentrated solution can be overcome through the application of pressure on the more concentrated solution side of the semipermeable membrane, Figure 2, in excess of the osmotic pressure of the solution. The reversal of the osmostic flow is the basis behind the reverse osmosis process used for water and wastewater treatment.

Reverse osmosis membranes are asymmetric films with a macroporous substructure underlying a dense surface layer, Figure 3. While there is agreement that separation occurs at the dense surface layer, there still remains some question as to the specific structure of this layer. Two distinct descriptions of surface morphology are supported by distinct transport theories labeled the solution diffusion theory and the pore theory. The solution diffusion theory characterizes the passage of molecules and ions across nonporous membrane boundary layers as occurring through a solution diffusion mechanism with surface pores being regarded as membrane imperfections that allow largely nonselective transport through them. The pore theory on the other hand proposes that materials are preferentially adsorbed onto the membrane surface and that their transport through the membrane occurs through the surface pores while no transport is assumed to occur by diffusion through the polymer matrix.

Both the solution diffusion theory and the pore theory have strengths and weaknesses. The application of either theory depends upon the specific problem at hand and the conceptual simplicity either theory has in quantitatively explaining experimental results (Johnston and Lim 1973). While an exact understanding of the mechanisms of flow through reverse osmosis membranes is not required for everyday utilization of the process, a general understanding of the possible transport mechanisms may allow for the expansion of reverse osmosis applications. Further explanations of the proposed mechanisms of flow through reverse osmosis membranes may be found in Hodgson (1970), Reid and Breton (1959) and Lonsdale and Podall (1972).

Operating Principles

The rate of transport of solvent through the semipermeable membrane in the reverse osmosis process is a function of the applied pressure, the differential osmotic pressure between solutions, the area and characteristics of the membrane, and the temperature of the solution.

The behavior of semipermeable membranes can be expressed by two

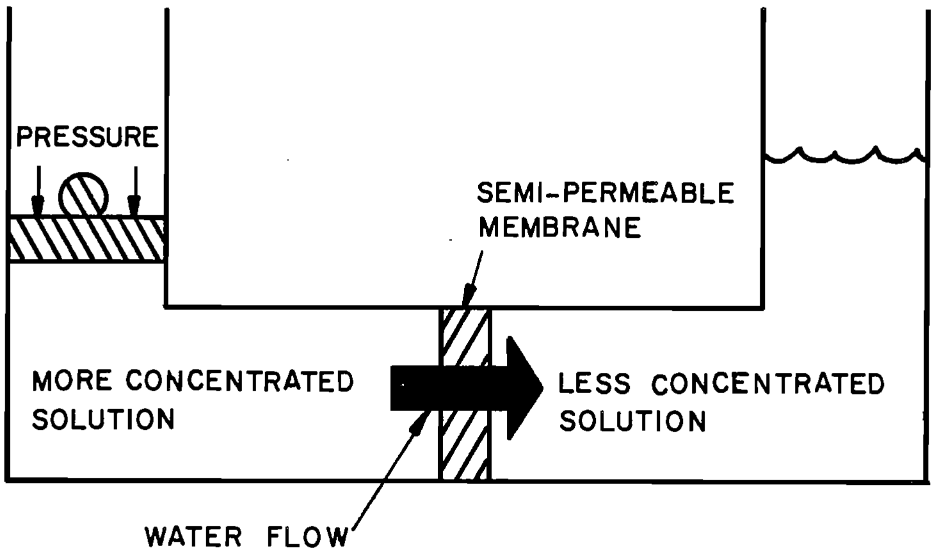


Figure 2. Simple reverse osmosis.

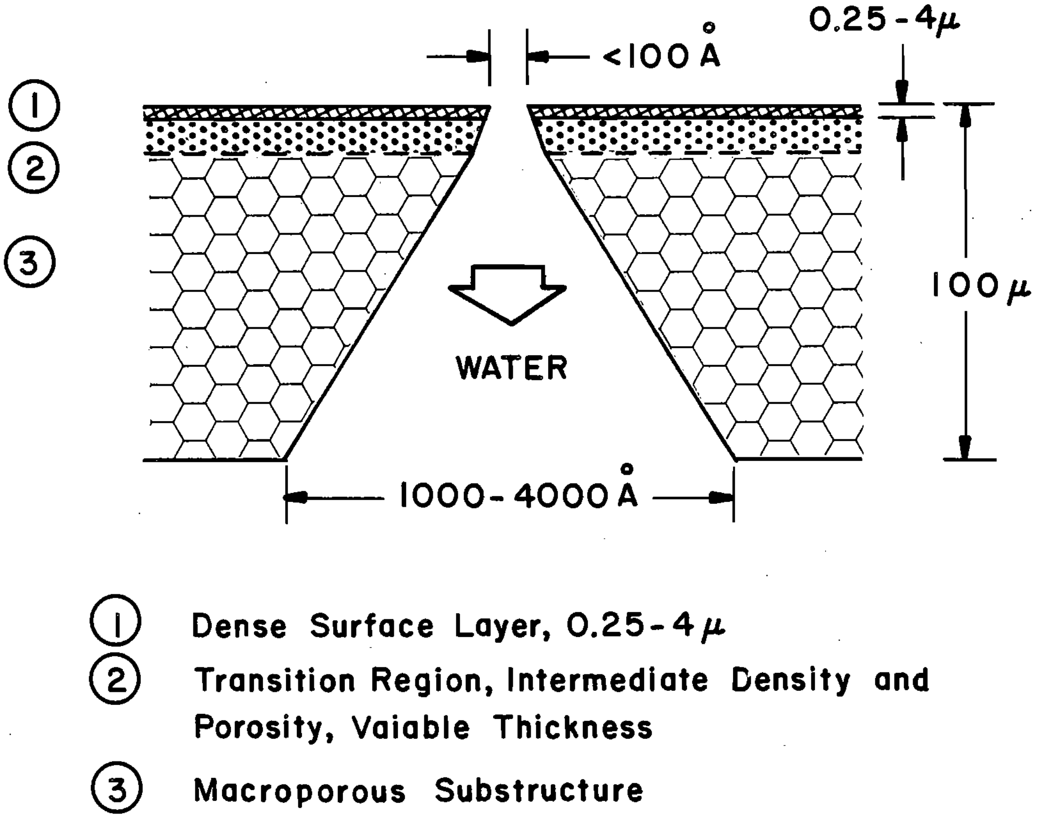


Figure 3. Asymmetric structure of typical reverse osmosis membranes (Johnston and Lim 1973).

basic equations, one describing the solvent or product water flow through the membrane and the other describing the salt flux through the membrane. The product water flow, F_w, is described as follows:

$$F_w = A(\Delta p - \Delta\pi) \quad . \quad . \quad . \quad . \quad (3)$$

where

F_w = product water flow, gm/cm^2-sec

A = water permeability constant, g/cm^2-sec-atm

Δp = pressure differential applied across the membrane, atm

$\Delta\pi$ = osmotic pressure differential across the membrane, atm

The salt flux is described by Equation 4 as:

$$F_s = B\ (C_1 - C_2) \quad . \quad . \quad . \quad . \quad (4)$$

where

F_s = salt flux, gm/cm^2-sec

B = salt permeability constant, cm/sec

$C_1 - C_2$ = concentration gradient across the membrane, gm/cm^3

Both the water and salt permeability constants depend upon the membrane and the procedures used in its manufacture.

These equations indicate that the water flux is dependent upon the applied pressure while the salt flux is not. This results in an increase in both the quantity and quality of product water as the applied pressure is increased. However, this improved performance is countered by an increased feed water salinity as the water flux is increased. The higher feed water salinity increases the salt flux through the membrane, and increases the solution osmotic pressure which in turn reduces the water flux through the membrane. The net result is a lower water flux and reduced water quality as the percent of feed water recovered is increased. The exact operating conditions for a particular application will generally depend upon the raw water quality, the final product water quality requirements, and the required water flux rate.

Historical Development

The phenomenon of osmosis has been studied for over 200 years. Nolet, in 1748, was the first to observe the passage of a solvent through a semipermeable membrane (Williams and Williams 1967). Dutroelot, Vicrordt, and Traub continued the early reverse osmosis work with animal membranes and artificial membranes during the 19th century (Burns and Roe 1979).

Pfeffer measured the osmostic pressure of solutions with varying concentrations in 1877 and showed that the product of the osmotic pressure and volume of a solution was constant at a constant temperature. He also observed that for a given solution, the osmotic pressure increased with an increase in temperature while the ratio of osmotic pressure to temperature remained constant (Williams and Williams 1967).

Van't Hoff built from Pfeffer's observations to show that the osmotic pressure, π, is equal to the product of the solute concentration, C, the absolute temperature, T, and the universal gas constant, R, as was shown in Equation 2. Once again, this relationship holds true for dilute solutions where Raoult's law is valid.

The first application of osmosis was proposed by Ostwald in the late 19th century (Williams and Williams 1967) in the form of a perpetual motion machine based on the difference in osmotic pressure caused by different membrane types. Osmotic pressure is independent of membrane type, however, and as expected, the machine did not work.

Direct osmosis has had practical use in determining molecular weights and in studying the thermodynamic properties of solutions. It was not until the 1950s, however, that scientists recognized the practical applications of reversing the process. In 1953, the U.S. Department of the Interior, through the Office of Saline Water, sponsored an investigation at the University of Florida of desalination by reverse osmosis. Reid and Breton conducted this study and found that cellulose acetate exhibited permeability to water with semipermeability to salts (Goff and Gloyna 1970).

In 1960 Loeb and Sourirajan developed a modified cellulose acetate membrane whose water permeability was some 500 times greater than that of the earlier films while still retaining a high degree of salt rejection. With their significant contribution, reverse osmosis technology began to leave the research stage.

Advancements in membrane technology have continued with the expansion of the reverse osmosis process for the solution of water quality problems. In an inventory of desalination plants with treatment capacities of 95 m^3/d (25,000 gpd) or more, El-Ramly and Congdon (1981) listed 447 reverse osmosis plants in the United States with a total treatment capacity of approximately 757,000 m^3/d (200 MGD). Of the total, 119,000 m^3/d (31.4 MGD) or 16 percent was for domestic use. As raw water quality deterioration continues with increased domestic, industrial, and agricultural use and as high quality water resources dwindle, the use of reverse osmosis as a water treatment option can be expected to increase.

CHAPTER II

PRETREATMENT

The purpose of pretreatment is to provide feedwater and brine streams with the physical and chemical properties necessary to prolong membrane life. Pretreatment steps are utilized to prevent premature deterioration of membranes, to minimize clogging of membranes due to particulate loading or chemical precipitation on the membrane surfaces, and to prevent bacterial growth on and within the membranes.

Speight and McCutchan (1979) suggested that to avoid costly system failure, pretreatment should be designed for the worst case raw water quality expected. The exact pretreatment requirements depend upon the quality of the raw water used and would include either physical or chemical processes or a combination of the two to reach the required pre-reverse osmosis water quality.

Particulate Removal

Reverse osmosis systems are not particulate removal devices and will clog rapidly during high particulate loadings. Proper operation of reverse osmosis systems requires a feedwater turbidity of less than 1 JTU (Buckley 1975) and various physical and chemical processes can be utilized for feedwater particulate removal pretreatment.

Filtration

Filtration is the most common pretreatment step to reduce membrane fouling from particulate matter. Dual media filtration, using sand and anthracite, allows deep penetration of solids into the filter bed and results in efficient filtration and long filter runs (Burns and Roe 1979). Other media, such as granular nonhydrous silicate (Adams and Brant 1977), activated carbon (Luttinger and Hoche 1974), and macroreticular resins, may be used depending upon the particular application and the corresponding economic considerations.

Cartridge filters are usually installed prior to reverse osmosis systems as an additional prefilter to protect the unit's membranes (Burns and Roe 1979). The cartridge filter media material is either cellulose, rayon, wool, or acrylic fibers with recommended effective sizes varying with the membrane configuration (Burns and Roe 1979).

Coagulation-Flocculation-Sedimentation

If feedwater with a high concentration of suspended material of a colloidal nature is to be treated using reverse osmosis, suspended solids removal prior to filtration may be required. Coagulation causes the neutralization of charges on the surface of the suspended colloids and destabilizes the suspension so that the slow mixing in the flocculation step allows particle aggregation and enhances particle removal through sedimentation and filtration.

Aluminum or iron compounds such as aluminum sulfate, sodium aluminate, ferric sulfate, and ferrous sulfate are used as coagulants. These compounds are acidic in nature and react with the alkalinity of the feedwater to form sulfates of magnesium, calcium, or sodium as well as hydroxide precipitates.

Scale Prevention

A number of chemical process options are available to control the formation of chemical precipitates that may clog and coat the reverse osmosis membranes.

pH Control

The adjustment of feedwater pH between 5.0 and 6.5 is used to prevent hydroxide and carbonate scaling based on the solubility product of the scale forming compounds. When the pH of the feedwater is controlled between 4 and 7, protection of membrane deterioration via hydrolysis is an added benefit.

For most applications, sulfuric acid is recommended for pH reduction (Osmonics 1975). Sulfuric acid is economical, is less corrosive than hydrochloric acid, and the sulfate ion results in a lower salt flux than monovalent ions. Phosphoric acid is not recommended for pH control due to the low solubility of calcium phosphate. When the concentration of calcium and sulfate ions are high in the feedwater, hydrochloric acid may be necessary.

When acidification is used to reduce the alkalinity of the feedwater, dissolved carbon dioxide diffuses through the membrane making the corrosion potential high in the product water. Consequently, some pH adjustment of the product water is also required either through decarbonation and/or lime or caustic soda addition.

Scale Inhibitors

The adjustment of feedwater pH is not effective against CaF_2 and $CaSO_4 \cdot 2H_2O$ scaling (Takahashi and Ebara 1978) and a scale preventing agent is needed. Sodium hexametaphosphate functions as a sequestering agent to form soluble complexes that keep calcium, magnesium, and iron salts in solution. Sodium hexametaphosphate is widely used in reverse osmosis installation especially for the inhibition of calcium sulfate precipitation.

Iron and Manganese Removal

The oxidized forms of iron and manganese can be deposited on reverse osmosis membranes in the form of particulate, colloidal, or slime layers and may cause serious damage to the membranes.

Aeration. Aeration may be used for the oxidation of iron and manganese to insoluble ferric hydroxide and manganese oxide. The oxidation of 1 mg/l of iron requires 0.14 mg/l of oxygen while 1 mg/l of manganese requires 0.24 mg/l of oxygen (EPA 1977). Soluble iron is oxidized readily through aeration, however, manganese oxidation requires the catalytic effect of contact with previously precipitated manganese oxide to be effective.

Ion exchange. Iron and manganese can be removed by sodium zeolite ion exchange in which the exchange bed may be either green sand or high capacity resin (Burns and Roe 1979). With the use of ion exchange removal of iron and manganese, care must be taken to prevent oxidation of the soluble iron and manganese forms in order to limit fouling of the ion exchange bed.

Softening. Iron and manganese can also be removed by lime-soda-ash softening. The iron is oxidized to ferric hydroxide while the manganese is oxidized to manganic hydroxide (Burns and Roe 1979). Flocculation and sedimentation are then employed to remove the softening sludge prior to reverse osmosis treatment.

Potassium permanganate/manganese dioxide greensand treatment. For small plants or for feedwater containing 1 mg/l or less of iron and manganese, the use of potassium permanganate as an oxidizing agent followed by filtration through manganese dioxide greensand is an economic alternative for iron and manganese removal. The potassium permanganate oxidizes the iron and manganese which then precipitates on the filter. If too little potassium permanganate is used, the filter itself oxidizes the iron and manganese, while when the potassium permanganate is in excess of the feedwater iron and manganese, the excess will regenerate the greensand filter. Due to the high cost of potassium permanganate and the zeolite bed, preaeration is sometimes used to preoxidize the iron and manganese.

Disinfection

Bacterial slimes may form during an extended shutdown of a reverse osmosis unit (DuPont 1977b). Microbial enrichment, or the movement of cellulosic degrading bacteria through the reverse osmosis membrane to colonize and proliferate within the membrane, can also occur during the operation of reverse osmosis systems (Hinterberger et al. 1974). To counteract this microbial growth and biological membrane fouling, some form of feedwater disinfection is required.

Hinterberger et al. (1974) showed that to reduce bacterial growth on reverse osmosis membrane surfaces, chlorination of the feedwater to a point of free chlorine residual was necessary. Disinfection of cellulose acetate membranes with the use of slug chlorine dosages at regular intervals is recommended, while continuous chlorine addition should generally be limited to 1 mg/l free chlorine residual (Burns and Roe 1979).

Polyamide and polyfuran membranes are susceptible to degradation from chlorine and other oxidizing agents. Zero chlorine residual is recommended for these membranes and disinfection is accomplished using a flushing solution of 0.75 percent by weight of a 30 percent formaldehyde solution (Burns and Roe 1979).

Oxidants

Chlorine is present in most municipal waters and is usually the most important oxidizing agent in water (Osmonics 1977), however, other oxidants such as chromic acid, ozone, and other halogens will affect reverse osmosis membranes in a similar manner.

Cellulose acetate membranes are the most resistant to oxidation with these membranes able to tolerate continuous free chlorine concentrations up to 5 mg/l and periodic free chlorine concentrations of 50 to 100 mg/l with little membrane oxidation (Osmonics 1977). Chromic acid at feedwater pH values of greater than 2.2 has also been used without membrane deterioration. Although cellulose acetate membranes are resistant to oxidation, some manufacturers are conservative in the allowable chlorine dosages they recommend, i.e., 0.5 mg/l continuous free chlorine concentration (Saltech 1978) and 1 mg/l (Burns and Roe 1979) to 5 mg/l (Saltech 1978) maximum free chlorine residuals.

Polyfuran and polyamide membranes are generally intolerant to oxidative degradation as stated above and oxidant removal is required in these reverse osmosis installations. When dechlorination of the feedwater prior to reverse osmosis treatment is required, sodium bisulfite is normally used at a dosage of 1.4 mg/l per mg/l of chlorine residual. Dechlorination can also be carried out using activated carbon adsorption (Speight and McCutchan 1979).

CHAPTER III

MEMBRANES

Membranes are the critical component of a reverse osmosis system. For effective operation, the membrane material must be highly permeable to water, highly impermeable to solutes, and able to withstand high feedwater pressures. Water recovery should be high to minimize both feed pumping costs and brine disposal costs. Membranes are a significant fraction of the capital costs of a reverse osmosis system and to be economical, the water flux rate must be large enough to produce a reasonable volume of product water per unit time (Lonsdale and Podall 1972). High flux rate requirements demand thin membrane walls. For long life, the membranes must be resistant to physical, chemical, and biological attack and to pH and temperature extremes (Kellar 1979). Finally, because pressure vessel costs are also high, the membranes should be capable of being cast into shapes with high packing densities, i.e., high membrane surface area to pressure vessel volume ratios (Lonsdale and Podall 1972). Unfortunately these requirements are often incompatible as one would expect and tradeoffs are inevitably made in the production and use of commercial membranes.

Cellulosic Membranes

Research began in the early 1950s to develop a reverse osmosis membrane with sufficient strength and product water flux to be of commercial interest in desalination applications (Chan and McCutchan 1978). Cellulose acetate was the first material found to provide significant electrolyte rejection from aqueous solutions (Reid and Breton 1959). Initial membranes could not be produced thin enough to provide reasonable water flux rates, however.

Research conducted at the University of California, Los Angeles, during the late 1950s was concerned with improving the water flux of the cellulose acetate membrane while maintaining its high salt rejection properties. Loeb and Sourirajan (1961) succeeded in increasing the water flux through these membranes without a decrease in their salt rejection through the addition of a pore producing agent.

This anisotropic membrane had an asymmetric structure consisting of a 0.2 to 0.5 μm thick dense surface layer underlain by a porous substructure and was a major breakthrough in the development of the reverse osmosis process. The thin, dense surface layer provided minimal resistance to flow and necessary solute retention characteristics, while the porous substructure provided structural support for the thin surface layer with little additional resistance to flow.

Chemically, cellulose acetate is a hydroxylic polymer of long chains of β-glucoside units with molecular weights of 25,000 to 65,000 that have been acetylated with acetic anhydride and hydrolyzed to reduce acetylation to between 38 and 43 percent. Cellulose acetate membranes are prepared from a solution consisting of the polymer dissolved in an appropriate solvent (usually acetone) along with a nonsolvent (water or formaldehyde) and an appropriate salt, both of which function as swelling agents. Membranes may be cast in either sheet or tubular form by physically spreading a desired thickness of this solution on an appropriate support under controlled atmospheric conditions. Evaporation is allowed to take place for a controlled period of time to permit solvent diffusion through the polymer and the membrane surface to produce the characteristic membrane asymmetry. This structure is gelled by immersing the film in a bath of water near 0°C.

In the as-cast state, these membranes reject only a small amount of sodium chloride, although they are relatively impermeable to high-molecular weight materials. The semipermeability is markedly improved by annealing the membranes in a water bath at temperatures between 60° and 90°C. During the annealing process, the permeability to water decreases by about an order of magnitude while the permeability to sodium chloride decreases by more than three orders of magnitude. By accurately controlling the temperature during annealing, a range of different salt rejecting membranes can be produced. Water permeability of the membrane is inversely, although not linearly, related to the salt rejection.

Although cellulose acetate has excellent permeability characteristics with productivity rates on the order of 0.5 to 0.7 $m^3/m^2/d$, it is limited in some applications because of poor chemical resistance to hydrolysis at a pH below 4 and above 8 and because of inadequate resistance to thermal induced hydrolysis above 38°C (Porter 1978). These membranes are also subject to deterioration by cellulase producing organisms (Burns and Roe 1979).

In an effort to improve the stability and usefulness of cellulose acetate membranes, several modified membrane types have been developed. Dow Chemical has developed cellulose triacetate hollow fiber membranes (Burns and Roe 1979) that result in improved salt rejection, improved resistance to microbial attack, improved stability to high and low pH and elevated temperature operating conditions, and improved resistance to membrane compaction as compared to cellulose acetate membranes. Membranes produced from a blend of cellulose triacetate and cellulose diacetate have also been developed (Burns and Roe 1979) that result in improved performance and operating stability over the Loeb-Sourirajan cellulose acetate membranes.

Polyamide Membranes

Since the development by Reid and Breton (1959) of cellulose acetate as a desalination membrane and the improvements in its water flux by Loeb and Sourirajan (1961), there has been a continuous search for new and better membrane materials. In 1967 DuPont introduced the asymmetric aromatic polyamide fiber. The polyamide materials are described by Burns and Roe (1979) as synthetic, organic, nitrogen-linked aromatic, substantially linear condensation polymers. Although the water permeabilities through these membranes are about an order of magnitude less than through cellulose acetate membranes, their packing density is about an order of magnitude higher (Belfort 1977). The inexpensive, compact area of the hollow fiber geometry makes these membranes competitive with the high flux cellulose acetate membranes.

As manufactured, the fibers have poor monovalent ion rejection capabilities. A coating of tannic acid is applied to the fibers to improve monovalent rejection. Productivity rates for this membrane material is in the range of 0.04 to 0.08 $m^3/m^2 \cdot d$ (1 to 2 $gal/ft^2 \cdot d$). Bicarbonate ion rejections are low at low pH conditions but improve with increasing pH. Low molecular weight organics are separated effectively by the polyamide membranes with the efficiency decreasing rapidly at a molecular weight of approximately 100 (Spatz and Friedlander 1978).

Shields (1979) reported that polyamide membranes are physically and chemically stable and consequently long membrane lives can be expected from them. Certain aromatic polyamides are stable during continuous operation over a pH range of 4 to 11 while this operating range may be broadened to between 2 and 12 for limited time periods. Extended usage at the extreme pH values may cause irreversible modifications to the membrane material and alter its separation ability however, and Kosarek (1979b) suggested a narrower permissible operating pH range of 3 to 9 with an optimum pH value cited of 5.5.

Polyamide membranes are capable of operating at higher temperatures than cellulose acetate membranes (Burns and Roe 1979) and Kosarek (1979b) indicated a safe operating range to 49°C. Polyamide membranes have an added advantage over cellulose acetate membranes in that they are essentially immune to biological degradation (Shields 1979) as microorganisms have not yet developed enzymes that react with synthetic polymers (Burns and Roe 1979).

The major disadvantage of the polyamide membranes is their extreme sensitivity to oxidants. Warranty requirements specify 0 mg/l feedwater chlorine concentration (Kosarek 1979b). Spatz and Friedlander (1978) suggest that whenever oxidants, especially chlorine, will be in the feedwater, polyamide should be carefully scrutinized and probably avoided, unless the pH is such that the oxidation potential is low.

Composite Membranes

The thin dense surface film and porous substructure of reverse osmosis membranes need not necessarily be made from one material. By optimizing the formation of each layer and sandwiching the layers together, a membrane with superior performance characteristics can be produced. The permeability of the membranes can be increased without a decrease in their salt rejection by reducing the dense film thickness. Belfort (1977) reported that composite membranes are able to desalinate seawater at a high flux rate of 1.02 $m^3/m^2 \cdot d$ (25 $gal/ft^2 \cdot d$) at 10.3 MPa (1500 psig).

Even with clean feedwater, the water flux through an anisotropic membrane decreases with time. This phenomenon is apparently the result of a creep process in which the dense surface layer grows in thickness by amalgamation with the porous substructure immediately beneath it. The effect of compaction is more pronounced with high flux membranes and at high temperatures. A major benefit of composite membranes is an improvement in their resistance to this compaction phenomenon (Porter 1978).

The composite membrane is similar in configuration to the asymmetric Loeb-Sourirajan cellulose acetate membrane. An ultra thin film of a semipermeable polymer is formed upon the finely porous surface of a highly water permeable support membrane. The water permeability of the thin film material, the thin film thickness, and the pore characteristics on the surface of the support membrane determine the water flux through these composite membranes. The thin film thickness ranges from 0.01 to 0.10 μm and can be varied and controlled with reproducibility. The composite membrane is greatly improved over the classical asymmetric membrane, however, by eliminating the ill defined area between the thin film and the porous substructure (Burns and Roe 1979). Additional freedom is provided in the preparation of the composite membranes including: independent selection of materials from which to prepare the ultra thin semipermable barrier and the finely porous supporting membrane; independent development and preparation of the thin film and the porous supporting membrane allowing for optimization of each component for its specific function; reproducible control over the thickness of the thin film as needed for different applications; and improved control over the porosity of the thin semipermeable barrier (Burns and Roe 1979). Several types of thin film membrane composites have been developed; however, polysulfone has been used the most in the commercialization of composite membranes (Sudak et al. 1979).

North Star Research and Development Institute developed a cross linked polyethyleneimine membrane, designated as NS-100 (Chian et al. 1975). The membrane has a dominant active layer of polyethyleneimine cross lined with m-toluene 2,4-diisocyanate, coated on a porous polysulfone support. The NS-100 was claimed to be the most promising membrane ever developed with respect to pH stability, permeate flux, and the removal of solutes, especially small polar organic compounds (Chian et al. 1975). At 10.3 MPa (1500 psig), this membrane was reported to have a flux of over 0.8 $m^3/m^2 \cdot d$ (20 $gal/ft^2 \cdot d$) with 99.5 percent salt rejection when used with synthetic seawater (Porter 1978). In addition, the membrane was reported to have excellent stability when used for alkaline feed water with pH's of 7 to 13. Spatz and Friedlander (1978) suggested that the membrane will fill a need in many processes for intermediate salt removal at elevated pH values. Its major drawback is that it is readily attacked by chlorine.

Burns and Roe (1979) described a furfuryl alcohol thin film composite, designated as NS-200. The membrane is prepared on a polysulfone support and has demonstrated 99 percent salt rejection and water fluxes of 0.73 to 0.81 $m^3/m^2 \cdot d$ (18 to 20 $gal/ft^2 \cdot d$) when tested on a 3.5 percent salt solution at 6.9 MPa (1000 psig) for 1000 hr.

Burns and Roe (1979) described a polyamide composite membrane, PA-100, prepared in a manner similar to NS-100 except that isophthaloyl chloride is employed for reverse osmosis barrier formation in place of toluene diisocyanate. The major drawback of the PA-100 composite membrane, as with other composite membranes, is its high sensitivity to chlorinated feeds which result in a rapid deterioration of the membrane. Research studies were conducted to modify the PA-100 system to make the membrane more tolerant of chlorinated feeds and to eliminate the added cost of dechlorination. The efforts led to the development of a polyamide composite membrane referred to as PA-300.

The PA-300 barrier is prepared from the interfacial condensation of an epichlorohydrin ethylene idamine (epiamine) condensate with isophthaloyl chloride (Burns and Roe 1979). Although the PA-300 membranes remain chlorine sensitive, compared to the PA-100 series they are much more stable in chlorinated feedwaters (Burns and Roe 1979).

Burns and Roe (1979) described a cellulose triacetate composite membrane with a 0.025 to 0.050 μm thick film that was formed on a finely porous cellulose nitrate cellulose diacetate support by dipping the latter in a dilute solution of cellulose acetate (2.83 percent). The film thickness is controlled by the concentration of the cellulose triacetate polymer in the solution and by the film withdrawal rate.

A new type of dry reverse osmosis asymmetric membrane is being developed and incorporated into sprial elements by Chemical Systems, Inc. (Burns and Roe 1979). The membranes, produced in the casting from a solution processed from quaternized cellulose triesters, are dry storable and wet-dry stable. Because of the presence of the quaternary ammonium groups, the new membranes have greater permeability and permselectivity than cellulose acetate membranes and are also more resistant to hydrolysis, chlorine oxidation, and biodegradation. Measured values for water flux and salt rejection were 0.92 $m^3/m^2 \cdot d$ (22.5 $gal/ft^2 \cdot d$) and 98 percent, respectively, on a 1 percent sodium chloride solution at 6.9 MPa (1000 psig) (Channabasappa and Strobel 1976).

Summary

The relative stability of four reverse osmosis membrane materials subjected to various operating conditions was investigated by Spatz and Friedlander (1978). The stability of membranes to low pH was in the order of polyfuran > cellulose acetate > polyethyleneimine > polyamide, while membrane resistance to high pH feedwater solutions was in the order of polyamide > polyethyleneimine > polyfuran > cellulose acetate. The stability of the membranes to oxidation by chlorine was in the order of cellulose acetate > polyetheleneimine > polyamide > polyfuran. The authors concluded that no one membrane material proved to be the best and the choice of membranes remains application specific. Additional membrane materials are expected to become available in the future that will not only provide improved physical and mechanical durability, but also enhanced chemical and biological stability while at the same time providing improved process reliability.

CHAPTER IV

MODULE CONFIGURATION

The membrane module houses the reverse osmosis membrane so the feed stream is sealed from the product stream. The module must have the mechanical stability to support the membranes when they are subjected to high pressures of 1.4 to 10.3 MPa (200 to 1500 psig). The module must also be constructed to prevent pressure leaks between feed and product streams and large pressure drops through the system. Hydrodynamically the module should be designed to minimize the buildup of both salt and fouling layers on membrane surfaces which impede membrane performance. The module should also provide a high membrane packing density to reduce capital costs of the pressure vessels and should accommodate uncomplicated membrane replacement. The four most common module configurations used are labeled the plate and frame, the tubular, the spiral wound, and the hollow fiber design.

Plate and Frame Modules

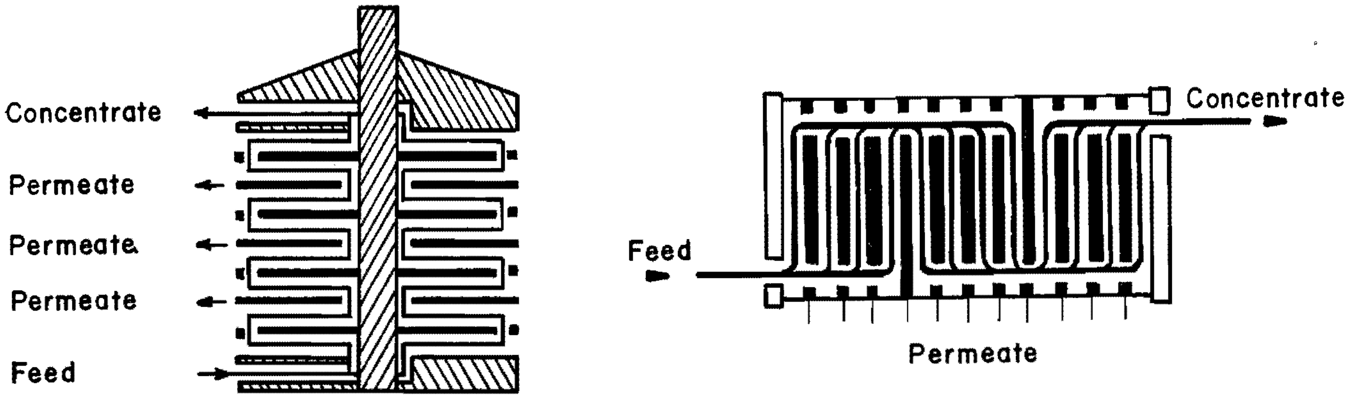
The first module configuration employed in large scale applications of the reverse osmosis process was the plate and frame system developed by Aerojet General Corporation (1966). The original design was similar in principle to the filter press and became extinct in the late 1960s due primarily to the difficulty and expense in changing degraded membranes (Belfort 1977). With each membrane mounted on an individual support device, the equipment and maintenance costs did not justify the productivity obtained from this original plate and frame configuration (Johnston and Lim 1973).

While the plate and frame configuration was abandoned in the United States, the Danish Sugar Corporation, DDS, continued the development of plate and frame systems (Nielsen et al. 1980). Through continual process improvement, the DDS developed a second generation plate and frame configuration shown in Figure 4(b). While the flow was conducted by spacer plates separating the membrane support plates in the original design, Figure 4(a), the second generation DDS design eliminated the spacer plates and allowed the formation of membrane channels from neighboring support plates, Figure 4(b).

This second generation design does not require a pressure vessel as each membrane is individually sealed by adjacent spacer plates, Figure 5. The new design has increased the operating efficiency of the plate and frame configuration; however, these modules remain susceptible to fouling, are difficult to clean and replace, and subsequently are still fairly costly.

Tubular Modules

The tubular module, Figure 6, is the simplest design of all modules used in reverse osmosis and was the first of the current commercial modules to be developed (Kellar 1979). The membrane is inserted into or coated onto the surface of a porous tube which is designed to withstand high operating pressures. Pressurized feedwater is introduced into one end of the tube and flows through the tube while the product water permeates the membrane radially. Tubes can be arranged as



(a) First generation plate and frame configuration.

(b) Second generation plate and frame configuration.

Figure 4. Plate and frame configuration of (a) first generation and (b) second generation design (Nielsen et al. 1980).

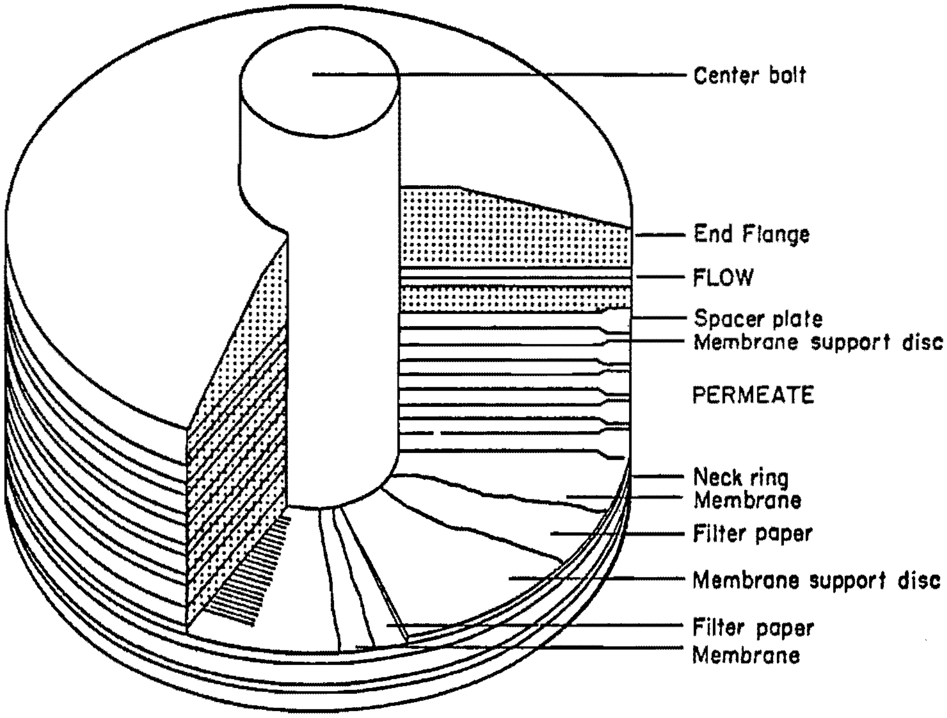


Figure 5. Second generation plate and frame configuration (OWRT 1979).

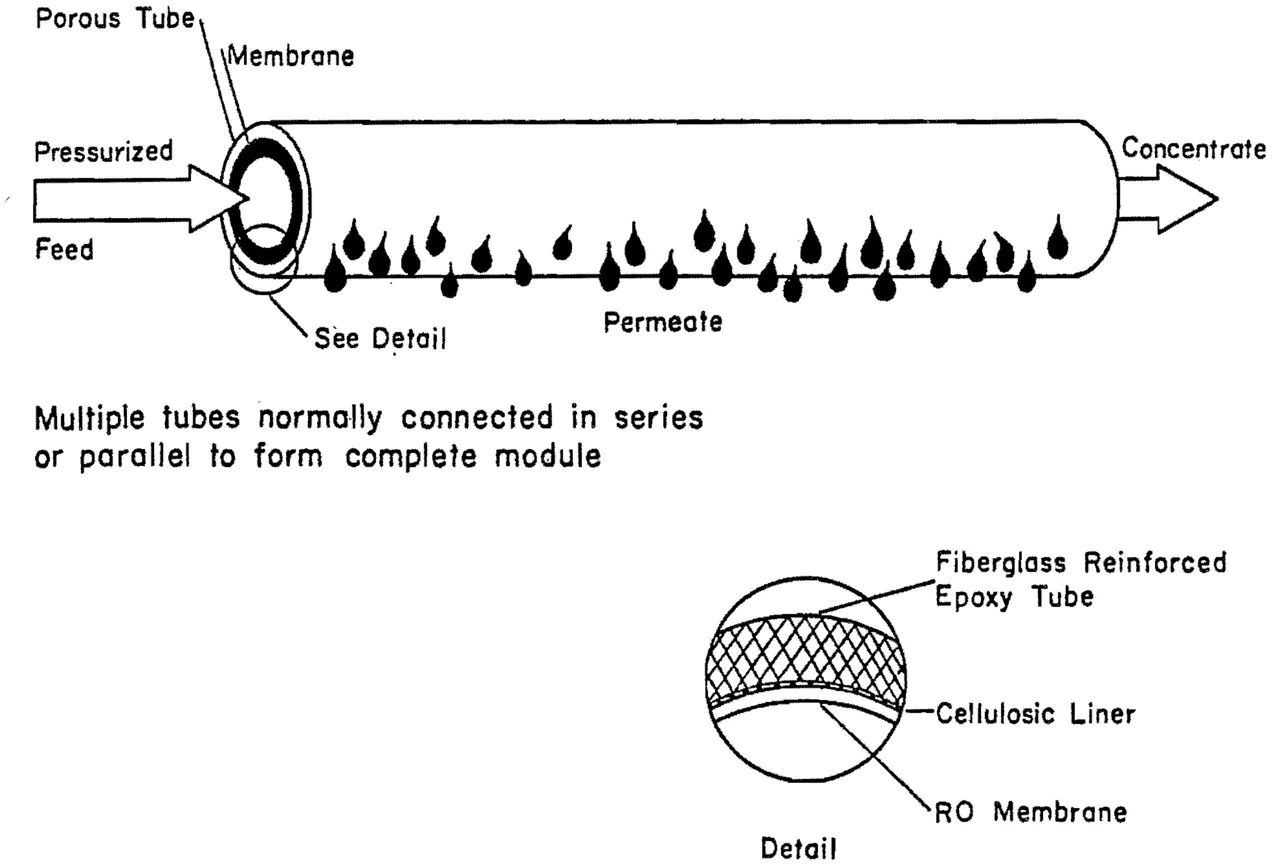


Figure 6. The tubular module element (OWRT 1979).

series or parallel. The tubular module was moderately successful during the late 1960s in applications such as chemical separations and food and drug processing.

The advantages of the tubular design relate to its ability to treat extremely turbid feedwaters and the ease by which it can be hydraulically or mechanically cleaned (OWRT 1979).

Disadvantages of the tubular configuration include high capital costs, high pumping costs related to high velocities required to prevent precipitation from forming on membrane surfaces, low water production rates per unit of module volume, and low packing densities.

Spiral Wound Modules

Spiral wound modules were introduced in the mid-1960s by Fluid Systems Division of Universal Oil Products and were a major step forward in producing large packing densities (Kellar 1979). The spiral wound module, Figure 7, contains two layers of semipermeable membranes separated by a woven fabric of nylon or dacron. A flexible envelope is formed by sealing the edges of the membrane on three sides. The open side is attached to a perforated central tube. A sheet of plastic netting, placed adjacent to the membrane envelope, separates the membrane layers during assembly and promotes turbulence in the feed stream during operation. The envelope and netting are wrapped

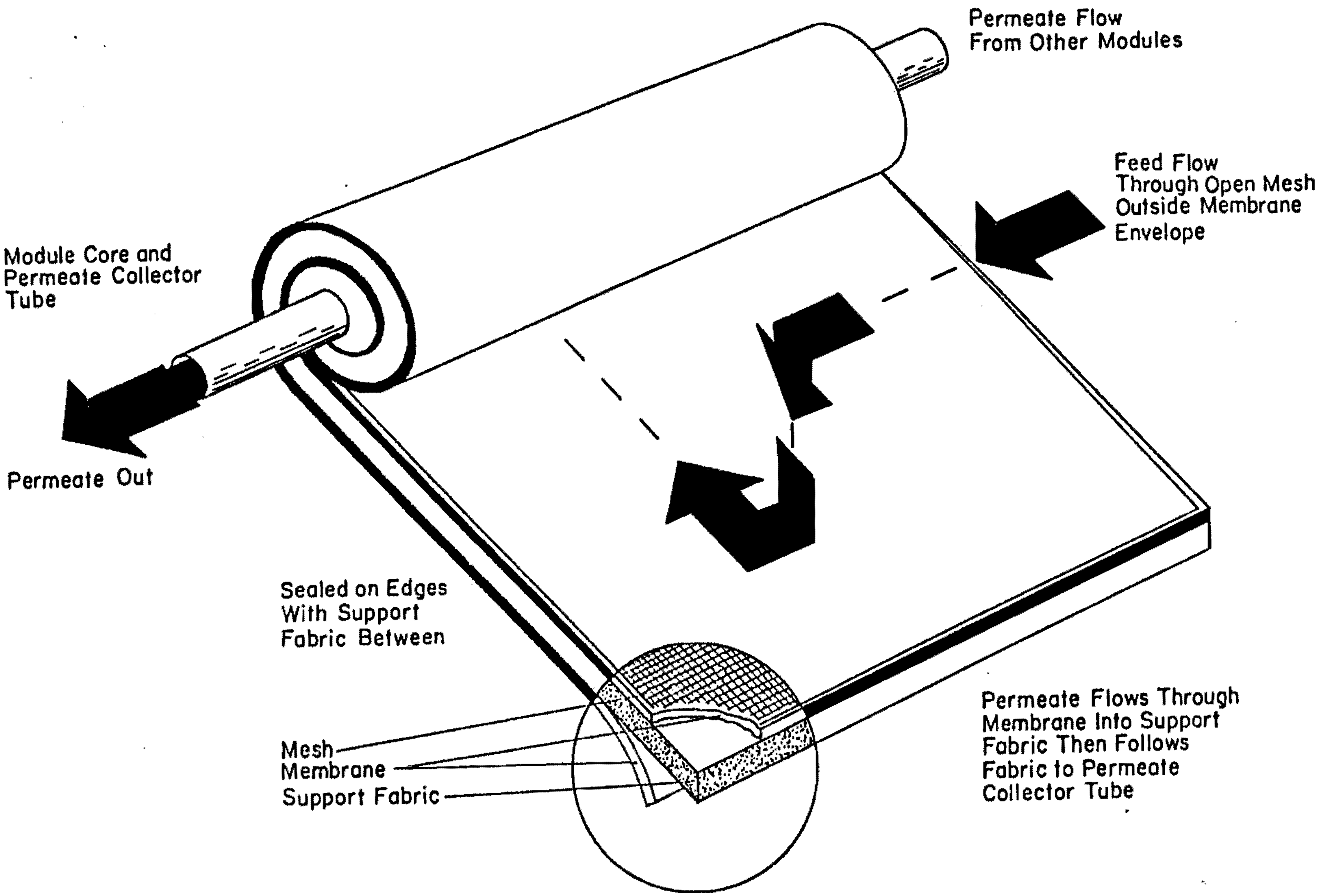


Figure 7. The spiral bound module element (OWRT 1979).

around the central tube in a spiral configuration similar to a window shade. The spiral wound element is then ready for insertion into a pressure container for use. Pressurized feedwater permeates through the membrane into the fabric. Flow channels direct the permeate to the perforated central tube for collection and removal from the system.

The spiral wound module has a high packing density and a low manufacturing cost. It can be chemically or hydraulically cleaned easily and enjoys a broad range of applications (OWRT 1979). The spiral wound modules can be unrolled and examined for defects and the product tube can be tested to locate leaks along the full length of the vessel. When membrane or product tube defects are located visually, or with dye, they can be remedied prior to rerolling. Spiral wound modules have also been popular because of their resistance to scale formation and fouling.

The pressure vessel can hold up to six membrane module elements in series with the module yielding a productivity of 0.6 to 1.2 $m^3/m^2/d$ (15 to 30 gal/ft^2/d). Product recovery ranges from 5 to 15 percent of the feed flow rate, while product side pressure drops through the module range from 206 to 276 KPa (30 to 40 psig).

The main disadvantage of the spiral wound modules is their sensitivity to high turbidity feedwaters due to the small feed flow passages that are subject to clogging if extensive pretreatment is not practiced. Dead spaces in the area between the element and the pressure vessel are susceptible to biological growth, while the O ring seals that separate the elements and the module end caps can be nicked or roughened allowing leakage of reject water into the product stream. A portion of the membrane is needed for adhesive attachment and results in nonproductive areas within the module. Finally, element assembly is performed by semi-skilled labor and variations in module quality can be expected.

Hollow Fiber Modules

The hollow fiber module, Figure 8, was first developed by DuPont in the late 1960s and was later also produced by Dow Chemical (Buckley 1975). DuPont uses aromatic polyamide membranes in its units while Dow Chemical uses cellulose triacetate membranes. The membrane material is spun into hair-like hollow fibers having an outer diameter of 85 to 200 μm. The fibers are bundled together in either a U-shape configuration for exterior brine flow or in a straight configuration for interior brine flow. The fibers are wrapped around a support frame with their open ends epoxied into a tube sheet, making sure the fibers are not blocked.

With exterior flow modules, the product permeates radially inward through the unsupported fiber. The product moves inside the hollow fiber bore to the product collection chamber. The exterior flow module is very compact, is low in cost, and can withstand high pressures of 2.8 MPa (400 psig). Its disadvantage is that it plugs easily and is difficult to clean because of the small spacing between the fibers in a bundle.

The interior flow modules are similar to heat exchangers. The feedwater flows into the bore of the hollow fibers at one end, moves along the inside of the fibers, and flows out of the other end of the unit. The product permeates radially outward through the fiber walls. The interior feed design possesses the characteristics of the exterior feed design in addition to providing controlled hydrodynamics of the feed which improves the ease of cleaning. This design is relatively new and no operating experience was reported in the literature.

Pressure vessels normally contain a single element. Productivity ranges

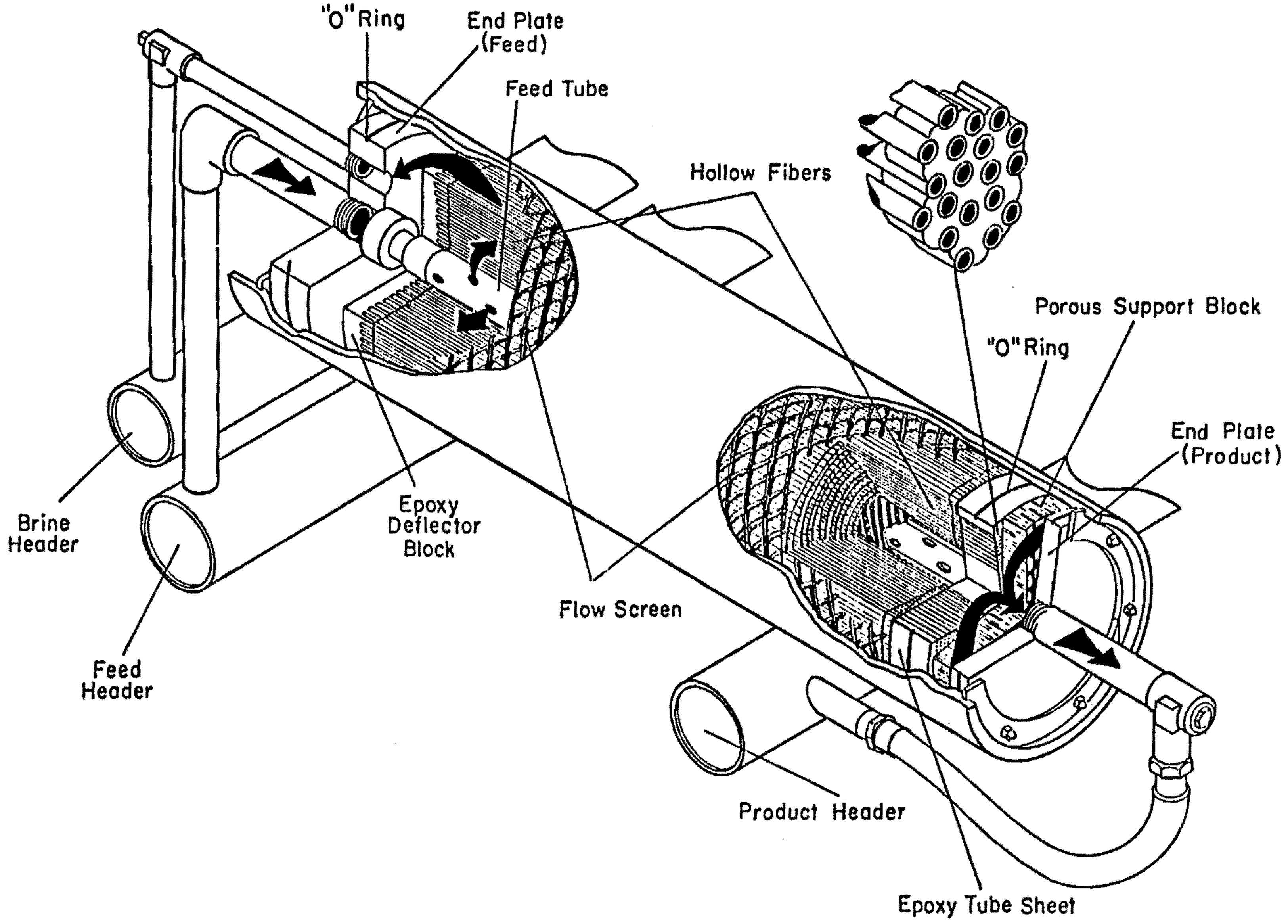


Figure 8. The hollow fiber module (DuPont 1977a).

from 0.12 to 0.24 $m^3/m^2/d$ (3 to 6 $gal/ft^2/d$) (Burns and Roe 1979). The elements have high packing densities of 39,400 m^2/m^3 (12,000 ft^2/ft^3) and are resistant to pressure collapse even to 4.1 to 6.9 MPa (600 to 1000 psig) (Porter 1978). Manufacturing costs are relatively low and systems based on this configuration are extremely compact (OWRT 1979). Broken fibers are claimed to be self healing by collapsing (Burns and Roe 1979). Product recovery per module is 50 to 60 percent of the feed flow rate. Because the fibers themselves are capable of withstanding high pressures, the encasing module is the major mechanical component of the complete unit and no support screens are required. The result is a comparatively low equipment cost requirement (Johnston and Lim 1973).

Even though this module configuration is economic, its susceptibility to fouling and the difficulty in cleaning the units requires extensive pretreatment even when treating relatively clean feedwaters (OWRT 1979). The pretreatment requirement severely limits the range of applications for this module configuration.

The hollow fiber modules, like the spiral wound module, have dead spaces between the product tube sheet and the pressure vessel in which biological growth can occur (Burns and Roe 1979). Additionally, membrane imperfections cannot be visually identified except by destruction and the large O-ring on the outside diameter of the product tube sheet is frequently a source of internal leakage. Up to 20 percent of the hollow fibers may be blocked by manufacturing defects on the face of the product tube sheet (Burns and Roe 1979) and by design, large membrane areas are unproductive due to the product tube sheet necessary to take the thrust from the 2.8 MPa (400 psig) pressure drop between the feed and product streams. Finally, limited flow velocities may occur in areas adjacent to the tube sheets resulting in nonuniform flow distribution through the fiber bundle.

Summary

As with membrane selection, module configuration selection becomes a matter of application specificity. All membrane configurations described, except the plate and frame design, are presently being used for water and/or wastewater treatment. The choice for a particular use will depend greatly upon the raw feedwater quality, the pretreatment requirements and costs, and the economics of the particular membrane module designs being considered.

CHAPTER V

MEMBRANE CLEANING AND MAINTENANCE

Even with pretreatment to reduce fouling and scaling of reverse osmosis membranes, reverse osmosis units require periodic cleaning and flushing. Shields (1979) indicated that a regular cleaning program will increase membrane life and maintain adequate membrane performance. Since chemical cleaning costs average less than $0.02 per 1000 gallons of product water (Shields 1979), routine cleaning is clearly a sound investment.

Johnston and Lim (1973) reported that product water flux will decline and membrane permeability will be reduced due to fouling of the membrane surface, densification of the polymer substructure from applied pressures, or irreversible chemical and/or physical damage to the polymer surface layer. The membrane surface layer can be damaged from hydrolysis of the ester group in cellulose acetate membranes or from physical abrasion by particulate materials in the feed solution. Colloidal gels or solid precipitates will foul the membrane surface, increase the effective osmotic pressure of the feed, and reduce the net driving force for flow across the membrane.

Inadequate operational procedures that may contribute to membrane fouling would include (Burns and Roe 1979): pretreatment upset conditions, improper equipment selection, inadequate flushing following shut down, failure of cleaning chemical injection systems, a lack of operator knowledge or proper execution, a low level buildup of precipitates over extended periods of time, inadequate interpretation of salt rejection and productivity data, and/or a change in the feedwater composition. Cleaning equipment, chemicals, and procedures are required at reverse osmosis installations to compensate for any of the above conditions.

Operational Considerations

Cleaning methods vary according to the type of reverse osmosis module being utilized. In general, cleaning or flushing is conducted at low system feed pressures and a brine concentrate flow rate approximately equal to the feed flow rate to minimize product water flow. Cleaning or flushing should be performed, as in normal operation, from membrane feed side to reject side, as reverse flow or back flushing may result in permanent damage to the membrane modules.

Cleaning solutions may be heated to improve cleaning efficiency and decrease the required cleaning time. However, the cleaning solution temperature must be monitored to ensure that it does not exceed the allowable maximum operating temperature of the membrane. Recirculation of the cleaning solution will increase its temperature and Burns and Roe (1979) suggest a maximum cleaning solution temperature of 35°C for safe system operation.

Cleaning procedures should be carried out when either the salt passage increases by 50 percent of normal operating levels, brine or product water flow rates decline by more than 5 percent at constant temperature and pressure conditions, or membrane module pressure drops increase by 50 percent (Burns and Roe 1979). If one cleaning cycle fails to improve performance, additional cleaning cycles should be performed. If cleaning is unsuccessful, reasons for the fouling should be determined and corrective measures taken before replacing the membrane elements.

In the event of an emergency shutdown, flushing the system with product water is recommended. This procedure will remove brine from the membrane modules and will reduce the potential for scale formation on the membranes (Burns and Roe 1979). Burns and Roe (1979) suggest providing an emergency flushing system on reverse osmosis systems consisting of an elevated product water storage tank with piping from the tank to the main header of the reverse osmosis unit. A conductivity meter can be used to shut a flush control valve when the conductivity of the brine stream reaches an acceptable level.

The nature and extent of membrane fouling is dependent upon the raw feedwater quality, the extent of pretreatment, and the degree of surface turbulence within the membrane modules. Fouling is caused by a number of different materials and their effect on system performance is summarized in Table 1. Because a variety of foulants exist that hamper reverse osmosis performance, a range of cleaning techniques has been developed. Specific chemical cleaning agents, their application, source of supply, and cost are provided in Appendix A. A summary of foulant characteristics and cleaning procedures is found below, while specific cleaning procedures are located in Appendix B.

Organic Foulants

Humic acid scale is generally the main organic foulant to be dealt with in reverse osmosis installations. Humic acid, a brown polymeric constituent of soil organic matter, is a polyelectrolyte whose molecular weight ranges from 2,000 to 500,000 with an average of 20,000 to 50,000. Scale formation is due to its ability to form insoluble precipitates with multivalent metal ions such as Fe^{+3} or Ca^{+2}. Organic colloids or proteins may also cause membrane fouling.

Johnston and Lim (1973) reported that fouling from adsorbed organics is sometimes of a nature that circulation of clean water through the system may be adequate to restore membrane performance. Some organic foulants may also be dissolved using pH adjusted water. Regular cleaning of the membranes is a necessity, however, and the most effective organic foulant cleaners are enzyme detergents such as Biz, Tertgazyme, or Bold.

Bacterial Growth

The large surface area of reverse osmosis membranes is an inviting environment for bacterial growth. Disinfection is required prior to reverse osmosis treatment as described earlier to limit microbial growth and biological fouling of the membranes. If the disinfection step is not successful, if the system is shut down for an extended period of time, or if the product brine becomes contaminated with microorganisms, membrane cleaning for bacterial slime removal will be required.

Generally, membrane sterilization and bacterial slime removal using a 0.75 to 1.0 percent by weight, 30 percent formaldehyde solution is recommended (Burns and Roe 1979). A thorough flushing of the membrane module banks and piping should be carried out before the plant is returned to service. The formaldehyde solution should be left in the modules if they are to be taken out of service.

If formaldehyde cleaning fails to restore membrane performance, flushing with a chlorine solution of 1 to 5 mg/l free chlorine residual is recommended

Table 1. Effects of membrane foulants (DuPont 1977b).

Foulant	General Symptoms		
	Salt Passage	Bundle Pressure Drop	Product Water Output
Hydrated oxides (iron, nickel, copper, etc.)	Rapid* Marked Increase (>2x)	Rapid* Marked Increase (>2x)	Rapid* Marked Decrease (20-50 percent)
Calcium Precipates (carbonates, sulfates, phosphates)	Significant Increase (10-25 percent)	Slight to Moderate Increase (10-50 percent)	Slight Decrease (<10 percent)
Colloids (Mostly aluminum silicates)	Gradual** Marked Increase (>2x)	Gradual** Marked Increase (2x)	Gradual** Marked Increase (>50 percent)
Mixed Colloids (iron, organics, and silicates)	Rapid* Increase (2 to 4x)	Gradual** Marked Increase (>2x)	Gradual** Marked Decrease (>50 percent)
Bacterial Slimes	Marked Increase (>2x)	Marked Increase (>2x)	Marked Increase (>50 percent)

*Within 24 hr
**Over several weeks

(Block 1977) only as a last resort. A maximum of one hour flushing is suggested to prevent membrane deterioration through chlorine oxidation. Chlorine cleaning cannot be used with polyamide and polyfuran membranes that are extremely chlorine sensitive.

Hardness Scale

Hardness scale consists of precipitates of carbonate hardness, i.e., calcium and magnesium carbonate; non-carbonate hardness, i.e., calcium and magnesium sulfate; and other calcium salts such as calcium fluoride and calcium phosphate. Hardness scale can be avoided by keeping product water recovery below 50 percent, by adding antiscale solutions such as sodium hexametaphosphate, or by controlling the pH of the feedwater in the acidic range where precipitation will not occur. Carbonate scale will resist mechanical flushing but can be dissolved in a warm weak acid solution of one to two percent citric acid. An ammonia citrate solution may also be used to remove these scales. Calcium sulfate scale is less easily dissolved than carbonate scale but is more easily removed by flushing. Block (1977) concluded that the EDTA $Na_4 \cdot 4H_2O$ (20 percent), NH_4HCO_3 (7 percent), and Zonyl FSA (0.005 percent) solutions adjusted to pH 7 gave the best results for calcium sulfate dissolution.

Boen and Johannsen (1974) reported that calcium deposits chemically identified as tri-calcium orthophosphate could be removed from reverse osmosis membranes by a 15,000 to 30,000 ppm (2 to 4 oz/gal) solution of EDTA (Questex or Versene 100) adjusted to a pH value of 7 with sulfuric acid. If sulfuric acid is used for cleaning solution preparations, the solubility limit of calcium sulfate may be exceeded and hydrochloric acid would be preferable for pH adjustment.

Takahashi and Ebara (1978) utilized sponge ball cleaning and scale preventing agents to limit hardness scale development in their units. Sponge ball cleaning is a physical abrasion method that is applicable only to tubular module membrane configurations and therefore has limited application.

Inorganic Colloids and Metal Oxides

Scales of clay-like materials composed of Si, Al, Ca, Mg, and Fe are very difficult to dissolve even without the restrictions imposed by the sensitivity of the reverse osmosis membranes and are only partially removed by some of the better performing cleaners tested in the laboratory (Block 1977). It was therefore recommended to prevent the formation of these deposits, rather than to try and remove them after they are formed. Pretreatment steps such as ultrafiltration or polymer coagulation are necessary to remove these fine particulate materials and prevent this form of membrane fouling.

DuPont (1980a) stated that in cases where iron and oxygen are present in the feedwater, iron fouling will occur despite the use of high quality filtration. This iron fouling will result in increased systems pressure drops, decreased product water flux, and increased salt passage. Allen and Shippey (1978) recommended that since iron materials cause cleaning difficulties, no iron should be allowed in future reverse osmosis system materials. In existing facilities, analyses should be performed for metals in product water samples before and after cleaning to monitor the presence of corrosion products. If corrosion products are detected, upstream pumps and hydraulic components should be checked for deterioration. All defective equipment and appurtenances should be replaced with bronze, stainless steel, or fiberglass reinforced materials for high pressure elements and PVC for low pressure elements to minimize iron oxide fouling.

Block (1977) found ammonium bifluoride, at 2 percent by weight adjusted to a pH of 4.3, to provide the best results for silicate scale removal from reverse osmosis membranes. A 2 percent by weight sodium phosphate solution adjusted to a pH of 12.4 was the next best silicate scale remover followed by ammonium fluoride and ROGA cleaning solution B. No chemical agents have been found to completely remove silica imbedded in membranes, nor are complex aluminasilicates, containing Ca, Mg, and Fe, completely removed with present cleaning solutions.

A 2 percent by weight citric acid solution, adjusted to a pH of 4 with ammonia hydroxide is recommended by DuPont (1980a) for iron hydroxide scale removal. Flushing the modules with product water prior to cleaning is advised since residual calcium and magnesium in the water in the modules will reduce the effectiveness of the cleaning solution by complexing with the citric acid. A green-yellow color is present in the cleaning solution when the citric acid content is in excess of the iron content on a molar basis. When there is more iron than citric acid, a red-brown color forms indicating that the cleaning solution should be changed. Block (1977) also found that iron and manganese hydroxide scale could be removed effectively by a 2 percent by weight sodium dithiorite solution, $Na_2S_2O_4$, adjusted to a pH of 3.6.

Membrane Rejuvenation

When a membrane has been subjected to severe cleaning procedures or cellulose deterioration, certain polymer and colloid solutions are reported to be effective in restoring membrane salt rejections (Burns and Roe 1979). Two rejuvenation procedures are provided in Appendix C. These procedures are effective only on intact membranes and are generally only temporary remedies especially when using colloid solutions as they are apt to wash out over a period of several weeks. Membrane productivity is reduced by 10 to 15 percent as well due to a loss of membrane surface area when the rejuvenation solutions plug membrane defects.

CHAPTER VI

REMOVAL OF INORGANICS USING REVERSE OSMOSIS

The major function of reverse osmosis systems is the separation of inorganic substances from a waste stream. A great deal of work has been devoted to the analysis of inorganic solute rejection by reverse osmosis membranes, however, general predictive models for membrane performance, especially when treating multicomponent feedwaters, have yet to be developed.

Single Component Systems

Sourirajan (1963) proposed a mechanism based on the Gibbs adsorption equation for the demineralization of aqueous sodium chloride solutions using porous membranes. The technique is applicable to inorganic solutes in aqueous solutions involving the preferential sorption of substances at interfaces. The order in which the given cellulose acetate membrane separated the various inorganic ions in aqueous solution was: strontium > barium > lithium > sodium > potassium and sulfate > chloride > bromide > nitrate > iodide. The given order is the same as the lyotropic series with respect to both cations and anions. Sourirajan (1963) concluded that the negative adsorption of solutes at liquid solid interfaces appears to offer a sound basis for the development of a practical technique for the separation of substances in solutions. While the parameters involved in the mechanism of the separation technique were clear, they were not sufficiently defined to make it possible to predict in detail the most successful system for a given separation problem.

Sourirajan (1964b) illustrated the general applicability of reverse osmosis as a separation technique for aqueous inorganic solutions. He also indicated the possible predictability of the separation and flow characteristics of porous cellulose acetate membranes and the concept that separations are similar for ions of the same valence. The applicability of reverse osmosis was tested with several commonly available inorganic salts in aqueous solutions using different samples of preshrunk Schleicher and Schuell cellulose acetate membranes. The extent of separation depended only on the pore structure and chemical nature of the membrane with respect to that of the solution. The ability of a cellulose acetate membrane to separate the inorganic ions in solution was found to be: citrate > tartarate > sulfate > acetate > chloride > bromide > nitrate > iodide > thiocynate, and magnesium, barium, strontium, calcium > lithium, sodium, potassium. This order is once again the same as the lyotropic series with respect to both cations and anions, although exceptions to the lyotropic series were found. The lyotropic order with respect to bivalent cations is Mg > Ca > Sr > Ba; Sourirajan found the corresponding separation order to be Mg > Ba > Sr > Ca at certain levels of solute separation.

From the data obtained by Sourirajan (1964b), Table 2 and Figure 9 were developed to predict the separation and flow characteristics of any cellulose acetate membrane for all solution systems illustrated, given the

Table 2. Separation of some related solutes aqueous solution under identical experimental conditions using S & S cellulose acetate membranes (Sourirajan 1964b).

Feed solution molality, 0.5M
Feed rate, 30 cc./minute
Operating pressure, 750 to 1500 p.s.i.g.

Mole % Salt Removed

NaCl	Sodium acetate	NaBr	$NaNO_3$	NaI	NaCNS	LiCl	CKl	NH_4Cl	$LiNO_3$	KNO_3	NH_4NO_3
0	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
10	14.	8.6	6.5	6.	5.	11.	9.	8.5	7.	6.5	5.
20	27.	16.5	13.5	13.	10.	21.5	18.	16.5	14.	13.	10.
30	40.	25.	20.5	19.5	15.	32.	27.	24.	21.	20.	15.5
40	51.5	33.	27.5	26.	20.	42.5	35.	32.	28.	27.	21.
50	62.5	42.	35.	32.5	25.	53.	44.	40.	36.	34.5	27.
60	71.	50.5	44.	40.	30.	62.5	53.5	49.	45.	42.5	34.
70	78.5	60.	54.5	48.	35.	72.	64.	58.5	55.5	52.	42.
80	86.	70.	65.5	58.	43.	81.5	75.5	69.	66.5	62.5	53.
90	93.	82.	80.	73.	59.5	91.	87.5	83.	80.	77.	71.
100	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.

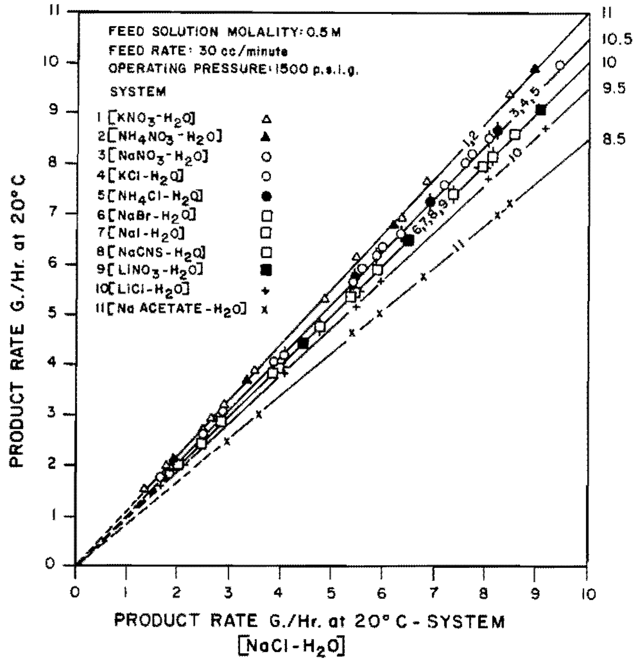


Figure 9. Flow characteristics of selected solution systems (Sourirajan 1964b).

characteristics of the membrane for any one of the above systems that contain monovalent cations and anions.

Hindin and Bennett (1969) conducted a study with cellulose acetate membranes dealing with membrane rejections of specific chemical species found in abundance in most treated wastewater effluents. An order of ionic rejection by the cellulose acetate membrane was found to be: $Al^{+3} > Fe^{+3} > Cu^{+2} > Na^{+} > NH_4^{+} > K^{+} > Cd^{+} > Mg^{+} > Ca^{+2}$. The authors stated that the trivalent cations reacted like Lewis acids and formed hydroxy complexes while most other cations formed hydrates. It was indicated that pH might be an important factor as the hydrogen concentration might dictate the form of the multivalent cation. An order of rejection of anions by the membrane was formulated as follows: $SO_4^{-2} > CrO_4^{-2} > Cl^{-} > HPO_4^{-2} > F^{-} = CN^{-} > NO_2^{-} > NO_3^{-} > B_4O_7^{-2}$.

Lonsdale et al. (1969) measured the rejection of cellulose triacetate and cellulose 2.5-acetate membranes on a number of solutes important in water quality. Phosphate and ammonia removals were evaluated at two pH values. Removal of nitrate and bicarbonate as well as other salts were also determined. The rejection of most of the salts was sufficiently high for both low flux and high flux membranes that it was concluded that there is little concern about product water quality in most applications of reverse osmosis, even when recoveries are high. Because of the high rejections of bicarbonates, the authors stated that the product water from reverse osmosis units will have a low buffer capacity. The pH value of the treated water should be close to neutral when applying reverse osmosis to the treatment of natural waters. Boron as boric acid was not highly rejected. Several compounds formed stable complexes with boric acid, however, and these complexed species were rejected.

Johnston (1975) described the selective rejection of various heavy metal chloride salts by cellulose acetate membranes. Interaction of divalent cations with a cellulose acetate membrane surface were generally uniform and were likely largely coulombic in origin. Selective solute rejection was dependent mainly on the interactions of the divalent cations with water in the bulk solution. Johnston concluded that the overall controlling criteria for these interactions appeared to be the partial molar free energies of hydration and the entropies of the ions in solution.

Rangarajan et al. (1976) studied the reverse osmosis separations of several inorganic salts in aqueous solutions involving polyvalent ions using porous cellulose acetate membranes. Free energy parameters for the Mg^{+2}, Ca^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Sr^{+2}, Cd^{+2}, Ba^{+2}, Pb^{+2}, Fe^{+3}, Cr^{+3} and SO_4^{-2} ions, and for the $MgSO_4$, $CoSO_4$, $ZnSO_4$, $MnSO_4$, $CuSO_4$, $CdSO_4$ and $NiSO_4$ ion pairs were determined. Free energy parameters offered a means of predicting reverse osmosis separations of inorganic salts in aqueous solutions involving the above ions and/or ion pairs using porous cellulose acetate membranes. Only membrane specifications in terms of a single reference solute such as sodium chloride were required to predict performance.

Johnston and Lim (1978) conducted both laboratory and pilot plant studies on the removal of inorganic contaminants by reverse osmosis using cellulose acetate membranes. A cellulose acetate membrane capable of rejecting 70 percent NaCl from a standard salt solution was found to reject more than 80 percent of each of the metals except Mg^{+2} as shown in Table 3. A membrane capable of rejecting 90 percent NaCl from a standard salt solution was found to reject more than 90 percent of all the metals.

Burns and Roe (1979) recognized that ion rejection values are relatively insensitive to membrane rejection differences, especially at high rejection values. They suggested the use of a reduction ratio as being more indicative of differences in reverse osmosis process performance. The reduction ratio is defined as the ratio of the solute concentration in the feed to the solute concentration in the product or permeate and is calculated as follows:

$$R_R = 1/(1-R) = C_F/C_P \quad . \quad . \quad . \quad (5)$$

Table 3. Metal removal efficiencies by reverse osmosis (Johnston and Lim 1978).

Metal Chloride	pH of 10 mg/l Solution	Percent Metal Removal*	
		$NaCl_{70}$	$NaCl_{90}$
(1) K^+	6.3	88.1	94.0
(2) Ba^{+2}	5.8	88.3	100.0
(3) Be^{+2}	4.3	83.8	97.0
(4) Ca^{+2}	5.9	80.8	94.1
(5) Cd^{+2}	5.5	85.1	98.3
(6) Co^{+2}	5.8	81.9	96.0
(7) Cu^{+2}	5.4	84.1	98.6
(8) Fe^{+2}	5.1	82.0	96.2
(9) Mg^{+2}	6.1	73.5	90.0
(10) Mn^{+2}	5.8	84.2	97.5
(11) Ni^{+2}	5.9	81.8	95.2
(12) Pb^{+2}	5.2	85.5	97.6
(13) Sn^{+2}	4.0	99.3	100.0
(14) Sr^{+2}	5.9	84.1	96.3
(15) Zn^{+2}	5.6	83.4	97.3
(16) Al^{+3}	4.4	97.3	100.0
(17) Cr^{+3}	4.2	99.1	100.0
(18) Fe^{+3}	3.4	100.0	100.0

*10 mg/l solutions tested at 1724 kPa (250 psi).

Separations noted are for metal removals from a 10 mg/l solution when permeated through the reverse osmosis static test cell.

where

R_R = the reduction ratio

R = percent rejection/100

C_F = solute concentration in the feed, mg/l

C_P = solute concentration in the product, mg/l

At 98 percent rejection, the reduction ratio is 50 to 1 while at 99 percent rejection, the ratio increases to 100 to 1. Reduction ratios for selected sodium and magnesium salts are shown in Table 4 and selected metal chloride reduction ratios are shown in Table 5.

Multicomponent Systems

Erickson et al. (1966) studied the desalination properties of membranes prepared from cellulose acetate-acetone-formamide solutions which were cured at three different temperatures. In studies of sea water and brackish water, the order of ion rejection was $SO_4^{-2} > Ca^{+2} > Mg^{+2} > HCO_3^- > Na^+ > K^+ > Cl^- > Br^-$. When more than two ions occurred in solution, the passage or rejection of one ion by the membrane was strongly influenced by the surrounding ionic environment. In systems containing a mixture of monovalent and divalent ions, the divalent ions were preferentially rejected at the expense of the monovalent ions. Alkaline earth metals as well as sulfates were strongly rejected indicating that the sign of the ionic charge has no bearing on rejection. Ions normally rejected by cellulose acetate membranes were rejected to an even greater extent in multisalt solutions, while ions which are usually passed easily were passed to an even greater extent.

Hinden and Bennett (1969) investigated ion rejection by cellulose acetate membranes. The authors found that, in general, the percent reduction of specific ions in the product water was greater than the reduction of the specific ion singly in aqueous solution, however, changes were not as apparent for anions as for cations.

Table 4. Reduction ratios of sodium and magnesium salts (Burns and Roe 1979).

	Sodium	Magnesium
SO_4^{-2}	106	670
OAc^-	88	-
HCO_3^-	60	-
F^-	58	-
Cl^-	31	190
Br^-	18	-
NO_3^-	10	130
CN^-	8	-
SCN^-	6	-

Agrawal and Sourirajan (1970) developed a simple method for predicting the performance of Loeb-Sourirajan type porous cellulose acetate membranes for low concentrations of mixed solute with a common ion in aqueous feed solution systems. The method requires only data on membrane specification and the applicable mass transfer coefficient for the corresponding single solute.

Mixon (1973) conducted bench scale studies with cellulose acetate and polyamide membranes to establish rejection efficiences for barium, cadmium, chromium, copper, lead, and zinc. Experiments were conducted using trace levels of the above metals singly, in combination, and at different concentrations, using potable waters, wastewaters, and brackish waters as feedwaters. Rejections for metals in mixtures showed no significant difference when compared with rejection for metals individually.

Sastri (1977) investigated the reverse osmosis characteristics of zinc salt solutions using cellulose acetate membranes. In general, Sastri found that product rates increased linearly

Table 5. Reduction ratios of metal chlorides (Burns and Roe 1979).

Basis: NaCl = 31/1
0.1 Molar Solutions
600 psig, 75°F
Hydration Numbers in Parentheses
Source: Reverse Osmosis of Single Salt Solutions, Havens Industries (1965)

	IIA	IIIB	VIII	VIII	IB	IIB	
Li 40/1 (3.4)							F 59/1 (1.8)
Na 31/1 (2.0)	Mg 190/1 (5.1)						Cl (0.9)
K 22/1 (0.6)	Ca 114/1 (4.3)		Co^{+2} 184/1	Ni^{+2} 110/1	Cu^{+2} 92/1	Zn^{+2} 119/1 (5.3)	Br 17/1 (0.9)
Rb 26/1*							
Cs 32/1 (0)	Ba 125/1 (3.0)	La 354/1 (7.5)					

*Prorated from a bromide test.

with increasing operating pressures and decreased slightly with increase in feed concentrations. For a given operating pressure, the separation of zinc nitrate was less than zinc chloride which was less than zinc sulfate. This trend was unaffected by feed concentrations of 100, 500, or 1000 mg/l zinc. A mixture of zinc nitrate and zinc chloride showed greater solute separation than a mixture of zinc nitrate and zinc sulfate. To determine the role of ion pairs, Sastri conducted experiments adding sodium sulfate to zinc chloride and zinc nitrate solutions. The result in both cases was increased solute separation which Sastri attributed to the formation of ion pairs in solution which were better separated than hydrated divalent zinc ions. He indicated that for solutions containing metal nitrate or metal chloride, solute separation could be increased by the addition of sodium sulfate.

Sastri (1978) conducted experiments with nickel salts using cellulose acetate membranes and found similar results to those given above with zinc salts. Sodium sulfate was added to nickel chloride and nickel nitrate solutions and resulted in increased solute separation. Sastri concluded that nickel ion pairs, $Ni^{+2}SO_4^{-2}$, were separated better than divalent nickel ions as was shown for zinc.

Rangarajan et al. (1978) presented an analytical technique for predicting reverse osmosis performance, ion separation and product rate, of cellulose acetate membranes of different surface porosities for different aqueous feed solutions containing two univalent electrolytic solutes with or without a common ion. The prediction technique requires only a single set of experimental data on membrane specifications given in terms of the pure water permeability constant and the solute transport parameter for sodium chloride, and the applicable mass transfer coefficient for the chosen feed solution system. The validity of their prediction technique was experimentally verified from reverse osmosis data for the feed solution systems $NaCl\text{-}KNO_3\text{-}H_2O$, $NaBr\text{-}KCl\text{-}H_2O$, and $NaCl\text{-}NaNO_3\text{-}H_2O$ using several cellulose acetate membranes.

Rangarajan et al. (1979) extended their analytical technique for predicting reverse osmosis performance, ion separation and product rates of cellulose acetate membranes of different surface porosities to aqueous solutions containing two electrolytic solutes involving a univalent cation, a divalent cation, two univalent anions, and a common univalent anion. The validity of their prediction technique was experimentally verified from reverse osmosis data for the feed solution systems $NaBr\text{-}MgCl_2\text{-}H_2O$, $NaCl\text{-}Mg(NO_3)_2\text{-}H_2O$, and $NaCl\text{-}MgCl_2\text{-}H_2O$.

Sastri (1979) studied the reverse osmosis separation behavior of calcium, magnesium, zinc, manganese, copper, aluminum, and iron as nitrate, chloride, and sulfate salts, and investigated the effect on solute separation of adding sodium sulfate to magnesium perchlorate and manganese nitrate solutions. It was concluded that ion pairs increase solute separation, and that for solutions containing metals, nitrates, or chlorides, solute separation could be increased by adding sodium sulfate.

Ionic Charge Relationships

Loeb and Manjikian (1965) reported the results of experiments with a reverse osmosis cellulose acetate membrane treating brackish water with a total dissolved solids content of 2500 mg/l, more than half of which consisted of divalent ions. Divalent ions were removed more effectively than monovalent ions and the authors indicated that reverse osmosis could be effective for desalinating waters having appreciable concentrations of calcium, magnesium, sulfate, or carbonate ions.

Govindan and Sourirajan (1966) observed that solute separation increased with an increase in valence of the ions and the effect was more pronounced with the variation of the valence of the anion. For solution systems involving ions of different valences, the relative separation data form unique lines characteristic of the membrane-solution system, similar to those obtained for solutions containing ions of the same valence. Product rate data showed a wide scatter for feed solutions containing ions of unequal valences.

In a study of the desalination properties of cellulose acetate-acetone-formamide membranes, Erickson et al. (1966) found that divalent ions were rejected to a greater extent than monovalent ions with no apparent regard to the sign of the charged ions. Complex multicomponent salt solutions exhibited the greatest preferential ion selectivity. Calcium, magnesium, and sulfate were rejected 10 to 30 percent better than the average of all ions in solution.

Sastri and Ashbrook (1976) studied the reverse osmosis separation of various heavy metal salts in the form of $CuSO_4$, $Cu(NO_3)_2$, $NiSO_4$, $NiCl_2$, $Ni(NO_3)_2$, $Fe_2(SO_4)_3$, and $Al(NO_3)_3$. Cations of the order of increasing solute rejection were $M^{+3} > M^{+2} > M^{+1}$. Sastri and Ashbrook found that metal sulfate salts were rejected to a greater extent than metal nitrate salts, indicating that the percent separation of the solute increased with an increasing value of the ion-pair equilibrium constant. Because the cellulose acetate membrane has a proton affinity, and in the case of an ion pair, both size and effective charge may prevent approach of the ion pair toward the membrane surface layer, the ion pair shows better separation than the hydrated cation.

Tan and Davis (1978) studied the reverse osmosis properties of polybenzimidazole membranes as effected by pH variations when treating monovalent and multivalent solute systems. Rejections of multivalent solutes were higher than those of the monovalent solute, sodium chloride. Below pH 2 sodium chloride rejection was low, while divalent solute rejections remained high.

Johnson and Lim (1978) used cellulose acetate membrane and found that trivalent ions were better rejected than lower valence ions and large ions were rejected better than small ions. The effect of metal concentration on percent rejection was examined for a few metal chlorides and only metals of lower valence showed a slight enhancement of removal efficiency with increased metal concentration.

Sastri (1979) found metal salts of trivalent cations to show the greatest separation with the order of salt rejection once again predictably $M^{+3} > M^{+2} > M^{+1}$. The separation of sulfates was greater than chlorides which was greater than perchlorates or nitrates. Sastri attributed the greater increase in sulfates to the presence of highly rejected metal-sulfate ion pairs in solution.

Nusbaum and Riedinger (1980) stated that rejection of individual ions is not meaningful as ions are present in water as compounds and pass through a membrane as charge balanced combinations. As shown in Table 6, within a chemical family, rejection generally decreased with increasing molecular weight. Rejection of an ionized species increased as the charge on the ion increased. Salts containing only monovalent ions showed poorer rejection than those containing divalent or trivalent anions or cations. Weak acids and bases that were only slightly ionized were poorly rejected as were dissolved gases.

Water and Wastewaters

Hauck and Sourirajan (1969) reported the performance of a few typical Loeb-Sourirajan type porous cellulose acetate membranes for the treatment of

Table 6. Rejection of various compounds by reverse osmosis at 400 psi (2800 kN/m^2), pH 6, and membrane type ROGA #4101 (Nusbaum and Riedinger 1980).

Compound	Rejection %	Compound	Rejection %
LiCl	96.4	SiO_2	92.3
NaF	97.1	H_3BO_3	44
NaCl	96.0	NH_4Cl	93.3
NaBr	92.3	$CuCl_2$	98.9
NaI	88.9	$CuSO_4$	99.6
$NaNO_3$	93.3	$NiCl_2$	99.4
$NaHCO_3$	97.4	$NiSO_4$	99.9
KCl	95.5	$FeCl_2$	99.7
$NaSO_4$	99.6	$AlCl_3$	99.2
$MgCl_2$	98.8	CO_2	0
$CaCl_2$	98.8	H_{25}	0
$MgSO_4$	99.8	HCN	0
NaH_2PO_4	99.8		

polluted waters. Using feed waters containing 300 to 800 ppm hardness expressed as $CaCO_3$, product waters containing 2 ppm or less could be obtained with 90 percent product recovery and an average initial flux of 65 $l/m^2/h$ (38 gpd/ft^2) at 6.9 MPa (1000 psig). The average separation of nitrate was 50 percent at an average product rate of 55.6 $l/m^2/h$ (32.7 gpd/ft^2) at 6.9 MPa (1000 psig), while phosphate was rejected 99 percent at an average product rate of 31.1 $l/m^2/h$ (18.3 gpd/ft^2) at 3.45 MPa (500 psig). It was concluded that the reverse osmosis process using the above type of porous cellulose acetate membranes had the potential of becoming an economic means of renovation of wastewaters to provide a product of acceptable quality for domestic use as well as for high pressure boilers. Table 7 shows that common water pollutants such as nitrates, borates, fluorides, chlorides, phosphates, ABS, and ammonium ions can be effectively removed by the reverse osmosis process.

The effect of reverse osmosis treatment on the natural bicarbonate buffering system was investigated by Milstead et al. (1971) using cellulose acetate membranes. The quality of the product water was dependent both upon the carbonate-bicarbonate equilibrium and the membrane permeability of the species involved in that equilibrium, namely CO_3^{-2}, HCO_3^-, H_2CO_3, CO_2, OH^- and H^+. The order of the carbonate species rejection was found to be $CO_3^{-2} > HCO_3^- > H_2CO_3 > CO_2$. At high feed pH values, the product water was less basic because of the nearly complete rejection of carbonate. At low feed pH values, the low rejection of CO_2 resulted in an acidic product water. The precise prediction of bicarbonate rejection and of product water pH in brackish water desalination was found to be complicated by the effect varying feedwater composition had upon individual ion rejection.

To determine if the type of water in which a metal ion was dissolved affected rejection results, Mixon (1973) conducted bench scale studies with cellulose acetate and polyamide membranes using potable, brackish and wastewaters as a feedwater source.

Table 7. Separation of selected water pollutants by reverse osmosis* (Hauck and Sourirajan 1969).

System	Solute Concentration. in Feed ppm	Product Solute Concentration ppm	Product Rate gpd/ft^2
$NaNO_3-H_2O$	492	87	27.3
$Na_2B_4O_7-H_2O$	524	16	26.1
$NaF-H_2O$	505	26	26.4
$NaCl-H_2O$	507	78	27.6
$ABS-H_2O$	95	1	20.9
$ABS-H_2O$	300	1	19.6
$NH_4NO_3-H_2O$	487	97	23.2
$Na_3PO_4-H_2O$	480	3	20.4

*Film H-4
Operating pressure 1000 p.s.i.g.
Product recovery 90%
pH of feed = 9.0.

Removal efficiences were essentially the same for barium, cadmium, cromium, and zinc from all the feedwaters, while copper removal from wastewater was significantly less than from potable or brackish waters.

Boen and Johannsen (1974) conducted pilot studies to determine the feasibility of applying reverse osmosis as an upgrading process for treated and untreated secondary effluents. Six commercially designed reverse osmosis pilot units with 1.136 to 3.785 m^3/day (3000 to 10,000 GPD) capacities were tested. The mean percent reduction of constitutents during the study is shown in Table 8. While secondary effluent is admittedly not the best source for drinking water, the data show that reverse osmosis consistently produced product water meeting primary and secondary regulations for those parameters monitored in the study. Colorado River water was also tested as representative of a high TDS, high sulfate water. Rejections were high for all constituents except boron and fluoride. The poor rejections for boron and fluoride were due to the acidified nature of the river water.

Buckley (1975) treated brackish well water in San Diego, California, by reverse osmosis. Rejection of 97 percent of the total dissolved solids was achieved with 75 percent feedwater recovery.

Johnson and Lim (1978) conducted reverse osmosis pilot plant studies for 9 months using chlorine free secondary effluent from an extended aeration pilot plant as feedwater. During this time, percent rejections for total hardness, TDS, and chlorides fluctuated very little and the sulfate ion concentration was constant. Total inorganic carbon removal was consistent, although not as stable as TDS. Neither removal efficiencies nor permeation rates were affected by the level of water recovery.

Glueckstern et al. (1978) described a 700 m^3/day reverse osmosis plant operating in Eilat, Israel, using brackish water with 6000 ppm TDS as a feed source. The plant produced 560

Table 8. Average percent reductions of constituents by various reverse osmosis configurations treating secondary wastewater effluents (Boen and Johannsen 1974).

Reverse Osmosis Configuration	TDS	Total COD	Diss. COD	Total Hardness	Ca^{+2}	Ortho-P	NO$_3^-$-N	Ammonia-Nitrogen	Cl$^-$	SO$_4^{-2}$
DuPont Hollow Fiber B-9 Modules Polyamide Fibers	88	90	90	95	96	93	84	--	91	94
Gulf Spiral Wound Cellulose Acetate	94	88	92	98	99	99	55	96	88	99
University Tubular Cellulose Acetate	97	93	96	99	99	99	84	99	97	99

mg/l TDS in the product water. Feedwater and product water analyses indicated approximately 90 percent rejection for the cations and anions measured.

Shields (1979) presented case histories of reverse osmosis plants in Europe and the United States using aromatic polyamide membranes. Feedwater TDS ranged from 200 to 42,000 mg/l and product water was produced meeting drinking water standards for TDS.

Sorg et al. (1980) reported the results of chemical analyses of effluent from reverse osmosis systems in Sarasota County, Florida. All of the reverse osmosis systems produced a high degree of treatment and rejection efficiencies of specific ions were close to the ranges reported in the literature. Differences in rejection values between systems were said to be due to specific design and operational differences and to differences in membrane age.

Huxstep (1981) evaluated low, 1.38 MPa (200 psig), and high, 2.76 MPa (400 psig), pressure reverse osmosis treatment for the removal of specific contaminants from drinking water. Two 170 m^3/day (45,000 gpd) pilot plant reverse osmosis systems were installed at the Charlotte Harbor Water Association Treatment Plant. As expected, the high pressure system performed in a superior manner to that of the low pressure system. Removal of natural constituents by each system varied with the substance measured; however, both systems achieved the highest rejection with sulfate and the lowest with sodium. TDS rejection by the high pressure system was approximately twice that of the low pressure system indicating the need for high pressure operations for adequate system performance.

Summary

General reverse osmosis performance predictive models dealing with a wide variety of multicomponent solute systems have yet to be developed. From a review of the literature related to inorganic solute removal by reverse osmosis, a number of performance characteristics can be recognized:

1. Multivalent ions are rejected more effectively that univalent ions in the order $M^{+3} > M^{+2} > M^{+1}$.

2. Co-ions affect the rejection of particular ions due to ion pair formation.

3. Undissociated or poorly dissociated compounds are only poorly rejected.

CHAPTER VII

REVERSE OSMOSIS REMOVAL OF THE INORGANIC CONTAMINANTS CONTROLLED BY THE NATIONAL INTERIM PRIMARY DRINKING WATER REGULATIONS

On June 24, 1977, the United States Environmental Protection Agency established the National Interim Primary Drinking Water Regulations (NIPDWR) (EPA 1976) to protect the health and welfare of the American public and to ensure them a supply of safe drinking water. Maximum contaminant levels (MCL) were set for ten inorganics and radionuclides, Tables 9 and 10, whose removal by reverse osmosis will be discussed below.

Arsenic

The National Academy of Science (1977) stated that the current MCL for arsenic of 0.05 mg/l provides a meager margin of safety. Sorg and Logsdon (1978) reported that arsenic is a common mineral in many western states and is probably present in many groundwater supplies serving small communities.

There is little data available on the removal of arsenic from drinking water by reverse osmosis. Polymetrics (1974) estimated a rejection range of 90 to 95 percent. Sorg and Logsdon (1978) concluded that since reverse osmosis is effective in removing most dissolved solids, it should be effective for arsenic removal.

Fox (1981) conducted tests on the removal of arsenic III and arsenic V, using both spiral wound cellulose acetate and hollow fiber polyamide membranes. Fox demonstrated that the removal of arsenic by reverse osmosis was dependent upon valence and independent of pH in the range of 4.6 to 6.5, operating pressure in the range of 1.2 to 1.7 MPa (170 to 250 psig), and feed water TDS concentrations. The arsenic MCL of 0.05 mg/l, could be achieved for a maximum feed water concentration of 6.0 mg/l of arsenic V, but could be achieved only with a maximum feed water concentration of 0.13 mg/l for arsenic III. If arsenic III were oxidized to arsenic V prior to reverse osmosis treatment, arsenic III removal should be as effective as arsenic V removal.

Huxstep (1981) presented results of pilot plant studies conducted on the removal of arsenic III and arsenic V by low 1.4 MPa (200 psig) and high 2.8 MPa (400 psig) pressure reverse osmosis systems. Removal of arsenic III ranged from 63 to 73 percent for the high pressure system and 12 to 42 percent for the low pressure system. Neither system achieved the arsenic MCL for the source water arsenic concentrations in the range of 1.1 to 4.2 mg/l. Assuming rejections of 65 percent for the high pressure system and 30 percent for the low pressure system, a 0.05 mg/l MCL could be achieved only for source water concentrations not exceeding 0.14 and 0.07 mg/l, respectively. Arsenic V removals of approximately 94 percent for the high pressure system and approximately 79 percent for the low pressure system were recorded. The MCL could be achieved for raw water arsenic V concentrations not exceeding 0.83 mg/l for the high pressure system and not exceeding 0.23 mg/l for the low pressure system. A comparison of arsenic III and V removals again indicates that arsenic

Table 9. National Interim Primary Drinking Water Standards for selected inorganic contaminants.

Contaminant	Maximum Contaminant Level mg/l (unless specified)
Arsenic	0.05
Barium	1
Cadmium	0.010
Chromium	0.05
Lead	0.05
Mercury	0.002
Nitrate (as N)	10
Selenium	0.01
Silver	0.05
Radium-226 and 228 (combined)	5 pCi/l
Gross alpha particle activity	15 pCi/l
Gross beta particle activity	4 millrem/yr

Based on a 2 l/day drinking-water intake, except for tritium and strontium-90. Average annual concentrations of tritium and strontium-90 assumed to produce a dose of 4 mrem/year or 20,000 and 8 pCi/l, respectively.

Table 10. National Interim Primary Drinking Water Standards for fluoride.

Temperature °F	Temperature °C	Maximum Level mg/l
<53.7	<12.0	2.4
53.8-58.3	12.1-14.6	2.2
58.4-63.8	14.7-17.6	2.0
63.9-70.6	17.7-21.4	1.8
70.7-79.2	21.5-26.2	1.6
79.2-90.5	26.3-32.5	1.4

The MCL for fluoride is determined by the annual average of the maximum daily air temperature for the location in which the community water system is situated.

V is more effectively removed than arsenic III.

Barium

Sorg and Logsdon (1980) stated that although barium is often detected in trace amounts in surface waters and drinking water, it is not a serious problem in most drinking water supplies. A few areas in the United States do have a barium problem, however. In northern Illinois, concentrations of barium in groundwaters commonly range from 2 to 7 mg/l and in one source a level of 19 mg/l was observed.

Mixon (1973) conducted tests to determine the effectiveness of reverse osmosis in removing barium from potable, brackish, and waste waters in solutions by itself and with five other metal salts. The overall mean removal of barium from all waters was greater than 90 percent. Mixon concluded that reverse osmosis could meet the MCL of 1.0 mg/l of barium for feedwater concentrations up to 7.7 mg/l.

Johnston and Lim (1978) conducted laboratory studies on the removal of barium by reverse osmosis using cellulose acetate membranes. Barium solutions of 10 mg/l were tested at 1724 kPa (250 psig) and a pH value of 5.8. Removals of 88.3 and 100 percent were reported for $NaCl_{70}$ and $NaCl_{90}$ membranes, respectively.

Sorg and Logsdon (1980) reported that for two short laboratory experiments conducted by the Drinking Water Research Division of EPA for removal of 7.0 mg/l barium from a northern Illinois groundwater, removals of 95 to 99 percent were achieved. It was stated that since reverse osmosis is very effective in removal of hardness, it should also be very efficient for barium removal.

Cadmium

Sorg et al. (1978) reported that cadmium was not expected to pose a problem for water utilities. Minute traces have been discovered in waters where lead, copper, and zinc are mined and processed. A more serious problem exists in surface water receiving wastewater from industrial plating operations, but even here the problem should be minimal due to the insolubility of cadmium carbonate and hydroxide complexes in waters with a high pH value. Cadmium is also a contaminant of zinc galvinized iron and corrosive water provides the potential to dissolve cadmium from distribution pipes into the distribution system.

McCabe et al. (1970) found only 14 out of 967 finished water supplies with cadmium concentrations exceeding the MCL of 0.01 mg/l. The source of cadmium was suspected to be the distribution system rather than the raw water source.

Several studies appear in the literature describing cadmium removal by reverse osmosis, however, the data is conflicting as to the effectiveness of reverse osmosis. Hindin et al. (1968) conducted laboratory tests with cellulose acetate membranes using raw water with cadmium concentrations of 0.097, 0.950, and 9.250 mg/l in the feedwater. Cadmium removals of 69 percent were observed indicating that the MCL of 0.01 mg/l could be met only for cadmium levels of 0.03 mg/l or lower in the feedwater.

Mixon (1973) reported cadmium removals of greater than 90 and 97.9 percent for initial feedwater cadmium concentrations of 0.10 and 0.96 mg/l cadmium, respectively. Cadmium removal was not affected when five other metals were added to the feed. On selected source testing, removal efficiencies for cadmium exceeded 98 percent for all potable, brackish, and wastewaters. Long term testing showed little effect on rejection efficiency. Mixon stated that reverse osmosis could produce an effluent that would meet the MCL of 0.01 mg/l for cadmium when treating influent feed water with concentrations less than 0.5 mg/l.

Houle (1974) evaluated a full scale reverse osmosis system for recycling wastewater from an electronics manufacturing plant. Cadmium rejections varied from 43 to 83 percent for feedwater cadmium concentrations in the range of 0.024 to 0.059 mg/l. The mean percent removal of 66 percent was essentially the same as reported by Hindin et al. (1968). Houle suggested that this low rejection may be due to resolution of the analytical technique used.

Johnston and Lim (1978) reported cadmium removals of 95.1 and 98.3 percent using cellulose acetate membranes with NaCl rejections of 70 and 90 percent, respectively. Cadmium solutions of 10 mg/l were tested at 1724 kPa (250 psig) and a pH value of 5.5.

Fox (1981) conducted tests with raw water cadmium concentrations ranging from 0.05 to 0.30 mg/l. Both spiral wound and hollow fiber systems achieved rejection rates exceeding 94 percent under all operating conditions. The pH values in the feedwater ranged from 5.4 to 7.0 and operating pressures ranged from 1.2 to 16 MPa (170 to 230 psig). No noticeable effect on cadmium rejection was observed with pH or pressure changes. The 94 percent rejection rate would satisfy the MCL for cadmium of 0.01 mg/l for influent feedwaters with cadmium concentrations of less than 0.16 mg/l.

Because of the low MCL for cadmium, percent rejection becomes significant. A low rejection rate of 69 percent would satisfy the MCL for raw water cadmium concentrations of only 0.032 mg/l, whereas a 98 percent removal would meet the MCL for raw water concentrations less than 0.5 mg/l. Because of the inconsistencies in cadmium removal data, it is difficult to assess the effectiveness of reverse osmosis in cadmium removal, indicating that more studies are needed in this area.

Chromium

Sorg (1979) reported that chromium was not expected to be a serious problem for water utilities because it is not commonly found in either ground or surface waters. McCabe et al. (1970) found only four finished water samples from 967 water supplies with total chromium concentrations exceeding the MCL of 0.05 mg/l. Sorg (1979) indicated that the principal source of chromium in natural waters is industrial in nature. The greatest potential for a chromium problem exists with water sources containing discharges from metal finishing, textile, and leather industries.

Hindin et al. (1968) conducted laboratory tests on chromium VI removal using cellulose acetate reverse osmosis membranes. Removals of 96.7, 95.0, and 93.5 percent were obtained for raw water chromium VI concentrations of 0.47, 5.0, and 49.6 mg/l respectively.

Mixon (1973) evaluated chromium VI removal using cellulose acetate membranes and obtained removals of 95.8 and 88.6 percent with raw water concentrations of 0.94 and 9.35 mg/l, respectively. No significant difference was observed in the rejection of chromium in a mixture with other metals compared with rejection of chromium alone. For selected source testing of potable, brackish, and wastewater, he found an overall removal efficiency greater than 93.7 percent. Long term runs had no appreciable effect on chromium removal. Mixon concluded that reverse osmosis could meet the MCL of 0.05 mg/l chromium for raw water concentrations less than 0.7 mg/l.

Johnston and Lim (1978) investigated chromium III removal using a laboratory static test cell with cellulose acetate membranes. At initial raw water concentrations of 10, 100, and 1000 mg/l chromium III, removals were greater than 99, 97.3, and 94.8 percent, respectively. On a 4.54 m^3/day (1200 gpd) pilot scale, they reported greater than 99 percent removal for initial raw water chromium III concentrations ranging from 0.15 to 7.3 mg/l.

Fox (1981) studied chromium III and chromium VI removal using hollow fiber and spiral wound membrane systems. Chromium rejection was found to be dependent upon valence and pH, and independent of operating pressure and initial raw water concentration. Chromium III removals ranged from 90 to 98 percent for feedwater initial concentrations from 0.071 to 0.80 mg/l. The hollow fiber membrane system reduced chromium III concentrations to below the MCL with a maximum initial feed concentration of 0.60 mg/l chromium III. The spiral wound membrane system performed better, meeting the MCL for raw water chromium III concentrations up to 1.1 mg/l. Chromium VI removals ranged from 94 to 97 percent for the hollow fiber membrane system and from 82 to 95 percent for the spiral wound membrane system. The hollow fiber membrane system could meet the MCL for initial feedwater concentrations less than 1.0 mg/l and the spiral wound system for initial feedwater concentrations less than 0.58 mg/l chromium VI.

Fluoride

Sorg (1978) reported that many small community water supplies are thought to have fluoride concentrations exceeding the MCL. Only limited data on fluoride removal by reverse osmosis was found in the literature. Hindin et al. (1968) conducted laboratory studies on fluoride using cellulose acetate membrane that showed fluoride concentration could be lowered from 58.5 to 1.0 mg/l.

Reverse osmosis equipment manufacturers report a wide removal range, from 40 to 96 percent. DuPont (1977a) stated fluoride removal is pH dependent ranging from 45 to 90 percent as the pH increases from 5.5 to 7.2. Data are based on brackish waters with fluoride concentrations of 1 to 10 mg/l and may not be applicable to waters with higher fluoride concentrations.

Fox (1981) substantiated that fluoride removal is pH dependent at low fluoride concentrations using hollow fiber and spiral wound membrane systems. The fluoride feed concentration was varied from 4.5 to 14 mg/l, the pH from 5.1 to 7.0, and the operating pressure from 1.2 to 1.6 MPa (170 to 230 psig) during the study. Product water with fluoride concentrations ranging from 0.3 to 4.9 mg/l was obtained. The spiral wound membranes produced 73 percent removal at pH 5.1 and 95 percent removal at pH 7. Hollow fiber membranes showed 50 percent removal at pH 5.1 and 92 percent removal at pH 6.8. Operating pressure did not affect fluoride removal for either membrane system.

Reverse osmosis was effective in removing fluoride at feedwater pH values above 6.5; however, Fox (1981) pointed out that the high pH value could cause calcium carbonate precipitation problems with waters of high calcium concentrations. Lowering the pH would prevent the problem of fouling but at the expense of fluoride removal. Blending of product water with feedwater to maintain the desired fluoride concentration in the effluent was suggested.

Huxstep (1981) presented results of pilot plant studies on fluoride removals by low 1.4 MPa (200 psig) and high 2.8 MPa (400 psig) pressure reverse osmosis systems. Fluoride concentrations ranged from 4.7 to 12.5 mg/l. Results showed consistent rejections of fluoride by both systems throughout the influent concentration range. Removals of 90.3 to 93.4 percent for the high pressure system and of 58.3 to 62.4 percent for the low pressure system were recorded. Product water concentrations for both systems increased with influent concentration due to the unchanging percent rejection. The product water fluoride concentration for the high pressure system did not exceed 1 mg/l, while the low pressure system product water fluoride concentration increased from 1.9 to 4.7 mg/l as the influent fluoride concentration was raised from 4.7 to 12.5 mg/l. The high pressure reverse osmosis system met the fluoride MCL even at the 12.5 mg/l influent concentration. The low pressure system would be applicable only for feedwaters with a fluoride concentration of 2 to 6.5 mg/l.

Lead

Sorg et al. (1978) stated that the principal problem with lead in drinking water comes from water distribution systems and not from lead in natural groundwater or polluted surface waters. Occasionally, however, lead is present in groundwaters at levels from 0.4 to 0.8 mg/l. Dutt and McCreary (1970) reported that 6.5 percent of 677 water samples collected from Arizona groundwaters had lead concentrations exceeding the MCL, with the highest level being measured at 0.52 mg/l lead.

Mixon (1973) conducted laboratory tests to determine the effectiveness of reverse osmosis in removing lead and found removals greater than 99.5 and 97 percent for initial lead concentrations of 0.95 and 9.3 mg/l, respectively. Tests for lead in combination with five other metals resulted in removals of 97.8 and 99.9 percent for initial source concentrations of 1.1 and 4.75 mg/l, respectively. In long term runs, lead rejections were stable.

Johnston and Lim (1978) recorded lead removals of 85.5 and 97.6 percent using a laboratory static test cell with cellulose acetate membranes rated at 70 and 90 percent NaCl removal, respectively. Lead solutions of 10 mg/l were tested at 1724 kPa (250 psig) and at a pH value of 5.2.

The results of studies of lead removal by reverse osmosis by Fox (1981) support the findings by Mixon (1973). Rejection rates for lead removal from drinking water were greater than 97 percent for both hollow fiber and spiral wound membrane systems. For raw water concentrations varying from 0.15 to 0.61 mg/l, both membrane systems produced product water with less than the minimum detectable resolution (0.005 mg/l) until raw water lead concentrations reached 0.23 mg/l. From 0.23 to 0.61 mg/l, the lead concentrations in the product water increased, but did not exceed the MCL of 0.05 mg/l. Fox (1981) stated that reverse osmosis can be an effective treatment technique for removing lead. Assuming a 97 percent removal rate, a single stage reverse osmosis unit could achieve the MCL treating water with lead concentrations less than 1.6 mg/l.

Mercury

EPA (1976) added mercury to the 1975 NIPDWR establishing an MCL of 0.002 mg/l. Sorg (1979) stated that because mercury is one of the least abundant metals in the earth's crust, it should not be frequently found in natural groundwater. Potential problems are seen with surface waters receiving wastewaters from industrial or manufacturing processes using mercury.

There is little data available on the removal of mercury from drinking water by reverse osmosis. Johnston and Lim (1978) investigated the use of reverse osmosis for the removal of heavy metals, pesticides, and other toxic chemicals from secondary wastewater effluent. One day batch tests, run with feedwater spiked with 5.0 and 9.0 mg/l of inorganic mercury, produced removals of 82.4 and 83.3 percent, respectively.

Sorg (1979) reported that the Drinking Water Research Division of EPA performed one day tests on mercury removal using hollow fiber polyamide and spiral wound cellulose acetate membrane systems. Results with a raw water source containing 0.008 mg/l inorganic mercury showed rejections of 25 percent for the spiral wound system and 79 to 81 percent for the hollow fiber system.

Sorg (1979) stated that even though the results of these two studies were not as high as the 95 to 98 percent rejection range for inorganic mercury estimated by equipment manufacturers (Polymetrics 1974 and Osmonics 1974), full scale reverse osmosis systems operated at high pressure and high recovery should achieve greater removals than pilot scale units performing under less than optimum conditions.

Nitrates

Sorg (1978) stated that nitrate excess is one of the most frequently reported drinking water regulation violations and is certainly a major problem for small communities in agricultural areas utilizing groundwater for drinking water purposes. Equipment manufacturers list a wide removal range (60 to 95 percent) for nitrate. Havens Industries (1965) reported 70 to 80 percent rejection for nitrate. Hindin et al. (1968) examined aqueous solutions spiked with 25 to 250 mg/l nitrate-nitrogen and recorded removals of 68 to 73 percent with a single stage reverse osmosis system.

Because the rejection of an ion or molecule by reverse osmosis is directly related to its size and valence, monovalent nitrate is not as effectively removed as divalent ions, such as sulfate. Other factors also affect nitrate removal efficiency, such as membrane type, number of operating stages, and operating pressure. Sorg (1978) pointed out that no reverse osmosis system has been installed solely for nitrate removal and therefore, no specific removal data are available for full scale systems.

Goodman (1975) reported that reverse osmosis could be used with waters containing high nitrate concentration. In experiments using a bore hole feedwater source, nitrate concentrations of 8 to 10 mg/l were reduced to 1.3 and 2.2 mg/l at recoveries of 33 to 60 percent, respectively. Total hardness was reduced from 280 mg/l to between 8 and 16 mg/l, and the pH was reduced from 7.6 to 6.2 due to removal of alkaline salts. In other experiments with hard river water at feed rates of 20 to 40 l/hr and 50 percent recovery, nitrates were reduced from 7.6 to 2.9, 9.6 to 3.1, and 8.4 to 2.8 mg/l nitrate.

Previous nitrate removal results were confirmed by Fox (1981) with removals ranging from 59 to 95 percent. His results demonstrate that reverse osmosis is an effective treatment, as the product water never exceeded the MCL of 10 mg/l of NO_3-N. Hollow fiber polyamide membranes showed rejections of 80 to 90 percent, independent of operating pressures of 1.2 to 1.4 MPa (170 to 200 psig) and feed pH (5.4 to 7.0). At an assumed rejection rate of 85 percent, hollow fiber membrane system could meet the MCL treating raw waters with less than 67 mg/l NO_3-N. Spiral wound cellulose acetate membranes were affected by pH as nitrate removals ranged from 51 to 95 percent. When the feedwater NO_3-N concentration was maintained at 13 mg/l and the feed pH was increased from 5.2 to 7.0, the rejection decreased from 80 to 70 percent. Fox was unable to account for this reduction in efficiency. Varying the operating pressure from 1.4 to 1.6 MPa (200 to 230 psig) had no effect on removal. Based on a rejection of 75 percent, the spiral wound system would meet the MCL treating waters with NO_3-N concentrations less than 40 mg/l NO_3-N.

Guter (1981) conducted experiments comparing the performance of five different reverse osmosis membranes for nitrate removal. The results showed a wide range of removal depending upon the membrane type. DuPont B-9, a hollow fiber polyamide membrane, achieved the best removal and had the highest water recovery.

Huxstep (1981) presented results of pilot plant studies conducted on the removal of nitrates by low 1.4 MPa (200 psig) and high 2.8 MPa (400 psig) pressure reverse osmosis systems with raw water NO_3-N concentrations ranging from 15 to 41 mg/l. Results of the testing showed removals of 75 to 80 percent for the high pressure system and removals of 6 to 24 percent for the low pressure system. Product water concentrations were below the 10 mg/l MCL for the high pressure system and above the 10 mg/l MCL for the low pressure system. Assuming 75 percent rejection for the high pressure system and 25 percent rejection for the low pressure system, the 10 mg/l NO_3-N MCL could be achieved only for raw water nitrate concentrations not exceeding 40 mg/l for the high pressure system and not exceeding 13 mg/l for the low pressure system.

Selenium

Sorg and Logsdon (1978) reported that because of possible carcinogenicity, the U.S. Public Health Service lowered the acceptable selenium limit in drinking water from 0.05 to 0.01 mg/l in the 1962 revised Public Health Service standards. EPA retained the 0.01 mg/l limit in their 1976 NIPDWR. Little information is available to determine the extent of the selenium problem. There is greater chance that it will be present in groundwaters than in surface waters as it is an uncommon pollutant in industry. Selenium is associated with uranium mining and has been reported in groundwaters in mining areas in Colorado, Arizona and New Mexico. Engsberg (1973) reported that 40 percent of 139 groundwater samples and 25 percent of 39 surface water samples in Nebraska exceeded the 0.01 mg/l selenium MCL.

There is little data on selenium removal by reverse osmosis. One manufacturer estimates removals at 90 to 95 percent (Polymetrics 1974). The Drinking Water Research Division of EPA performed two experiments using a small portable reverse osmosis unit with cellulose acetate membranes (Sorg and Logsdon 1978), with Cincinnati tap water spiked with 0.1 mg/l selenium IV as the feedwater. Selenium IV rejection was found to be independent of feedwater pH from 7.3 and 6.3, and feedwater TDS concentration from 360 and 3000 mg/l.

Johnston and Lim (1978) reported selenium removals of 97.9 and 99.4 percent for two different cellulose acetate membranes rated at 70 and 90 percent NaCl rejection, respectively. In their tests, the influent selenium concentration was 10 mg/l, the pH value was 6.8, and permeate flux for the $NaCl_{70}$ and $NaCl_{90}$ membranes was 4.94 and 2.53 $ml/hr/cm^2$, respectively.

Fox (1981) stated that unlike conventional coagulation treatment methods for selenium removal, selenium removal from drinking water by reverse osmosis was found to be independent of valence. Source water concentrations of selenium IV less than 0.12 mg/l were reduced to below the MCL of 0.01 mg/l. A hollow fiber system produced a product water that met the MCL for raw water selenium IV concentrations less than 0.5 mg/l, while a spiral wound system met the MCL for source water selenium IV concentrations less than 0.6 mg/l. Both systems produced a reduction in selenium concentration exceeding 98 percent. Percent removal of selenium IV was unaffected by either an operating pressure range from 170 to 230 psig, an increase in TDS to 1000 mg/l with calcium chloride, or a range of pH value from 5.0 to 6.1.

Fox (1981) found selenium VI removals from both reverse osmosis systems exceeded 98 percent. As with selenium IV, variations in feedwater pH from 4.5 to 6.5, operating pressure from 1.1 to 1.2 MPa (160 to 180 psig) and from 1.6 to 1.7 MPa (230 to 250 psig), an increase in raw water TDS from 285 to 1000 mg/l, and raw water selenium VI concentrations less than 0.5 mg/l had no effect on selenium VI removal.

Assuming 98 percent selenium removal efficiency, a single stage reverse osmosis system would meet the MCL for raw water selenium concentrations of less than 0.5 mg/l.

Silver

Sorg (1978) stated that silver should not be a problem in either surface or groundwaters, except in a few isolated cases. McCabe et al. (1970), in their 1969 Community Water Supply Survey, did not find a sample of finished water that had a silver concentration exceeding the MCL of 0.05 mg/l. No data were found in the literature for the removal of silver by reverse osmosis but equipment manufacturers claim removal ranges of 93 to 95 percent (Polymetrics 1974) and 94 to 96 percent (Osmonics 1974).

Radiation

Sorg and Logsdon (1978) indicated that radium is a problem in northern Illinois, central and western Florida, and in uranium mining areas of the Rocky Mountain States. Schliekelman (1976) reported that 151 of 241 towns monitored in Iowa had water supplies with detectable amounts of radium 226, 19 of which exceeded the MCL of 5 pCi/l. Gilkeson (1978) found more than 300 wells in northern Illinois exceeding 3 pCi/l of gross alpha with some containing up to 15 pCi/l of radium 226. The Sarasota County Health Department in Florida found that 40 out of 59 water supplies they tested had radium 226 concentrations of 0.3 to 22 pCi/l with 25 exceeding the MCL of 5 pCi/l (Sorg et al. 1980).

Brink et al. (1978) treated a brackish well water for Greenfield, Iowa, with a total solids content of 2200 mg/l in a reverse osmosis unit installed in 1971. Raw, product and reject water samples were collected and analyzed for radium 226. At 69 percent recovery, the radium 226 concentration was reduced from 14 pCi/l in the raw water to 0.6 pCi/l in the product water.

Kosarek (1979a) reported that reverse osmosis membranes have provided product water with less than 5 pCi/l from feedwater levels of radium ranging from 30 to 750 pCi/l. In addition to removal of radium, reverse osmosis reduced alpha radiation 85 to 96 percent and beta radiation 95 to 99 percent.

Carnahan et al. (1979) conducted studies on the removal of iodine 131, strontium 85, and cesium 134 by reverse osmosis. Reverse osmosis was capable of removing the isotopes but not to acceptable levels. Post treatment with carbon adsorption and ion exchange would be required to produce a potable water.

Sorg et al. (1980) studied radium 226 removal by eight reverse osmosis systems in Florida and found removals of 87 to 98 percent from waters containing radium concentrations ranging from 3.2 to 20.5 pCi/l. Sorg and Logsdon (1980) stated reverse osmosis is a good treatment method for most radionuclides and is most advantageous for the treatment of small drinking water supplies containing a mixture of radionuclides that would require the combination of several treatment methods to be effective.

Subramanian and Sastri (1980) conducted laboratory tests on radium 226 removal using cellulose acetate membranes. Feedwater was obtained from leaching uranium mine tailings. Feed radium 226 concentrations were considerably higher than those found in drinking water sources, 390 to 910 pCi/l; however, they concluded that reverse osmosis is one of the best methods available for alleviating radium contamination from a water source.

Huxstep (1981) presented results of pilot plant studies on radium 226 removal by low 1.4 MPa (200 psig) and high 2.8 MPa (400 psig) pressure reverse osmosis systems at the Charlotte Harbor Water Association Treatment Plant. One set of grab samples was analyzed and results showed excellent radium removal of 97.4 percent for the high pressure system and moderate radium removal of 61.7 percent for the low pressure reverse osmosis system.

Summary

While no treatment method is ideal for removing all contaminants, reverse osmosis has been shown to be effective for the removal of most of the contaminants controlled by the NIPDWR. The significant characteristic of the reverse osmosis process is its ability to remove contaminants from water supplies that would otherwise require a combination of treatment methods for their purification.

CHAPTER VIII

REMOVAL OF ORGANICS USING REVERSE OSMOSIS

While reverse osmosis has its primary application to inorganic solute separation from a flow stream, it has a significant advantage over other demineralization systems in that it also effectively rejects many organic contaminants.

Single Component Systems

Sourirajan (1963) presented data indicating the relative effectiveness of reverse osmosis membranes for the separation of selected organic substances from aqueous solutions. Results indicated the following order of organic solute rejection:

n-PrOH > EtOH

Iso-PrOH > PrOH

Iso-BuOH > n-BuOH

Tert-BuOH > sec-BuOH > n-BuOH

Acetaldehyde > ethyl alcohol > acetone > acetic acid

Sourirajan (1964a) stated that for any given membrane material, the degree of separation and rate of permeation varies with the porous structure variation within the film. The chemical nature of the membrane surface was found to determine the direction of separation for a given feed system. Operating pressure was shown to affect the separation and flow characteristics of a cellulose acetate membrane for the system n-heptane-EtOH. The variation of product flow rate and alcohol enrichment indicated that the separation process involved capillary liquid flow through the porous film.

Sourirajan (1965) conducted additional studies of the separation and permeability characteristics of a cellulose acetate membrane for several organic solutes in aqueous solution. The effects of the chemical nature of the solute, solute concentration, and operating pressure and temperature on the performance of the membranes were investigated. Data indicated the following order of membrane rejection:

n-PrOH > EtOH > n-BuOH

Iso-PrOH > n-PrOH

Tert-BuOH > sec-BuOH > iso-BuOH > n-BuOH

Glycerol > ethylene glycol > n-PrOH

Acetaldehyde > EtOH > acetic acid

Propionic acid > acetic acid

NaCL > any of the above organic solutes

The permeability of the cellulose acetate membrane was affected by its contact with aqueous organic solutions. The extent of solute separation decreased, but only slowly, with an increase in the feed concentration, while the corresponding product rate decreased more rapidly. Percent solute removal increased with an increase in the operating pressure in the range from 3.4 to 10.3 MPa (500 to 1500 psig). The extent of solute separation decreased and the product rate increased with an increase in the operating temperature.

Sourirajan and Sirianni (1966) indicated the possible applicability of the membrane separation technique for studying the solution properties of surface active substances and illustrated the use of high flow porous cellulose acetate membranes for the removal of detergents from aqueous solutions by reverse osmosis. Several polyoxyethylated nonionic surface active agents (Tritons) in aqueous solutions were examined. An increase in the feed rate increased both the extent of solute separation and the product rate presumably because of higher turbulence in the cell and less solute concentration buildup at the film surface.

Kimura and Sourirajan (1968) analyzed the reverse osmosis separation data for the system sucrose-water using a number of Loeb-Sourirajan type porous cellulose acetate membranes. The solute transport parameter for sucrose was shown to decrease with an increase in its boundary concentration. A new method of expressing membrane selectivity on a relative scale was given. The predictability of membrane performance for the separation of sucrose in aqueous solution and the effect of membrane compaction on solute separation were also illustrated and discussed. Only the initial specifications of the film, given in terms of the pure water permeability constant and the solute transport parameter for sodium chloride, were required.

Merten et al. (1968) studied organic solute removal by reverse osmosis systems and indicated that significant permeation rates were observed only for some small, usually oxygenated organics. The authors indicated that retention in a homologous series increases with increasing molecular weight. At a constant molecular weight, retention increases with increasing branching. Retention of compounds with molecular weights below 100 could not be relied upon. Low permeation rates were observed for compounds of a molecular weight of 200 or above. Low molecular weight nitriles and amines showed moderate retention similar to oxygenated compounds of similar molecular weight.

Lonsdale et al. (1969) conducted laboratory studies on two low molecular weight organic solutes, urea and dextrose. Dextrose showed rejections of greater than 99 percent, whereas urea was rejected at a rate of less than 45 percent.

Hindin et al. (1969) investigated the removal of organic compounds by reverse osmosis. Certain organic species form colloidal particles, aggregates, milcelles, or macromolecules in an aqueous medium. Examples of such species include detergents such as LAS and ABS, soaps, motor oils, DDT, TDE, proteins, starch, cellulose, humic acids and tannins. The authors observed solute rejections of 80 to 99 percent for those species existing in the colloidal, aggregate, micelle, or macromolecular form. Reductions of 50 to 80 percent were obtained for those species existing as dispersed aggregates or discrete molecules in true solution with vapor pressures greater than that of water. Reductions of 14 to 40 percent were obtained for those molecules more volatile than water such as p-chloro nitro-benzene and low molecular weight esters. While reverse osmosis was shown to be effective in separating some organic materials from aqueous solutions, the authors noted that compounds with significantly higher vapor pressures than water, such as phenol, may appear in significant quantities in the product water.

Kaup (1973) stated that small hydrogen-bonding nonelectrolytes and simple straight-chain organics of four carbons or less that possess hydrogen-bonding abilities pass easily through reverse osmosis membranes. The rejection of organic substances was observed to increase as the molecule became large, sterically complex and/or polyfunctional. Organic acids and amines were shown to be permeable to the membrane in their free state, while they were relatively impermeable when neutralized to salts. Acetic acid passes through cellulose acetate as a free acid but is rejected at 98 to 99 percent as the sodium salt.

Klein et al. (1975) investigated the separation of trace organics from aqueous systems. The retention of a particular solute by a polymer membrane was found to be related to both physical interactions and ionic forces that determine the solubility of the solute in the membrane phase. Ionizable compounds, such as benzoic acid, benzene sulfonic acid, and amines were easily rejected by both cellulose acetate and ethyl cellulose membranes. In the salt form, their rejection was even more pronounced. Rejection of weakly ionized compounds was a function of pH, and the more highly charged the species, the greater was its rejection. Polyacids, phosphoric acids, and other highly charged species including humic and tannic acids showed the expected high rejections. The high rejection of glutaraldehyde when contrasted with the low rejections of glycols, alcohols, and sugars indicated that solubility is indeed a good indicator of solute rejection. In general, aldehydes, ketones, and aromatics are less effectively rejected than ionized or highly hydrogen bonding compounds.

Matsuura et al. (1976a, 1976b) investigated the use of free energy parameters of various carboxylic acids and undissociated aliphatic organic solutes for the prediction of their separation from aqueous solution by reverse osmosis membranes. The authors showed that solute separation in reverse osmosis systems can be predicted for many organic solutes from data on membrane specifications given in terms of a pure water permeability constant and a membrane solute transport parameter for sodium chloride. On the basis of a firm physicochemical criteria approach to reverse osmosis, Matsuura et al. offered a practical technique for predicting solute transport parameters for organic solutes used in conjunction with membranes of different surface porosities.

Chian and Fang (1976) extended the use of physicochemical criteria for the analysis of organic solute separation by reverse osmosis through the use of five membrane materials. The separation of organics was shown to depend both upon the characteristics of the membrane material and the nature of the solute. Within a given solute group, separation was shown to increase with the size, branching and degree of ionization of the solute. The physicochemical criteria and pressure effects on solute separation with cellulose acetate membranes held for other membranes used in the study. This allowed the presentation of generalized guidelines for the choice of appropriate membrane materials for different reverse osmosis applications. For membranes with an appropriate surface structure, the more nonpolar the membrane material is, the better the solute separation will be, especially for low molecular weight polar organic solutes commonly found in water and wastewaters. For high molecular weight and/or less polar organics, the choice of a favorable engineering system becomes more important than that of the membrane material. For separating dissociable compounds, improving the separation can be made by increasing the degree of ionization with proper pH adjustment.

Matsuura et al. (1977) stated that free energy parameters and the hydrophobic nature of a solute governed the separation of one to nine carbon alcohols in dilute aqueous solutions using porous cellulose acetate membranes. The separation of many alcohol solutes could be predicted based on membrane specification of pure water permeability and the solute transport parameter for sodium chloride. The authors concluded that the prediction technique could be extended to a wide variety of organic solutes whose separation by reverse osmosis was governed by polar, steric, and/or nonpolar effects.

Johnston and Lim (1978) studied the effectiveness of reverse osmosis in removing specific toxic organic substances using cellulose acetate membranes rated at 70 and 90 percent NaCl rejection. Complex cyanides and nitrilotriacetic acid were almost completely removed by both membranes with the $NaCl_{70}$ membrane achieving twice the permeation flux of the $NaCl_{90}$ membrane. The rejection of sodium cyanide was significantly less than for the complex potassium tetracyanonickelate II, with the $NaCl_{90}$ membrane removing 15 percent more sodium cyanide than the $NaCl_{70}$ membrane at approximately half the permeation flux.

Johnston and Lim (1978) investigated the rejection efficiency of phenol and substituted phenols using cellulose acetate membranes and found essentially no separation for phenol and p-chlorophenol. Sixty percent rejection was observed for napthol, while p-cresol exhibited negative separation.

Kurokawa et al. (1979) applied solution theory to the prediction of reverse osmosis rejection of organic solutes from aqueous solution assuming that the rejection is primarily determined by the distribution of solute between the membrane and the aqueous solution. The authors concluded that solution theory could serve as a basis for predicting solute rejection by reverse osmosis if membrane parameters were reasonably estimated.

Hsieh et al. (1979) studied the reverse osmosis separation of polyethylene glycol (PEG) solutes in aqueous solutions in the concentration range of 50 to 5000 mg/l of solute using porous cellulose acetate membranes in the operating pressure range from 172 to 690 KPa (25 to 100 psig). Necessary physiochemical data were generated and practical techniques were developed for predicting membrane performance in terms of solute separation and product rates for the separation of PEG solutes in aqueous solutions from a single set of experimental data for a reference feed system of PEG.

Multicomponent Systems

Ironside and Sourirajan (1967) reported on reverse osmosis separation techniques for water pollution control using porous cellulose acetate membranes. Feedwater containing 370 and 512 mg/l, respectively, of the anionic surface active agents sodium dioctyl sulphosuccinate and sodium alkyl-benzene sulphonate were reduced to less than 0.5 mg/l and 0.6 mg/l, respectively, at product water rates of 0.98 m^3/m^2/day (24 gpd/ft^2). Feedwater containing a 10.4 percent acidic brown lignin solution had the lignin content reduced to 0.035 percent at a product water rate of 0.66 m^3/m^2/day (6.2 gpd/ft^2). The operating pressure was 6.89 MPa (1000 psig) for both tests. Ironside and Sourirajan showed that reverse osmosis could separate water polluting ingredients from the feed solutions yielding product waters of acceptable quality at significant production rates.

Hinden et al. (1969) investigated the permeation of chemical species in a multiple component aqueous solution and found evidence that suggested that organic solute transport through cellulose acetate membranes was a function of solute vapor pressure. The rejection of methyl formate was markedly greater in a solution of three other low molecular weight esters than when it was in a solution by itself. Rejection of 2,4-D isopropyl ester and chlorophenol was found to be decreased in a mixture of phenol, p-chloro nitrobenzene and ethyl acetate indicating that synergistic effects assisted these nonvolatile species in permeating the membrane. Amino acids and monocarboxylates did not react as other organic molecules did indicating that some mechanism, other than that based upon solute vapor pressure, also effects solute transport through cellulose acetate membranes.

Kopecek and Sourirajan (1970) reported that reverse osmosis is applicable for the separation of binary mixtures of alcohols and/or hydrocarbons, including azeotropic and isomeric mixtures. No simple generalizations were possible regarding the direction of separation, however, due to the complex nature of preferential sorption in reverse osmosis. Hydrocarbons tended to collapse the porous structure of the cellulose acetate membranes and Kopecek and Sourirajan stated that some other type of membranes have to be utilized for feed mixtures containing hydrocarbons.

Sourirajan and Matsuura (1971) conducted reverse osmosis experiments for glucose-water, maltose-water, lactose-water, ethylene glycol-water, propylene glycol-water, and ethylene glycol-propylene glycol-water systems. Their results showed that the prediction technique developed for aqueous solution systems containing mixed inorganic solutes with a common ion was applicable for systems containing nonionic mixed organic solutes.

Nomura et al. (1978) investigated reverse osmosis of some aromatic compounds in a 1-propanol solution using porous cellulose acetate membranes along with some factors which influence organic solute permeability. Data for a number of benzene derivatives showed that only phenol was rejected while others were enriched. Solute permeabilities for compounds with various substituent groups had the following order: $-OH < -CH_3 < -H < -Cl < -NH_2 < -NO_2$. For the benzene, naphthalene, and anthracene series, the permeability was related to the molar volume of solutes and varied as follows: benzene > napthalene and anthracene. Two factors governed the permeation behavior through the membrane, namely a partition coefficient and a diffusion coefficient. When the steric effect was absent, the partition coefficient was a dominant factor in solute permeation. The partition coefficients were closely related to the dipole moment of solutes and the authors concluded that their results could provide a method of prediction for the reverse osmosis separation of organic compounds on the basis of liquid chromatographic analysis.

Chlorinated Organics/Pesticides

Lonsdale et al. (1969) conducted laboratory studies on the rejection of chlorinated hydrocarbons representative of various pesticides and herbicides using cellulose acetate membranes. The compound 2,4-dichlorophenoxyacetic acid showed rejections of greater than 93 percent, while the rejection of 2,4-dichlorophenol was negative as was observed with phenol. The 34 percent negative rejection of the dichlorophenol exceeded that observed with phenol, approximately 20 percent, and may indicate that flow coupling between phenol and water is increased by the presence of chlorine atoms. The authors stated that most phenolic compounds will not be highly rejected and they observed a large reduction in product water flux with feed phenolic compound concentrations as low as 5×10^{-4} M. Rejection data of p-dichlorobenzene indicated that chlorinated hydrocarbons in general would be expected to be poorly rejected. Cellulose acetate membranes would therefore not remove many chlorinated organic pesticides and herbicides from natural waters.

Edwards and Schubert (1974) presented an excellent literature review of refractory organic removal by carbon adsorption and reverse osmosis and determined the selectivity of a number of cellulose acetate membranes for aqueous solutions of several 2,4-dichlorophenoxyacetic acid salts. Rejection of these salts was observed to decrease rapidly with time and the authors concluded that reversible sorption of the solute by the membranes was occurring in their study.

Chian et al. (1975) evaluated cellulose acetate and cross-linked polyethylenimine membranes for the removal of a wide variety of pesticides including chlorinated hydrocarbons, organophosphates, and miscellaneous pesticides. From a material balance, it was determined that appreciable amounts of these pesticides were adsorped onto the polymeric membrane materials. The chlorinated hydrocarbons showed the highest adsorption potential with the exception of lindane, followed by trifuluralin and captan in the miscellaneous group along with all the organophosphates. Randox and atrazine showed the poorest adsorption. It was found that the more nonpolar a membrane was, the greater was the removal of the pesticides analyzed. Removal of pesticides in natural waters was expected to be even greater than that observed in the lab due to complexes formed between the persistent pesticides and humic and fulvic acids. While greater than 99.5 percent removals were obtained for the nonpolar pesticides by the polyethylenimine membrane, such as the organophosphates and the chlorinated hydrocarbons, removal of more polar pesticides was less satisfactory. The authors concluded that pesticide removal from aqueous solutions can be explained partially by the polar effect of the solute and partially by the adsorption of the pesticide onto the membrane materials. The extent of adsorption was shown to be governed by van der Waals-London forces and by hydrophobic bonding between pesticide molecules and the polymeric membrane materials.

Seevers and Deinzer (1976) investigated the characteristics of cross-linked polyethyleneimine-toluene-2,4-diisocyanate membranes with regard to adsorption, desorption and permeation of the pesticide methoxychlor during osmotic pumping using water and ethanol as cosolvents. The rejections for ethanol and methoxychlor were determined to be 35 and 99.5 percent, respectively. Ethanol was significant in the adsorption-desorption kinetics for methoxychlor. A mechanism was proposed which indicated that when a molecule of methoxychlor adsorbs to the membrane, two ethanol molecules are released, one from the membrane and one from the solvation sheath surrounding each methoxychlor molecule. Rate constants for the methoxychlor adsorption and desorption were determined and the equilibrium constant was calculated. An expression for the adsorption isotherm relating the quantity of adsorbed methoxychlor to its concentration in solution and to the concentration of ethanol in solution was obtained and the membrane adsorption density at saturation was found.

Johnston and Lim (1978) investigated the use of cellulose acetate membranes in removing toxic organic substances. Their study included chlorinated hydrocarbon and organophosphate pesticides. All pesticides analyzed were completely removed by the membranes with the exception of malathion which was rejected at 79.0 and 93.5 percent by the $NaCl_{70}$ and $NaCl_{90}$ membranes, respectively. The high removal efficiencies were presumably due to adsorption as the solute concentrations in the concentrate were consistently lower than that of the feed while little or no solute was detected in the permeate. The reappearance of chemicals as contamination in later experiments indicated that previously adsorbed molecules were dissolving and travelling with the permeate through the membrane. Adsorption appeared to take place on top of a membrane with the adsorbed molecules migrating through the membrane and being eluted in the permeate as the membrane became saturated with the chemical. The separation of the chemicals declined over time and it was concluded that reverse osmosis was an impractical process for removing these strongly sorbed substances from water. It was suggested that the polymeric membrane material could be better employed as an adsorbent than as a physical membrane separation technique for these chemicals.

Malaiyandi and Blais (1980) investigated the separation characteristics of cellulose acetate membranes for trace levels of lindane in water. Lindane was poorly separated by the cellulose acetate membranes. It was found that once exposed to this contaminant, reverse osmosis membranes of the cellulose acetate type remained contaminated and slowly released the pollutant to the product water long after the contaminated feed source had been removed. Such an event in clinical or potable water treatment plants using reverse osmosis units would, in effect, contaminate the quality of the product water for a prolonged period. Malaiyandi and Blais stated that this form of membrane impairment, which is not usually tested for during routine maintenance of reverse osmosis plants, should be guarded against.

Drinking Water Treatment

Deinzer et al. (1975) investigated the concentration of organic compounds in Cincinnati, Ohio, drinking water using cellulose acetate membranes. The reverse osmosis concentrates showed the presence of hydrocarbons, alkyl phthalates, a tetrachlorobiphenyl isomer, 2,4,6-trichlorophenol, 1,1,3,3-tetrachloro-acetone, phthalic anhydride, and barbital. Certain classes of compounds, such as the aromatics, were found to be adsorbed to cellulose acetate membranes rather than being rejected, yet the authors concluded that reverse osmosis was useful for the concentration of trace organic contaminants in large volumes of drinking water.

Cabasso et al. (1975) examined and tested the use of membrane materials for the separation of trace organic solutes from drinking water to facilitate toxicological sample preparation. Cellulose acetate, cellulose acetate butyrate, ethyl cellulose, polyamide, and polyurea NS-1 membranes were evaluated. The mechanism by which a membrane rejected the passage of certain solutes while permitting water transport was not resolved. However, the ability of a solute to form hydrogen bonds correlated with its apparent formation of bonds with the membranes.

Dissociated solutes, polyhydric alcohols, and paraffins experienced greater rejections by cellulose acetate membranes than did undissociated phenols and organics capable of ionizing. Rejection of organics generally increased with the degree of branching and with the number of carbon atoms for compounds within the same functional group. However, there were exceptions caused by other unknown factors being involved in the permeability mechanism.

The NS-1 polyurea membrane showed much higher rejections for organics than did the cellulose acetate membrane. The ability of a solute to permeate this type of membrane structure was a reflection of its ability to penetrate the cross linked surface. The nature of the functional group was less important in rejection by the polyurea membrane than by the cellulose acetate membrane. Polyurea membrane rejection was shown to be related to a large extent to system operating pressure. Polyurea was found to be effective over a wide range of pH, however, the sensitivity of the membrane to chlorine was its major limitation.

Polyamide membranes showed rejections similar to the polyurea membrane but were also sensitive to chlorine. A two unit series of cellulose acetate and polyamide membranes was proposed that would remove high molecular weight products and salts in the first cellulose acetate stage and low molecular weight solutes in the second polyamide stage.

Cabasso et al. (1975) concluded that reverse osmosis is feasible for concentrating and recovering organic solutes from water with the degree of recovery varying with the solute-membrane combination. While a membrane's rejection of salts might indicate mechanical integrity, the authors found it did not indicate the membrane's true potential for concentrating organics. The applied pressure was found to influence solute recovery and might be crucial in the concentration of low molecular weight organics. The highly cross-linked surface structure of the polyurea limited molecular penetration by the solute, while for the cellulose acetate membrane, chemical interaction was the dominant factor of retention behavior. Cellulose acetate membranes showed the least overall rejection of organics but were chlorine resistant and showed excellent salt rejection and water permeability. They served as a satisfactory first separation membrane for the polyurea and polyamide membranes which showed good rejection characteristics toward a wide variety of solutes.

Carnahan et al. (1979) tested a 600 gph reverse osmosis unit designed to meet the United States Army's requirements for producing water in a combat environment. Three chemical contaminants, agents GB, VX and BZ, were tested in feed solutions to the reverse osmosis unit. The agents GB and VX are organophosphate compounds similar to malathion and parathion. GB was the most difficult agent to remove by reverse osmosis due to its low molecular weight. A polyamide membrane was shown to perform better than a cellulose acetate membrane, however, neither membrane produced an acceptable product water. The authors indicated that reverse osmosis could remove chemical contaminants from water but post treatment with carbon adsorption was required to produce a potable water.

McCarty (1980) found the removal of trace organics at Water Factory 21 by reverse osmosis to be relatively ineffective for the trace organics evaluated. He concluded that reverse osmosis is effective when high molecular weight or humic materials comprise the major portion of the TOC or COD. However, since reverse osmosis is expensive, other membrane systems specifically designed for removal of high molecular weight materials were thought to be more attractive.

Coleman et al. (1980) concentrated the organics in 1.5 m^3 (400 gallons) of Cincinnati, Ohio, drinking water by reverse osmosis. Analysis of the concentrate identified polychlorinated biphenyls (PCBs), chlorinated aromatics, and many polynuclear aromatics (PNA). Altogether, approximately 460 compounds were identified, including 41 PNAs, 15 PCBs, and a number of amines, amides and other halogenated species.

Wastewater Treatment

Sourirajan (1965) investigated the applicability of cellulose acetate membranes for the concentration of a propionic acid/water mixture, a natural maple sap, and two industrial lignin wastes. Solute separation ranged from 100 percent for the maple sap to 65 percent for the propionic acid/water mixture. Sourirajan concluded that reverse osmosis was applicable for the separation of a wide variety of industrial solutes in aqueous or non-aqueous solutions.

Merten et al. (1968) investigated organic solute separation from a number of food processing wastes. Citrus juice residues, which are largely hydrocarbon in nature, were much better retained than were the aromatic components of apple juice which are largely esters, alcohols, and aldehydes. Protein retention of 98 to 99 percent in fish processing wastes, sugar retention of 99.9 percent in maple sap residue, and BOD and COD retentions of 90 to 99 percent were also recorded.

Hauck and Sourirajan (1969) presented performance data for CA-NRC-18 type porous cellulose acetate membranes used for the treatment of secondary effluent. Average BOD removals of 85.8 and 80.8 percent at 6.9 and 3.45 MPa (1000 and 500 psig), respectively, and 90 percent recovery were recorded for raw water feed BOD concentrations from 21 to 46 mg/l. Average ABS removals of 93 percent were recorded for average product rates of 1.33 and 0.746 $m^3/m^2/$day (32.7 and 18.3 gpd/ft^2) at 6.9 and 3.45 MPa (1000 and 500 psig) for raw water feed ABS concentrations from 0.4 to 2.0 mg/l. Hauck and Sourirajan concluded that reverse osmosis had the potential of becoming an economic means of wastewater renovation.

The permeation of a number of organic compounds found in sewage effluents was investigated by Hindin et al. (1969) and a comparison of the percent reductions of specific species in sewage effluent, aqueous multicomponent systems, and singly in solution was made. Percent reductions for each species in the sewage effluent, with the exception of ethyl acetate, was the same or greater than that obtained in either multi- or single component systems. It was believed that if permeation data were known for a species singly in solution, a close approximation of the percent reduction of a specific species in sewage could be estimated.

Boen and Johannsen (1974) conducted a pilot study to determine the feasibility of applying reverse osmosis to untreated and treated secondary effluents. While they acknowledged that organics can be a significant factor in membrane fouling, the DuPont Polyamide, Gulf Spiral cellulose acetate, and Universal cellulose acetate reverse osmosis systems they used succeeded in producing average total COD reductions of 90, 88, and 93 percent, respectively, for feedwater total COD concentrations ranging from 6 to 60 mg/l. For soluble COD, the three systems yielded average COD reductions of 90, 92, and 96 percent for influent COD concentrations ranging from 6 to 60 mg/l.

Reinhard et al. (1979) investigated the removal of trace organics by advanced waste treatment. A pilot reverse osmosis plant using spiral wound membrane elements was used to treat activated-carbon and mixed-media filter effluent. No significant removal of volatile compounds was observed through the reverse osmosis process. The reverse osmosis unit was effective in overall COD removal indicating that while the more volatile and low molecular weight substance permeated the membranes, many organics were rejected by the reverse osmosis system.

Summary

While reverse osmosis possesses a major advantage over many other membrane processes in its ability to reject organic contaminants, the nature and extent of this organic solute rejection is, as with inorganic solute rejection, completely dependent upon the nature of the organic material being considered. The application of reverse osmosis to organic contaminant removal was reviewed by Nusbaum and Riedinger (1980) and their comments are summarized as follows:

1. Low molecular weight, nonpolar, water soluble organic species tend to pass through reverse osmosis membranes.

2. Rejection of low molecular weight organic acids and amines followed the same pattern as inorganic acids and bases, i.e., undissociated species are poorly rejected while the salts are readily rejected.

3. Phenols, chlorinated hydrocarbons, pesticides and low molecular weight alcohols are poorly rejected or permeate slowly through reverse osmosis membranes.

4. The highly rejected organic species include:

a. Large complex organic molecules which cause color or interfere with coagulation and filtration.

b. Chlorination-interfering nitrogen-containing molecules.

c. Lignins, humic acids, fulvic acids, detergents, and many other organics occurring in wastewater discharges.

The application of the reverse osmosis process for organic removal is extremely flow stream specific, however, it can prove to be an effective water treatment or wastewater renovation process under the proper circumstances.

CHAPTER IX

REMOVAL OF MICROORGANISMS

The removal of microorganisms from drinking water is essential in disrupting the cycle of waterborne diseases in a population. Chlorination is the primary control measure in the United States for microbial contamination of drinking water. Because of the costs associated with disinfection and the possible production of harmful halogenated organic compounds, methods are being developed to reduce the raw water chlorine demand and the potential for halogenated organic formation through pretreatment. Reverse osmosis is one of these pretreatment options.

Bacteria

Originally, reverse osmosis was hoped to be a potential disinfection process that could compete with chlorination. It was found early (Otten and Brown 1973) however, that reverse osmosis could not be relied upon for the complete retention of bacteria. Otten and Brown concluded that either pretreatment or post treatment would be necessary to prevent bacterial contamination of the distribution system from the reverse osmosis unit.

Ford and Pressman (1974) evaluated a prototype reverse osmosis unit for coliform and virus removal. The prototype unit was preceded by cationic polyelectrolyte addition and prefiltration and was followed by hypochlorination. The unit successfully reduced the level of both coliforms and an f_2 virus to undetectable limits.

Hinterberger et al. (1974) investigated the capability of reverse osmosis to remove bacteria from water and found that bacteria with physical dimensions greater than viruses penetrated the reverse osmosis membranes. This passage of bacteria was attributed to tiny holes in the membrane surfaces due to manufacturing defects and to other imperfections in the cross linkages of the cellulose acetate. The authors also pointed out that full scale plants with large membrane areas would be expected to produce treated water of a higher microbial count than small pilot scale units due to the greater probability of membrane imperfections in the larger units. The presence of membrane defect holes was confirmed by Melzer and Myers in 1971, when they showed pore diameters in some membranes 200 times greater than the average pore opening.

Deinzer et al. (1978) reported that it is possible to disinfect wastewater by reverse osmosis if membranes with a pore size smaller than viruses are used. They pointed out, however, that capital costs, membrane replacement costs, and pumping costs make reverse osmosis far more expensive than chlorination for wastewater disinfection. Additionally, for drinking water disinfection, reverse osmosis alone is not suitable because it produces no residual effect for distribution system protection.

Cooper and Straube (1979) investigated microorganism removal from sewage by reverse osmosis. Both coliform and seeded animal virus removal through the reverse osmosis unit was significant, greater than 99.99 percent; however, results of the investigation indicated that some form of disinfection would be required if the product water was to be used for domestic purposes.

Nusbaum and Riedinger (1980) stated that complete rejection of bacteria, fungi, and viruses by reverse osmosis depends on having a membrane free of all imperfections and that the probability of having such a membrane is very low. They indicated that while organisms may penetrate the membrane, colonize and proliferate, continuous or intermittent disinfection relieves this problem.

Viruses

Compared with other water and wastewater treatment processes, virus removal by membranes processes has not been extensively investigated. Most of the early work with virus removal using reverse osmosis has dealt with concentrating and purifying viral stocks (Chian and Sellerdorf 1969 and Wang et al. 1969). Some membrane manufacturers claim that no viruses should appear in the product water, citing virus size and membrane transport theories as reasons for viral rejection.

Hinden et al. (1968) collected a small volume of product water from a reverse osmosis unit treating a feedwater inoculated with coliphages T7 and X175. Without concentrating the viruses in the product water, an attempt was made to isolate them by directly plating samples of the product water onto EMB auger previously inoculated with E. coli. This product water was found to be free of viruses.

Sorber (1971) inoculated various concentrations of coliphage T2 and poliovirus in the feedwater of a bench scale reverse osmosis unit and evaluated the rejection of these viruses by commonly used commercial grade asymmetrical cellulose acetate membranes. Limited numbers of virus pentrated the membranes. The virus penetration was attributed to random areas of imperfect cross linkages of the cellulose acetate in the dense layer of the membrane. All of the cellulose acetate membranes used rejected high percentages of viruses and produced a product water of excellent quality except in two experiments where mechanical failure of the membranes was observed.

The prototype reverse osmosis unit utilized by Ford and Pressman (1974) that incorporated cationic polyelectrolyte addition and prefiltration followed by hypochlorination was shown to reduce f_2 virus to undetectable limits. Dual media pressure filtration following polyelectrolyte addition when used as a pretreatment step for the reverse osmosis unit yielded 99.99 percent f_2 virus removal from a natural feedwater. When viruses were added to feed water without prefiltration, virus penetration resulted in reverse osmosis removal of 97.3 percent from a feedwater containing 10^6 virus units. Virus removal through prefiltration ranged from 91 to 99.99 percent using polymer addition, while practically no virus removal was attained without the polymer.

Summary

Because of inherent imperfections in reverse osmosis membranes produced during their manufacture, the complete rejection of microorganisms is not considered feasible. Pretreatment processes used in conjunction with reverse osmosis have, however, been shown to be highly effective in removing microbial contaminants from both water and wastewater streams.

Many of the organic and inorganic compounds that interfere with disinfection and increase the chlorine demand of a water are removed in the reverse osmosis process. This reduces the chlorine dosage required for effective disinfection and is of significant economic importance, especially in water treatment applications in which a chlorine residual is required for protection of the distribution system.

CHAPTER X

PERFORMANCE EVALUATION OF REVERSE OSMOSIS INSTALLATIONS

To review and evaluate the design, operation, and maintenance of commercial reverse osmosis installations and to identify problem areas in those installations, questionnaires were sent to 117 reverse osmosis installations in the United States and 11 other countries (Appendix D). Replies were received from 28 of the installations contacted, 24 percent, of which 5 were no longer in operation. Plant closings were the result of a number of items ranging from the utility's acquisition of improved raw water to the inability of the utility to afford the high cost of replacement membranes. While financial considerations were important in a number of plant closings, operator opinions were received that suggested that better plant design and operation could have extended plant life and reduced product water costs.

Water Sources and Treatment Objectives

By far the greatest source of feedwater for the reverse osmosis installations replying to the survey was groundwater, 88 percent. Since Utah has not accepted reverse osmosis for surface water treatment (Scanlon 1980), groundwater would also be expected to be the predominant feedwater source for reverse osmosis installations in the state.

The major use of reverse osmosis product water cited was drinking water, (76 percent), while boiler feedwater (10 percent), and cooling water (3 percent) were also specified treatment objectives. Groundwater injection for seawater intrusion protection, and deionized water for medical use were also specified for product water use.

Pretreatment

Ninety-five percent of the plants reporting the use of pretreatment employed some type of chemical addition. To control calcium carbonate scale, sulfuric acid was used at 95 percent of the sites and hydrochloric acid was used at 5 percent. To prevent calcium sulfate scaling, a threshold scale inhibitor was used at 75 percent of the installations. This scale inhibitor was sodium hexametaphosphate at 93 percent and sodium zeolite at 7 percent of the plants.

Particulate removal by coagulation, flocculation, and sedimentation was carried out by 25 percent of the installations prior to reverse osmosis treatment. Mechanical filtration, excluding cartridge filters, was used at 50 percent of the plants. Green sand filters for iron and manganese removal were used at 20 percent of the plants, while dual media filters were used at the remaining facilities. Chlorination as a pretreatment step was performed at 20 percent of the plants.

Filter problems were not uncommon. Tar and other substances coagulating in manganese green sand filters were mentioned at one plant, and the problem was corrected by thorough and frequent backwashes. One site reported that a low silt density index was difficult to attain until a Culligan multi media filter was installed. At one site, the micron cartridge filters became plugged with sand and weekly filter cleaning was necessary. When a silt density index test was run, the index was high and the membranes no longer qualified for warranty.

System Operation

Cellulose acetate membranes were used at 71 percent of the plants while 29 percent used polyamide membranes. Hollow fiber and spiral wound modules of one to three sections per module were equally divided among the plants responding to the survey.

The system operating time reported by the various plants was application specific with plants operating from 2 to 24 hours per day, 2 to 7 days a week and all but two plants operating 52 weeks per year.

The product recovery rate reported from the plants ranged from 30 to 83 percent and averaged 57 ±8 percent. Solute rejection efficiency averaged 86 ±17 percent, ranging from 17 to 99 percent.

Because product recovery is not 100 percent efficient, a large quantity of concentrated brine may have to be disposed. Methods of brine disposal were found to vary with geographical location. Total containment ponds were used most frequently, 42 percent, followed by tidal canals, 17 percent, and ocean disposal, 13 percent. Disposal into tidal canals entailed combining the reject stream from the reverse osmosis system with surface runoff and discharging this mixture into a navigable waterway. In the United States, a permit issued by EPA is required for this disposal method. Other brine disposal schemes included injection wells; its use in an energy recovery turbine; disposal in a salt barrens, a percolation pond, and a sewage lagoon; mixing it with the outfall of a sewage treatment plant; and its discharge into a sewer system.

Membrane cleaning was carried out at the plants surveyed using citric acid for inorganics (53 percent) and using BIZ for organic foulants (27 percent). Membrane cleaning procedures were carried out on fixed schedules ranging from every 3 weeks to every 2 years, or on schedules based upon the occurrences of membrane fouling.

Alarm and automatic shutdown procedures for membrane fouling and membrane or system failure occurrences were utilized in 90 percent of the plants surveyed. High-low pressure, pH, and electrical conductivity sensing devices were most commonly used by the plants in their alarm systems. Other sensing devices used in the alarms were for feed levels to ensure a water supply to the reverse osmosis unit and for storage levels to ensure unit shutdown when storage capacity was reached.

Only one plant responding to the questionnaire, the Yuma test facility, did not posttreat their product water. Disinfection was practiced at 90 percent of the facilities using chlorine (93 percent) and iodine (7 percent). Degasification was practiced at all plants for the removal of dissolved carbon dioxide and hydrogen sulfide and for pH adjustment.

Operators

Training and maintenance experience of the operators at the reverse osmosis installations responding to the survey are summarized in Tables 11 and 12. At five sites, maintenance was performed by outside personnel, either by service contract, by the government, or by outside sections of the utility operation and maintenance department.

To improve operator and maintenance training, a training program or school specifically for reverse osmosis operation was recommended by each plant reporting. Additional recommendations were that manufacturers should offer short courses to teach reverse osmosis

Table 11. A summary of operator training and experience.

	Number
Prior experience in RO	3 (12 percent)
Prior experience in water and/or wastewater	12 (48 percent)
On the job training	10 (40 percent)

Table 12. A summary of operator maintenance training and experience.

	Number
Prior experience	6 (40 percent)
No prior training or experience	3 (20 percent)
On the job training	6 (40 percent)

systems operation, instrumentation, mechanics, cleaning and maintenance; that reverse osmosis should be included in state certification and operator training; and that training should be included in the overall cost of plant design and in the annual municipal budget.

Operating Problems and Recommendations

Membrane fouling and subsequent product water flux declines were the most common operating problems identified. Long filter backwash cycles and regular membrane flushing were recommended for improving performance. Substantial pretreatment was suggested especially for surface feedwaters to prevent rapid membrane fouling. A silt density index of less than 3 was identified as a desirable maximum allowable pretreatment product water quality parameter to ensure adequate operating cycles. Flushing with a formaldehyde solution was also recommended to prevent bacterial growth on membranes when a plant is to be down for over 24 hours.

The inadequacy of operating personnel was identified as a major potential cause of operating problems and a number of suggestions were presented to correct this problem. Periodic evaluations of operator instructions were suggested and the need for daily supervision was stressed. While manufacturers adequately lecture on a system's automatic capabilities, the human operator oriented instructions reportedly are severely lacking. Adequate training is required for successful system operation and it was suggested that plant start up by qualified, field-experienced individuals is essential if adequate plant performance is to be expected.

Recommendations For Future Reverse Osmosis Installations

Because of the potentially severe impact of raw water quality on membrane fouling and process performance, the importance of a complete and thorough investigation of the raw water source was stressed by a number of respondents. An adequate pretreatment train was emphasized along with cleaning connections on all units even those that were expected to require only infrequent cleaning. The proper development and construction of wells was also felt to be important as system failures due to well casing corrosion and subsequent membrane fouling were identified.

Effective process monitoring was felt to be limited by inadequate reverse osmosis plant design. It was suggested that more sampling points, meters, pressure gages, and alarms be installed in reverse osmosis systems to allow individual membrane module performance monitoring. This added information would aid in the detection of faulty O rings, faulty membrane modules, or insufficient pretreatment processes that result in progressive membrane fouling.

CHAPTER XI

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Summary and Conclusions

Reverse osmosis membranes represent a significant portion of the capital cost of reverse osmosis systems. Because of this, a great deal of research and system development has been devoted to membrane performance optimization. Cellulose acetate membranes were the first to be developed and although they are stable to low pH conditions and resistant to chlorine oxidation, the cellulose acetate membranes are susceptible to bacterial attack and high pH conditions. Polyamide membranes, synthetic organic nitrogen-linked aromatic condensation polymers, operate at higher temperatures than cellulose acetate membranes and are resistant to bacterial attack and high pH conditions but are unstable in low pH waters and are extremely sensitive to chlorine oxidation. Composite membranes, produced by forming a thin surface layer over a porous support substructure, have been developed in an effort to optimize the formation of the separate layers to produce membranes with superior overall performance. These composite membranes remain highly susceptible to chlorine oxidation, however. No single membrane is the best for all applications and research is ongoing to develop an ideal membrane with chemical and biological stability and improved process performance.

Four membrane module configurations have been developed: the plate and frame, the tubular, the spiral wound, and the hollow fiber modules. All configurations except the plate and frame design are being used in water and/or wastewater treatment applications at present. The choice of a particular membrane module configuration for a particular application will be a function of raw water quality, pretreatment requirements and costs, module costs, and the economics of the overall system required.

Membrane fouling is a major cause of reverse osmosis system failure and an effective pretreatment program is essential. Pretreatment may include filtration, coagulation, flocculation, sedimentation, pH control, aeration, ion exchange, softening, disinfection, dechlorination, or a combination of the above to insure proper process performance. Routine membrane cleaning and system maintenance is a good investment as these practices will be effective in reducing the occurrence and extent of membrane fouling.

The major purpose of reverse osmosis systems is for the rejection of inorganic solutes from aqueous solutions. Inorganic solute rejection is a function of ionic charge and hydrated radius and decreases in the order of trivalent, divalent, and monovalent ions. Co-ions have been shown to affect the rejection of particular ions due to ion pair formation and undissociated or slightly dissociated compounds are poorly rejected.

Reverse osmosis membranes possess the ability to reject a number of organic solutes in addition to inorganic solutes as described above. Large complex organic molecules, some nitrogen containing molecules, lignins, humic and fulvic acids, and detergents are among the organic species highly rejected by reverse osmosis membranes. Low molecular weight, nonpolar, water soluble compounds tend to pass through reverse osmosis membranes; however, as with inorganic solutes, while the undissociated forms are poorly rejected, these species in the salt form are readily rejected. Phenols, chlorinated hydrocarbons, pesticides, and low molecular weight alcohols have been found to be poorly rejected or to permeate slowly through reverse osmosis membranes, and the possibility of adsorbed organics being released into the product water should not be overlooked.

The production of reverse osmosis membranes is not 100 percent error free, subsequently, the complete retention of viruses, bacteria, and other larger microorganisms is not considered possible. The major advantage of the reverse osmosis process from the standpoint of microbial contaminant removal is in its ability to reject organic and inorganic compounds that interfere with disinfection.

The survey of full scale reverse osmosis installations revealed that inadequate raw water source investigation and subsequent inadequate pretreatment systems, along with inadequate personnel training led to the bulk of process failures and occurrences of membrane fouling.

From an extensive literature review and analysis of the full scale reverse osmosis plant survey, the following conclusions can be made:

1. Reverse osmosis is most applicable to water supplies with several contaminants that would otherwise require a combination of treatment methods for their removal. Reverse osmosis is particularly useful for water supplies containing high TDS and one or more other contaminants.

2. Feedwater composition variability, temperature, and source must be thoroughly known prior to the design of a reverse osmosis system.

3. Pretreatment should be designed for the worst possible case and should include colloidal removal processes such as coagulation and filtration to inhibit membrane fouling.

4. Regular filter backwashing, routine membrane cleaning, and equipment maintenance is required to ensure adequate process performance.

5. Disinfection following reverse osmosis treatment is required if product water is to be used for domestic purposes.

6. Dissolved gases will permeate reverse osmosis membranes and posttreatment degasification systems will be required for carbon dioxide and hydrogen sulfide removal.

7. To prevent microbial membrane enrichment and membrane fouling and deterioration, reverse osmosis systems should be flushed with product water during emergency shutdowns and should be sterilized during extended shutdowns.

8. Operator training for reverse osmosis system operation and maintenance should be improved.

Recommendations

Future designs of reverse osmosis systems should be made with the following items being considered:

1. Raw feedwater sources should be comprehensively surveyed and the best water quality source should be developed to reduce the requirements and costs of pretreatment and to limit membrane fouling.

2. Hydrogeologic investigations should assess the potential intrusion of undesirable water into raw water well fields.

3. PVC, ABS, fiberglass or stainless steel casing should be used in the construction of wells to minimize the potential of membrane fouling from corrosion products.

4. Feed and product water monitoring along with pretreatment process performance monitoring should be included in normal operating procedures to detect and remedy membrane fouling or deterioration that may occur.

5. Pressure gages, flow meters for the permeate and concentrate, and sampling taps for the permeate and concentrate should be standard equipment to allow effective membrane performance monitoring.

6. Alarms and automatic shutdown provisions should be provided for membrane protection using high/low pressure, pH, and EC sensing devices.

7. Operators should be trained in proper reverse osmosis operating procedures and defined maintenance schedules should be established.

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APPENDICES

Appendix A
Chemical Cleaning Reagents for Reverse Osmosis Membranes

Table A1. Chemical cleaning reagents (DuPont 1977b).

Chemicals	Foulants						
	$CaCO_3$	$CaSO_4$ $BaSO_4$ $SrSO_4$ CaF_2	SiO_2	Metal Oxides	Inorganic Colloids	Biological Matter	Organics
Hydrochloric Acid[a] (HCl)(pH 4.0)	X				X		
2.0 wt. % Citric Acid + NH_4OH (pH 4.0)	X			X	X		
5 wt. % Nutek NT-600	X						
2 wt. % Citric Acid + NH_4OH (pH 8)		X					
1.5 wt. % Na_2EDTA[c] + NaOH (pH 7-8) or 1.5 wt. % Na_4EDTA + HCl (pH 7-8)		X					
1.0 wt. % Na Hydrosulfite ($Na_2S_2O_4$)		X		X			
NaOH (pH 11.0)[b]			X		X		X
2.0 wt. % Citric Acid + 2.0 wt. % Na_2EDTA + NH_4OH (pH 4.0)	X			X			
0.5 wt. % "Biz"[d] + NaOH (pH 11.0)			X		X		X
1 wt. % Drewsperse 738					X		
1 wt. % NaHMP				X	X		X
1/4 wt. % Formaldehyde followed by 0.25 wt. % "Biz" (with phosphate)						X	

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[a] A lower pH may be more effective. Consult the RO system manufacturer for assistance.

[b] A higher pH may be more effective. Consult the RO system manufactuer for assistance.

[c] EDTA is ethylenediaminetetracetic acid.

[d] "Biz" (with phosphate) is a product sold by Proctor & Gamble, USA. For alternative detergents consult the RO System manufacturer for assistance.

Table A2. Chemicals cleaning reagents for reverse osmosis membranes (Burns and Roe 1979).

	Chemical	Cost, $	Scale(s)	Source	Recommended Cleaning Procedure
1.	Cleaning Solution A				
	Citric Acid (2.0 percent)	0.50/lb	Iron Hydroxides	FS	Use at highest available temp. up to 120°F for at least 45 min at maximum rate available up to 10 gpm/vessel.
	Triton X-100 (0.1 percent)	0.50/lb			
	Carboxy Methyl Cellulose (0.001) percent)				
	Adjust pH to 3 with NH_4OH				
2.	Citric acid (2.0 percent) adjusted to pH 8 with NH_4OH	0.50/lb	$CaSO_4$ and $CaHO_4P$	DuPont	Circulate, followed by water rinse.
3.	EDTA (1.5 percent), pH = 8 with NaOH	1.00/lb	$CaSO_4$ and $CAHO_4P$	DuPont	Circulate and flush temp. up to 120°C.
4.	Cleaning Solution B				
	Sodium Tripolyphosphate (2.0 percent)	0.29/lb	Humic Acid Salts of Ca and Mg	FS	Use at highest available temp. up to 120°F for at least 45 min at maximum rate available up to 10 gpm/vessel.
	Triton X-100 (0.1 percent)	0.50/lb			
	Carboxy Methyl Cellulose (0.001 percent)	0.76/lb			
	Versene-100 (39 percent solution of EDTA) (2.0 percent)	1.00/lb (100 percent basis)			
	Adjust pH to 7.5 with H_2SO_4				
5.	EDTA (2.0 percent Versene-100)	1.00/lb	"Silt" and Organic Fouling	Dow	Pressure less than 75 psi, flush for 2 hr, then run with permeate for 15 min, temp. less than 35°C.
	Triton X-100 (0.1 percent)	0.50/lb			
	Trisodium phosphate (2.0 percent) pH 7.5 adjusted with H_2SO_4 or HCL	0.27/lb			
6.	Ammonium Bifluoride (2.0 percent)	0.41/lb	SiO_2	ROGA W.R. Grace	Circulate and flush.
7.	HCl to pH 4.0		$CaCO_3$	DuPont	
8.	Citric Acid to pH 4.0	0.50.lb	$CaCO_3$	DuPont	
9.	Nutek NT-600 or -500 (5.0 percent)		$CaCO_3$	Dupont	

Table A2. Continued.

Chemical	Cost, $	Scale(s)	Source	Recommended Cleaning Procedure
10. H_2SO_4 or HCl, Adjust feedwater to pH 2.0-3.5		Fe or $CaCO_3$	Dow	Normal operating pressure.
11. Citric Acid (2.0 percent) pH 2.5		Mn, Fe, $CaCO_3$	Dow	Recirculate 30 min, repeat if flush is not clear.
12. Citric Acid (2.0 percent), NH_4OH to pH 4	0.50/lb	Fe, Ni, Cu, Mn Hydroxides Silicates	DuPont	
13. Citric Acid (2.0 percent) Na_2 EDTA (2.0 percent) NH_4OH to pH 4	--	Fe, Ni, Cu, Mn Hydroxides	DuPont	
14. Sodium Hydrosulfite (4.0 percent)		Fe, Ni, Cu, Mn Hydroxides $CaSO_4$, $CaHO_4P$	DuPont	
15. SHMP (1.0 percent)		Silicates	DuPont	
16. Citric Acid (2.4 percent) Ammonium bifluoride (2.4 percent)		Severe $CaCO_3$ of silica	Dow	Circulate 30 to 60 min, manufacturer's direction.
17. H_2SO_4 or HCL to pH 2.0-3.5		$CaCO_3$ or Fe Fouling	Dow	Maximum 4 hr at operating pressure.
18. Citric Acid t(2.0 percent) pH 2.5	0.50/lb	Mn, Fe, or $CaCO_3$	Dow	Maximum 3 hr, circulate 1/2 to 1 hour. Flush with permeate and repeat if flush not clear.
19. Biz Detergent, pH 9.4 (0.25 percent solution)	--	Organics Humic Acid	DuPont, Dow W.R. Grace	
20. Cl_2 (1.0-5.0 ppm residual (Cl_2) from hypochlorite or gaseous Cl_2 injection (not for periodic cleaning, only if other methods fail) pH 6.5-7.5	--	Organics	Dow	Maximum time 60 min circulate for 15 min, then flush, check for free Cl_2 in feed and effluent. If free Cl_2 is not in effluent after 15 min, reflush with fresh solution.

Table A2. Continued.

Chemical	Cost, $	Scale(s)	Source	Recommended Cleaning Procedure
21. Caustic, NaOH, pH 11 max.		Organics Silicates	DuPont only	
22. Drewsperse 732 (1.0 percent)		Organics	DuPont	
23. Cleaning Solution EBZ, pH 7.0 EDTA Na_4 $4H_2O$ (20 percent) NH_4HCO_3 (7 percent) Zonyl FSA (0.005 to 0.01 percent)		$CaSO_4$	W.R.Grace	
24. Sodium Dithionite (2.0 percent $Na_2S_2O_4$, pH 3.6		Fe	W.R.Grace	

Appendix B
Reverse Osmosis Membrane
Cleaning Procedures

Table B1. DOW iron or carbonate foulant cleaning procedure (Burns and Roe 1979).

Solution:	H_2SO_4 or HCl addition through acid feed system
Injection rate:	As necessary to reduce feedwater pH to 2.0-3.5
Time:	4 hr maximum
Procedure:	Inject acid to lower feedwater pH to 2.0 minimum and note changes in salt passage and pressure drop over hour. Discontinue if salt passage increases significantly after the first hour.

Table B2. DOW silt and organic foulant cleaning procedure (Burns and Roe 1979).

Solution:	Two percent Versene 100; 0.1 percent Triton X-100; 2.0 percent Trisodium phosphate; mixed with permate water
pH:	Adjust solution pH to 7.5 with HCl or H_2SO_4
Flow Rate:	20-30 gpm per DOWEX 20K permeator
Pressure:	Less than 75 psig
Quantity:	30 gal of formulation for each DOWEX 20K permeator
Procedure:	Flush each stage of permator for approximately 2 hr and then rinse with permeate for 15 minutes. The solution temperature must not exceed 30°C.

Table B3. DOW manganese, iron or carbonate foulant cleaning procedure (Burns and Roe 1979).

Solution:	2 percent citric acid in permeate (pH = 2.5)
Flow Rate:	20-30 gpm per DOWEX 20K permeator
Time:	3 hr maximum
Quantity:	30 gallons per 20K permeator
Procedure:	Flush system thoroughly using permeate. Introduce citric acid flush. Recirculate 30 to 40 min. If solution turns to red-brown color, repeat the procedure. Flush with permeate. If permeate is not clear, repeat the procedure.

Table B4. DuPont "BIZ" detergent flushing procedure (Burns and Roe 1979).

Solution:	0.5 percent BIZ in permeate (4 lb/100 gal)
Flow Rate:	10-20 gpm per 8 in. unit
Pressure:	50-150 psig
Time:	1 hr minimum
Quantity:	7.5 gal for each permeator plus 10-20 gal for piping and hoses plus 100-150 gal in tank
Procedure:	Flush once through 30 gal of product per permeator (discard permeate and reject). pH 6.0 minimum. Flush 20-25 percent of the cleaning solution to drain. Recirculate effluent and product to tank. Flush for 2 hr minimum.
Alternate:	Flush 15 min. Soak 15 min. Cycle until effluent is no longer discolored. Flush with feedwater less than 200 psi until no foaming occurs. (Shake sample in jar).

Table B5. ROGA solution B cleaning procedure (Burns and Roe 1979).

Solution:	2.0 percent sodium tripolyphosphate; 0.1 percent Triton X-100 (Rohm & Haas); 0.001 percent percent carboxy methyl cellulose; 2.0 percent Versene 100 (39 percent solution); 1.0 percent formaldehyde (optional)
Flow Rate:	35 gpm per element
Pressure:	Less than 60 psig
Temperature:	Highest available. Less than or equal to 120°F (40°C)
Time:	45 min recirculation

Appendix C
Reverse Osmosis Membrane Rejuvenation Procedures

Table C1. DOW membrane surface rejuvenation treatment (Burns and Roe 1979).

Solution: GELVA (Monsanto) C-5 V-16 10 wt. percent mixed with permeate

pH: Not below 6.0

Flow Rate: Rated feed flow for system

Pressure: Rated system pressure

Quantity: 15 g of 10 percent solution for each gpm of feedwater

Procedure: Mix GELVA with the required amount of permate following recommendations for safe handling provided by the manufacturer.

Addition of ammonium hydroxide or household ammonia may be helpful in reducing the viscosity and getting the GELVA into solution.

The RO system should be thoroughly flushed after any cleaning attempt and any hypochlorite or acid addition pumps shut off for the duration of this procedure.

The system should then be started up and operated at its normal pressure, flow rate, and recovery.

By means of a chemical injection pump, the prepared solution should be pumped into the feedwater system at a rate to yield 20 ppm active GELVA in the feed. Continuous monitoring of the product water salinity during this period is critical.

Continue injection until salt passage declines to the desired level or for a maximum of 15 min. (If salt passage does not decline significantly, do not treat further.) Allow the system to operate another 15 min with no injection and note if salt passage remains stable.

Because rejection is restored by coating a portion of the available membrane surface area, a consequential decline in productivity is often seen with the increase in salt rejection.

If the permeate is used for potable water, the system should be flushed at rated conditions for at least 4 hr before the product water is once again collected for use.

Table C2. ROGA sizing rejuvenation treatment (Burns and Roe 1979).

Unit should be cleaned with the most thorough procedure available.

Unit should be restarted with normal operating parameters and performance checked.

Unit should be checked for flow and condition at each pressure vessel any any abnormally high vessels probed.

All bad "O" rings should be replaced and all leaking modules replaced (no amount of permaloid will overcome one or two fair-sized leaks).

Set the pH of the operating unit to 7.0 (or turn acid off).

Use a 3-4 percent (dilute 12 percent stock 3:1) solution of Colloid 189 for injection with acid pump.

The Colloid 189 solution should have a pH of 8-9. If not, adjust with NH_4OH.

Start injection to give 15-25 ppm polymer in feed stream.

Continue injection until performance levels out.

Stop injection of polymer and flush out pump into system with product water adjusted with NH_4 to pH 8.

Run unit for 15 min at pH 7.0 to flush out any residual polymer in system.

Start acid for standard unit operation (pH 5-6).

Mix up a 5 percent solution of $ZnCl_2$ in product water adjusted to pH 4.0 with HCl.

Begin injection at 10-20 ppm for one hour or so.

Performance should stabilize after $ZnCl_2$ injection has ceased.

Appendix D

Reverse Osmosis Installations Included in Operational Survey

Table D1. List of reverse osmosis installations to which questionries were sent, their response, and operational status as of April 1982.

State/Country	Location	Name	Reply	In Operation
Alaska	Fairbanks	Univ. Alaska Power Plant		
	Newtok	Newtok School		
	Sheldon Pt.	Sheldon Pt. School		
	Stebbins	Stebbins School		
Arizona	Phoenix	Bureau Land Mgmt.		
	Tucson	Hughes Aircraft Co.	X	Yes
	Yuma	Bureau of Reclamation	X	Yes
California	Burbank	City of Burbank		
	Escondido	City of Escondido		
	Fountain Valley	Orange County Water District	X	Yes
	Gaviota	State of California at State Beach		
	Pittsburgh	Dow Chemical USA		
	Romona	San Diego Country Estates		
	San Luis Obispo	AT&T Relay Station		
Colorado	Englewood	Consolidation Coal Co.		
	Fort Lyons	Verterans Administration Hospital		
	Lamar	AT&T Relay Station		
Florida	Boca Raton	Pheasant Walk Estates		
	Bonita Springs	Imperial Harbor MH Estates		
	Bradenton	Christian Retreat Camp		
	Bryn Maur	Bryn Maur Camp Resort		
	Cape Coral	City of Cape Coral	X	Yes
	Christmas	KOA Campground		
	Englewood	Fiveland Investment Utility	X	Yes
	Estero	Estero Woods Village		
	Flagler Beach	Oceanside Acres Apts		
	Ft. Myers	Burnt Store Utilities		
	Ft. Orange	Riverwood Park		
	Ft. Pierce	Ft. Pierce Jai Alai		

Table D1. Continued.

State/Country	Location	Name	Reply	In Operation
	Ft. Pierce	Harbor Branch Foundation		
	Ft. Pierce	Ocean Village		
	Harbor Hts.	Charlotte Harbor Water Assn.		
	Jensen Beach	River Club Condos	X	Yes
	Kay Pase	Rotonda West Utilities		
	Key Largo	Card Sound Golf Club		
	Key Largo	Florida Keys Aqueduct Authority	X	No
	Key Largo	Ocean Reef Club		
	Key West	Florida Keys Aqueduct	X	Yes.
	Long Boat Key	Westchester Condos		
	Marineland	Marineland		
	Melbourne	Cove South Beaches		
	Melbourne	Chuck's Steak Hosue		
	Miami	Reverage Canners		
	Naples	Pelican Bay Improvement District		
	New Smyrna Beach	Sugar Mill Country Club Estates		
	Nokomis	Bay Lakes Estates MHP		
	Nokomis	Fairwinds Condominium Village		
	Nokomis	Kingsgate TTP		
	Nokomis	Lake Village MHP		
	Nokomis	Lyons Cove Condominium		
	Nokomis	Nokomis Elementary School		
	Nokomis	Palm 'n Pines MHP		
	Nokomis	Sorrento Shores	X	Yes
	Ormond Beach	1414 MHP Corporation		
	Ormond Beach	Kingston Shores		
	Osprey	Sarasota Bay MHP		
	Osprey	Southbay Yacht and Racquet Club		
	Palm Beach	Harbor House		
	Ponce Inlet	City of Ponce Inlet		
	Punta Gorda	Punta Gorda Isles Inc.	X	Yes
	St. Augustine	Marineland	X	Yes

Table Dl. Continued.

State/Country	Location	Name	Reply	In Operation
	Sanibel Island	Island Water Assn.		
	Sarasota	Camelot Lakes MHP		
	Sarasota	Myakka Valley Campgrounds		
	Sarasota	Pelican Cove Subdivision		
	Sarasota	Peterson Manufacturing		
	Sarasota	Workmens Electronics Corp		
	South Bay	Gulf & Western Corp.	X	Yes
	Stuart	Indian River Plantation	X	Yes
	Stuart	Joes Point		
	Stuart	Ocean Tower		
	Venice	City of Venice		
	Vero Beach	Bryn Mawr Beach Station		
	Vero Beach	Village Green		
	West Palm Beach	Palm Beach County Utilities	X	Yes
	West Palm Beach	Riverside Memorial Chapel		
Illinois	Homewood	Surmas Restaurant		
Indiana	Hillsdale	City of Hillsdale		
Iowa	Alta	Municipality of Alta	X	Yes
	Greenfield	Greenfield Municipal Water Works		
Montana	Decker	Decker Coal Co.	X	Yes
Nevada	Jean	Town of Jean		
New Mexico	Albuquerque	Mesa Rica Water Co.	X	Yes
	Conchas Dam	Conchas Dam	X	Yes
North Carolina	Ocracoke	Town of Ocracoke		
North Dakota	Dickinson	Jim Nelson		
	Parshall	City of Parshall		
	Reeder	Russell Earsley	X	Yes

Table Dl. Continued.

State/Country	Location	Name	Reply	In Operation
Ohio	Medina	Days Inn	X	No
Oklahoma	Tulsa	Lake County Mobile Homes		
Pennsylvania	Hastings	City of Hastings		
Texas	Dallas	Universoty of Texas	X	Yes
	Fabens	Indian Cliffs Ranch		
	Muleshoe	U.S. National Park Service	X	No
Utah	Hill AFB	Hill AFB	X	Yes
	Moab	Texas Gulf Corporation	X	Yes
	Salt Lake City	Morton Salt Company	X	Yes
	Salt Lake City	N. L. Industries		
Wyoming	Fontanelle	AT&T Relay Station		
	Muddy Gap	AT&T Relay Station		
	Sheridan	Pieter Kiewit & Sons		
Washington, D.C.		Blue Plains Sanitary Treatment Plant		
Bahamas	Grand Bahamas Isl.	Grand Bahama Hotel		
	Paradise Islands	Paradise Utilities		
	Paradise Islands	Resorts International		
Bermuda	Hamilton	Bermuda Properties		
Canada	Brandoz Manitoba	Manitoba Water Service Board	X	Yes
Dominican Republic	Santo Domingo	Inter Continental Hotel		
Israel	Eilat	Mekeroth		
Mexico	Holvox	Village of Holvox		
	San Felipe	City of San Felipe		

Table Dl. Continued.

State/Country	Location	Name	Reply	In Operation
Puerto Rico	Maniti	Schering Corporation		
	Prasa	Aqueduct & Sewer Authority		
Saipan	Mariana Islands	Intercontinental Hotel	X	No
Saudia Arabia	Riyadh	Intercontinental Hotel		
South Caicos Isl.	Sharjah	Admiral Arms Hotel	X	No
Virgin Islands	St. Croix	Schuster Water Service		
	St. Thomas	Frenchman's Reef		
	St. Thomas	Virgin Islands Housing Authority		

Appendix E
Operational Survey

July 31, 1981

Ladies and Gentlemen:

The Utah Division of Environmental Health is currently evaluating the use of reverse osmosis in the treatment of drinking water. We would be most grateful if you could fill out the enclosed questionnaire as completely as possible. Annual reports or data sheets containing similar information will be of equal value. Your answers will help us evaluate reverse osmosis with respect to design, operation, and maintenance criteria. Hopefully we can benefit from your experience and avoid any problem areas that you have encountered.

We have tried to make the questionnaire as short and as simple to answer as possible. If there are any questions you cannot answer, do not worry about it. If insufficient space is provided for an answer, feel free to use the back of page. The answers from all the reverse osmosis plants responding to the questionnaire will be summarized. Unless you indicate otherwise, your plant and name will be listed as a contributor to our findings and your answers will remain confidential. Finally, you will be sent a copy of our findings.

Thank you very much for your time and consideration in this matter.

Cordially yours,

E. Joe Middlebrooks
Dean, College of Engineering

EJM/jmj

Enclosure

Questionnaire

1. Prepared by ____________________ ________________ Date: __________
   Name Title

   Representing ______________________________ Phone: __________

   Address ____________________ ______________ ______ ______
   Street City State Zip

2. Objective of Treatment

   ___ Drinking Water
   ___ Wastewater
   ___ Boiler Feedwater
   ___ Cooling Water
   ___ Other (Please Indicate) ____________________

3. Source of Water

   ___ Municipal
   ___ Private
   ___ Other (Please Indicate) ____________________
   ___ Surface
   ___ Well (Please Indicate Depth) ________________
   ___ Other (Please Indicate) ____________________

4. Water Requirements

   Expressed in Units __________

   Maximum Flow _____ Duration _____
   Minimum Flow _____ Duration _____

   Average Flow _____ Hours/Day _____
   Days/Week _____ Weeks/Year _____

   Total Gallons Per Day ________

5. Is Water Storage Available?

   ___ No
   ___ Yes (Please Indicate Storage Capacity) __________

6. Current Cost of Raw or Treated Water in ¢/1000 Gal (Please Indicate) _____

7. Electricity

   ¢/KWH (Please Indicate) ________
   Frequency of Power Outages ________
   Reserve Power Source
   ___ No
   ___ Yes (Briefly Describe) ________

8. Labor

Briefly Describe operator's training and experience.

Briefly describe maintenance's training and experience.

What would you recommend to improve operator and maintenance training? (Describe Briefly)

9. Pretreatment

___ Chemical Addition (Please Indicate Chemicals and Concentrations)

__________________ __________________
__________________ __________________
__________________ __________________

___ Coagulation
___ Flocculation

___ Sedimentation
___ Filtration (Please Indicate Type) __________

___ Clarification
___ Disinfection (Please Indicate Type) __________
___ Other (Please Identify)
__________ __________
__________ __________

Please provide a brief sketch of pretreatment.
EXAMPLE:

Raw Water → Chemical Addition → Flocc → Sediment. → Filter → Reservoir
↑ Chemicals (into Chemical Addition)
↓ Sludge (from Sediment.)

→ Buffer Tank → R.O.

Briefly describe any problems you have encountered in pretreatment and recommendations for avoidance.

10. Pumps

A. Type
___ Centrifugal
___ Vertical Turbine
___ Multistage Process
___ Positive Displacement
___ Other (Please Indicate) __________

B. Spare Pumps/Motors
Indicate Number __________

C. What System Feed Pressure is used for running your RO unit?

Min ______
Ave ______
Max ______

D. Briefly describe any significant problems you have encountered with pumps and recommendations for avoidance.

11. Reverse Osmosis

a) System designed by (Please Indicate) ____________________

b) Operation

Hr/day _____ Days/Week _____ Weeks/Yr _____

How long has unit been in operation? ____________

c) Does unit have polishing membrane filter?

__ No

__ Yes (Please Indicate) _____ Size _____

d) Flow rate. Please indicate units ________

	Min	Ave	Max
Feed			
Permeate			
Concentrate			

e) Concentrations. Please indicate units if other than μmhos/cm

	Min	Ave	Max
Feed			
Permeate			
Concentrate			

f) Membranes

Manufacturer (Please Indicate) ____________________

Type

__ Cellulose Acetate

__ Polyamide

__ Other (Please Indicate) ________

Configuration

__ Spiral Wound

__ Hollow Fiber

__ Plate and Frame (Flat Membrane)

__ Other (Please Indicate) ________

Diameter

__ 4"

__ 6"

__ 8"

__ Other (Please Indicate) ________

Flux Rate (Please indicate in units of flow per surface area per time.)

Min ________ Ave ________ Max ________

g) Brine or Concentrate Disposal

___ Recycled to Feed
___ Used to Run Pump
___ Total Containment Pond
___ Other (Please Indicate) ____________

h) Cleaning. If applicable, please indicate.

1. Cleaning Solution Used
2. How Often Used
3. Procedure

i) Is RO provided with alarm or shutdown provisions?

___ No
___ Yes (Briefly Describe)

j) Equipment

Pressure gages up and downstream of polishing filter?
___ Yes ___ No
Flowmeters for permeate and concentrate?
___ Yes ___ No
Taps for sampling permeate and concentrate?
___ Yes ___ No
EC meters at sampling points?
___ Yes ___ No

k) If possible, please provide sketch of membrane module arrangement.

l) Briefly describe any significant problems you have encountered in RO unit and recommendations for avoidance.

12. Post-treatment

___ pH adjustment
___ $CaCO_3$ addition or Langlier Index Adjustment
___ Ion Exchange

___ CO_2 Removal (Please indicate type) _____
___ Disinfection(Please indicate type) _____
___ Other (Please indicate type) __________
___ Other (Please indicate type) __________

Please provide brief sketch of post-treatment if possible.

Briefly describe any significant problems you have encountered in posttreatment and recommendations for avoidance.

13. Cost

			Operating cost ¢/1000 Gal			
Capacity GPD	Capital Cost	Power	Chemicals	O&M	Membranes	Total

14. Based on your experience, briefly describe any recommendations or suggestions you would give to future RO installations with respect to:

DESIGN:

OPERATION:

MAINTENANCE:

Once again, thank you for your time and consideration.

Sincerely,

E. Joe Middlebrooks