# MEMBRANE SEPARATION TECHNOLOGIES FOR TREATMENT OF HAZARDOUS WASTES

Author: **Janet Corson MacNeil**
Environmental Strategies Corporation
San Jose, California

Referee: Ulric P. Gibson
*Technical Support Services*
C. C. Johnson & Malhotra, P. C.
Silver Spring, Maryland

## I. INTRODUCTION

Membrane separation processes, such as reverse osmosis, ultrafiltration, and electrod alysis, use selective membranes to separate a contaminant from a liquid phase (such water). Separation is achieved using a differential driving potential across the membrane attract or push the mobile component through the membrane. The major driving force acro the membrane may be the result of hydrostatic pressure (reverse osmosis and ultrafiltratio or electrical potential (electrodialysis).

Since the 1950s, membrane separation technologies have been used to desalinate brackis and sea water in order to provide supplementary sources of potable water in semiarid regions However, it was not until recently that the potential of these processes for treating hazardo wastes was recognized. Membrane separation processes can be used to (1) reduce the volun of an aqueous waste stream, (2) recover or purify water from an aqueous waste, and ( concentrate and/or recover the contaminant. These recycling/waste reduction options a becoming more desirable due to several factors:

1. EPA has banned the land disposal of certain wastes, which forces generators to se alternative hazardous waste management methods.
2. Under the Hazardous and Solid Waste Amendments of 1984 (HSWA), hazardo waste generators must certify that they are implementing waste minimization program
3. Generators risk significant potential liability when they send their wastes offsite f treatment and/or disposal. If the receiving facility ever becomes subject to a feder or state cleanup action, the generator could be liable for cleanup costs.
4. Waste reduction and recycling efforts reduce expensive waste treatment and dispos costs and may result in substantial savings of raw materials and water.

## II. OVERVIEW OF MEMBRANE SEPARATION TECHNOLOGIES

Although membrane separation technologies are all capable of separating contaminan from a liquid, each method utilizes a different separation mechanism and is applicable treatment of different waste streams. A brief summary of the capabilities of reverse osmosi ultrafiltration, and electrodialysis is provided below.

Reverse osmosis effectively removes dissolved inorganics (e.g., metals, metal-cyani complexes, and other ionic species) and high molecular weight (>120) organics (e.g pesticides) from aqueous waste streams.[2] It is generally applicable for treatment of wast with total dissolved solids (TDS) concentrations of up to 50,000 mg/ℓ.[2] With more high concentrated wastes, the operating pressures required to overcome the osmotic pressure

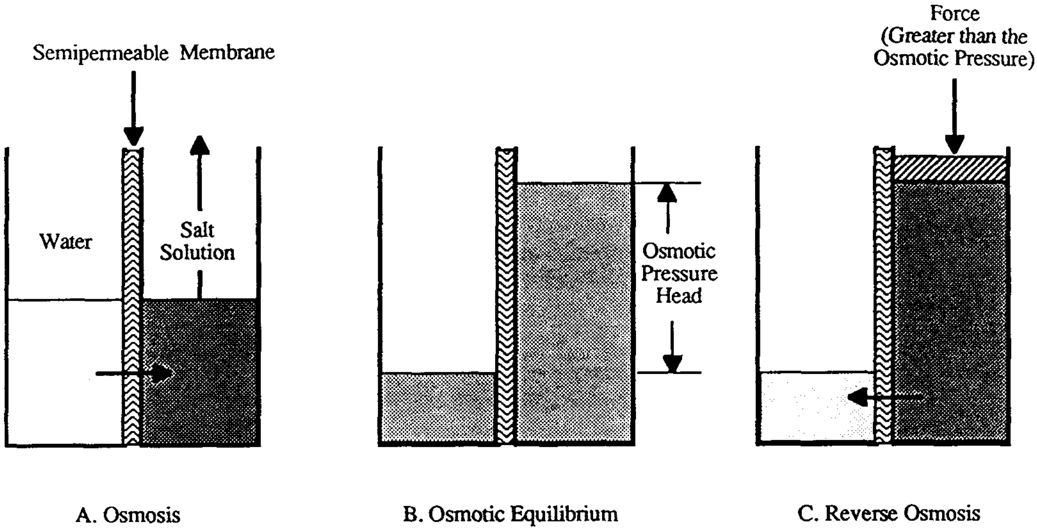


FIGURE 1. The principles of osmosis and reverse osmosis.

the solution become prohibitively high. The purity of recovered waste is relatively high and is usually suitable for reuse.[3] The maximum achievable concentration of salt in the reject stream is limited to approximately 70,000 ppm due to osmotic pressure considerations.[4]

Ultrafiltration generally separates high molecular weight (>300), nonionic organics and particulates from waste streams.[5] It is particularly effective for removing suspended solids, oil and grease, large organic molecules, and complexed heavy metals from waste waters.[3]

Electrodialysis is used to remove ionic species from water. It produces moderate quality product water.[3] The reject stream can be concentrated to between 10 and 25% solids (100,000 to 250,000 ppm) in one stage with feed solutions as low as 1000 ppm.[4] Electrodialysis can generally produce concentrate streams ten times the concentration of that produced via reverse osmosis. However, nonionic contaminants cannot be concentrated and the permeate is not as pure in dissolved ionic concentration as that produced by reverse osmosis.[6]

## III. REVERSE OSMOSIS

Reverse osmosis (also called hyperfiltration) is based on the principle of osmosis, which occurs when two solutions of different concentrations are separated by a semipermeable membrane. During osmosis, water flows from the solution with the lower concentration of solute (e.g., salt or contaminant) through the membrane into the solution containing the higher concentration of solute (Figure 1). The flow continues until an equilibrium osmotic pressure is achieved (i.e., the concentration of the salt or contaminant in the water is equal on both sides of the membrane). If pressure greater than the osmotic pressure is applied to the more concentrated solution, the naturally occurring osmotic flow is reversed. This process, which causes the water to flow through the membrane from the more concentrated to the less concentrated solution, is called reverse osmosis. The osmotic pressure that needs to be overcome is proportional to the dissolved salt concentration of the solution and the temperature of the solution; it is completely independent of the membrane.[7] Osmotic pressure can be determined from Equation 1:[8]

$$\pi = 1.12(T + 273) \sum m_i \tag{1}$$

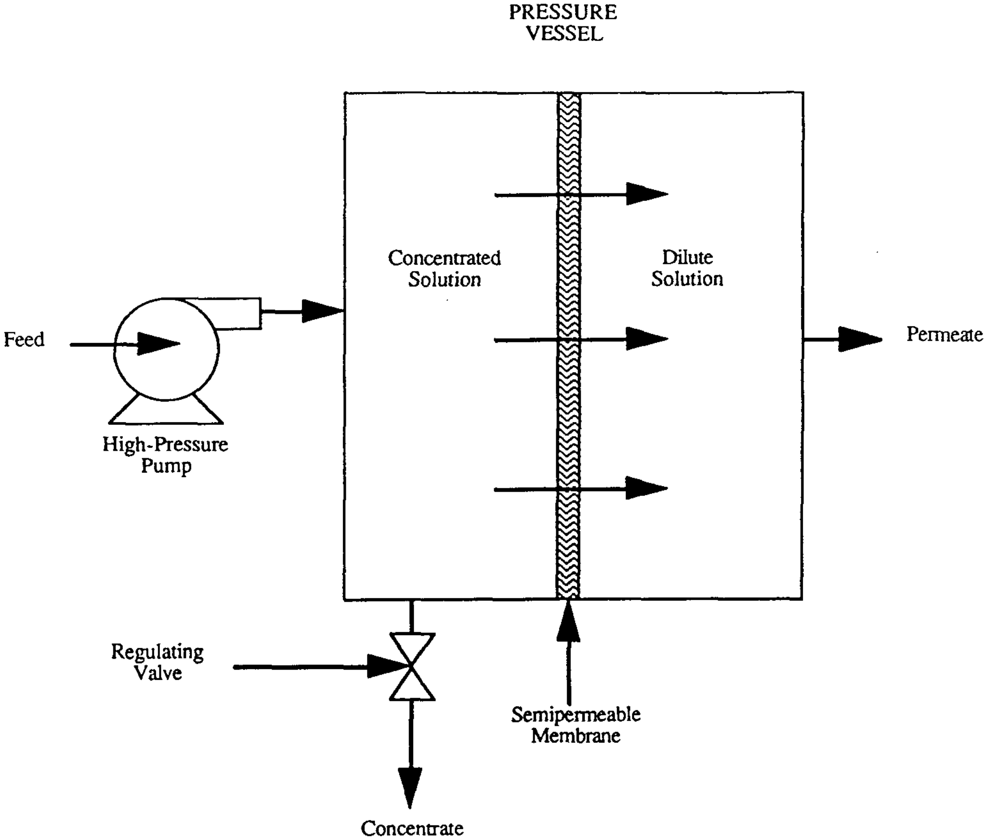


FIGURE 2. Schematic diagram of a reverse osmosis system. (From McArdle, J. L., Arozarena, M. M., and Gallagher, W. E., *A Handbook on Treatment of Hazardous Waste Leachate*, EPA/600/8-87/006 [PB87-152328], U.S. Environmental Protection Agency, Cincinnati, 1987, 61. With permission.)

where $\pi$ = osmotic pressure, pounds per square inch (psi); T = temperature, °C; and $\Sigma mi$ = summation of molalities of all ionic and nonionic constituents in the solution.

As a rule of thumb, each 1000 ppm of dissolved ionized solute increases the osmotic pressure by about 10 $lb_f/in.^2$ (0.07 MPa).[3,9] Reverse osmosis operating pressures generally range from 400 to 1500 $lb_f/in.^2$ (2.8 to 10.3 MPa).[2]

## A. Reverse Osmosis Design Factors

A basic schematic diagram of a reverse osmosis unit is shown in Figure 2. The feed solution is pumped into a pressure vessel containing a semipermeable membrane, where it is separated into two effluent streams known as the permeate and the concentrate. The permeate (the purified water that passes through the membrane) is recovered at atmospheric pressure, while the concentrate (the reject stream containing solutes or suspended solids that cannot pass through the membrane) is let down to atmospheric pressure via a flow-regulating valve. Because no heat is added and no phase change is involved, reverse osmosis is an effective process requiring relatively low energy input.[4] Energy requirements are on the order of 10 kWh/1000 gal product water (2.6 $kWh/m^3$ product water).[10]

The performance of a reverse osmosis system is often measured in terms of flux, conversion, rejection, and salt flow rate. Each of these design factors is discussed in detail in the following.

### *1. Flux*

The flux (sometimes called productivity) of a membrane depends on factors such as: membrane thickness, membrane porosity, temperature, differential pressure across the membrane, salt concentration, and flow velocity of water through the membrane.[11] It can be calculated as follows:[12]

$$J = A(\Delta p - \Delta\pi) \tag{2}$$

where J = water flux per unit area of membrane (gal/ft$^2$/day or m$^3$/m$^2$/day); A = membrane water permeability coefficient; $\Delta p$ = hydrostatic pressure difference across the membrane; and $\Delta\pi$ = osmotic pressure difference across the membrane.

Working membrane fluxes usually range from 2 to 200 gal/ft$^2$/day (0.08 to 8 m$^3$/m$^2$/day).[13]

Membrane flux is increased by increases in pressure, feed rate, and temperature.[13] However, it gradually decreases with time due to slow densification and fouling of the membrane structure.[11] The membrane must be replaced when the flux has reached a minimum acceptable value. Useful membrane life is typically 2 to 3 years or longer.[5]

### *2. Conversion*

The performance of a reverse osmosis system may also be characterized in terms of conversion (sometimes referred to as recovery), which is defined as:[8]

$$Y = 100\ Q_p/Q_f \tag{3}$$

where Y = percent conversion; $Q_p$ = product water flow rate; and $Q_f$ = feedwater flow rate.

In other words, conversion is the percentage of the feed flow which is pumped through the membrane.

It is usually desirable to operate reverse osmosis systems with a conversion as high as possible.[14] Conversion may be controlled by adjusting the flow rate of the reject stream exiting a reverse osmosis module. If a module is operated at low conversion, the concentrations of the reject stream and the feed water are almost the same. If conversion is increased, the average salt concentration on the feed side of the membrane increases. This consequently increases the osmotic pressure and decreases the flux because it is necessary to operate at higher feed pressures to overcome osmotic pressure effects (see Equation 1).[3] Consequently, conversion is often limited by pumping pressures, which are impractical above 1000 $\text{lb}_f/\text{in.}^2$ (6.9 MPa) for most applications.[6]

Conversion rates range from 10 to 15% for spiral-wound modules to 50% for hollow fiber modules.[8] (These module types are discussed below.) Higher overall conversion rates may be obtained by installing multiple modules in series or by using a large recycle stream.

### *3. Rejection*

Rejection is used to measure the amount of salt (solute) that is not allowed to pass through the membrane. It is defined by:[8]

$$C = 100\% - 100\ C_p/C_f \tag{4}$$

where $C_p$ = salt concentration in the product stream and $C_f$ = salt concentration in the feed stream.

### *4. Salt Flow Rate*

No membrane is capable of rejecting 100% of the salt in the feedstream.[6] Leakage of salt through the membrane is expressed by the following equation:[8]

## Table 1
## FACTORS THAT AFFECT MEMBRANE PERFORMANCE

| Factor | Cause | Methods of reduction |
|---|---|---|
| Membrane fouling | Deposition of soluble material (e.g., calcium carbonate, calcium sulfate, and hydrous metals), organics, suspended solids, colloidal particles, and other contaminants on the membrane surface; biological growth may also be a source of fouling | Pretreatment (e.g., filtration, pH adjustment, carbon adsorption, chlorination, coagulation of colloidal matter or a combination of treatment methods) |
| Membrane compaction and compression | Excessive temperatures | Reduction methods have not been successful to date |
| Hydrolytic deterioration of the membrane | Operation of the reverse osmosis system outside of the membrane pH tolerance levels, biological and chemical attack, and exposure to chlorine | pH adjustment of feed |
| Concentration polarization | Accumulation of solute on the membrane surface; the accumulated boundary layer interferes with the transport of water across the membrane | Increase of fluid turbulence to decrease the thickness of the boundary layer; adjustment of the module conversion so that less solvent leaves the feed solution |

Adapted from George, D., *Water Reuse*, E. J. Middlebrooks, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, 1982, chap. 10.

$$Q_s = \Delta C K_s A/t \qquad (5)$$

where $Q_s$ = flow of salt through the membrane; $\Delta C$ = salt concentration differential across the membrane; $K_s$ = permeability coefficient of salt passing through the membrane; A = membrane area; and t = membrane thickness

This equation indicates that the rate of salt flow is proportional to the salt concentration differential and is independent of applied pressure. Therefore, an increase in operating pressure will increase water flux (Equation 1) without changing the salt flow through the membrane.

### B. Factors That Affect Membrane Performance

The productivity and useful life of reverse osmosis membranes may be affected by several factors: fouling, compaction, hydrolytic deterioration, and concentration polarization. The causes and methods of reducing these problems are summarized in Table 1.

#### *1. Pretreatment*

Because of the susceptibility of membranes to chemical attack and fouling, pretreatment of waste streams is often necessary prior to reverse osmosis treatment. Pepper has compiled a detailed summary of pretreatment methods used in desalination applications.[16]

Pretreatment costs typically range from \$0.15 per 1000 gal (\$0.04 per $m^3$) for filtration to more than \$1.00 per 1000 gal (\$0.26 per $m^3$) for extensive treatment including chemical conditioning and ion exchange (1980 dollars).[12]

Several methods of predicting the degree of pretreatment required have been investigated. The Silt Density Index (SDI) has been used as a measure of particulate and oil fouling potential. High SDI values indicate greater fouling potential and thus the need for more

## Table 2
## PHYSICAL AND CHEMICAL LIMITATIONS OF REVERSE OSMOSIS MEMBRANES

| Membrane material | pH limits | Maximum temperatures | Other limitations |
|---|---|---|---|
| Cellulose acetate | 2.5—7 | 29—50°C (85—122°F) | Biologically degradable |
| Aromatic polyamides | 4—11 | 35—46°C (95—115°F) | Cannot tolerate chlorine |
| Thin film composites | <1—13 | 46—79°C (115—175°F | Can tolerate moderate chlorine levels (100 ppm) |

Adapted from MacNeil, J. and McCoy, D., *Standard Handbook for Hazardous Waste Treatment and Disposal*, Freeman, H. M., Ed., McGraw-Hill, New York, 1988.

extensive pretreatment methods, while SDI values of less than five have been reported to indicate little need for pretreatment.[17] A permanganate demand test has also been used to determine if a process can be operated for an extended period of time without fouling. However, both the SDI and permanganate demand test failed to accurately predict flux decline due to fouling in tests performed by Kinman et al.[18]

### *2. Membrane Cleaning*

In addition to pretreatment, regularly scheduled cleaning of the membranes will increase membrane life and help insure good membrane performance. The cost of chemical cleaning averages less than \$0.02 per 1000 gal (\$0.005 per $m^3$).[19] A comprehensive guide to membrane cleaning has been compiled by Eisenberg and Middlebrooks.[20]

## C. Reverse Osmosis Membrane Materials

Membranes are the critical component of a reverse osmosis system. Factors to consider in selecting a membrane material include performance, cost, ease of fabrication, serviceability, and resistance to environmental factors such as pH, temperature, and pressure.[21] The most popular reverse osmosis membrane materials are cellulose acetate, aromatic polyamides, and thin film composites (consisting of a thin film of a salt-rejecting membrane on the surface of a porous support polymer). The temperature, pH, and other limitations of these materials are presented in Table 2. Although all commercially available membranes exhibit excellent tolerance to certain chemical extremes, none has yet been developed that will satisfactorily function in all extremes.[23]

### *1. Cellulose Acetate Membranes*

In 1953, the U.S. Department of Interior's Office of Saline Water sponsored the development of a synthetic semipermeable membrane with adequate physical strength and product water flux to be economically feasible for desalination applications.[24] Under this program, Reid and Breton studied several potential membrane materials and discovered that cellulose acetate had suitable salt rejection properties.[25] However, the material could not be made thin enough to obtain practical flux rates.

Soon after, Loeb and Sourirajan developed an asymmetric cellulose acetate membrane that exhibited flux rates more than ten times those observed by Reid and Breton and had excellent salt-rejection properties.[5,26] This major technological breakthrough established reverse osmosis as an economically feasible process for desalination and made large-scale development possible. The asymmetric membrane consists of a dense, salt-rejecting surface skin (about 0.2 to 0.5 μm thick) supported by a spongy, porous substructure (about 50 to 100 μm thick). The skin provides a barrier to the transport of salts and impurities across the membrane, while the porous support layer allows diffusion of the product water into a collection system. The substructure has pores 0.1 to 1.0 μm in diameter, whereas the skin has pores estimated to be approximately 10 Å in diameter.[27]

A typical average water flux for an asymmetric cellulose acetate membrane is 2.5 gal/ft$^2$/day (0.1 m$^3$/m$^2$/day) per 100 lb$_f$/in.$^2$ (0.7 MPa) of applied pressure for salt rejection of greater than 95%.[28] Cellulose acetate has excellent permeability characteristics; however, it exhibits poor pH and thermal resistance (Table 2). Even so, the tolerance of cellulose acetate to oxidants and its good resistance to chemical attack make it useful for the treatment of industrial wastes.[29]

### 2. *Aromatic Polyamide (Hollow Fiber) Membranes*

DuPont introduced reverse osmosis modules containing asymmetric aromatic polyamide (aramid) membranes in 1970.[8] These modules were hollow fiber configurations that became known as Permasep units (see discussion of hollow fiber modules below). Each hollow fiber has an outside diameter of approximately 80 μm and an internal diameter of about 40 μm.[12] The product flux for these membranes (1.9 gal/ft$^2$/day at 399 lb$_f$/in.$^2$ or 0.075 m$^3$/m$^2$/day at 2.75 MPa) is about an order of magnitude less than experienced with cellulose acetate membranes. However, the surface area packing densities (12,200 ft$^2$/ft$^3$ or 40,000 m$^2$/m$^3$) of aromatic polyamide membranes are about an order of magnitude higher.[12,30] Productivity rates are approximately 1 to 2 gal/ft$^2$/day (0.04 to 0.08 m$^3$/m$^2$/day), and the membranes have extremely good organic removal with a cutoff of 100 mol wt.[29] Aromatic polyamide membranes have longer membrane life expectancy due to their high chemical and physical stability (see Table 2).[19] The membranes are also capable of operating at higher temperatures than cellulose acetate membranes and are essentially immune to biological degradation.[15,28] On the other hand, aromatic polyamide is very sensitive to oxidants such as chlorine.[31]

### 3. *Thin-Film Composite Membranes*

The most recent reverse osmosis membrane to be developed is the thin-film composite membrane, which emerged in the mid-1970s.[8] This membrane type is similar to the asymmetric cellulose acetate membrane developed by Loeb and Sourirajan (described previously). However, the thin-film composite membrane optimizes performance by using different materials for the thin dense skin and the porous substructure. The supporting porous material is usually a polysulfone polymer, while the composition of the thin film (ranging in thickness from 0.01 to 0.10 μm) can be tailored to the specific application.[3] Polyether, polyester/amide, polyamide, and polyurea have all been used as materials for the thin film in composite membranes.[3] Eisenberg and Middlebrooks have described several types of composite membranes that have been developed.[29]

In general, the reverse osmosis industry is moving in the direction of composite membranes due to their superior performance characteristics.[32] Composite membranes perform better than cellulose acetate membranes in almost all respects, including water flux, salt rejection, temperature and pH stability, and pressure requirements. Higher fluxes (25 to 35 gal/ft$^2$/day or 1 to 1.4 m$^3$/m$^2$/day) and high salt rejections (95 to 99% rejection with a 2000 mg/ℓ salt solution) at considerably lower pressures (200 to 400 lb$_f$/in.$^2$ or 1.4 to 2.7 MPa) are possible.[33] In addition, composite membranes provide improved resistance to compaction.[27]

## D. Reverse Osmosis Membrane Module Configurations

After a membrane type is selected for a specific application, it must be incorporated into a module or permeator that protects the fragile membrane from the high system operating pressures. In order to be practical, membrane modules must:[13,34]

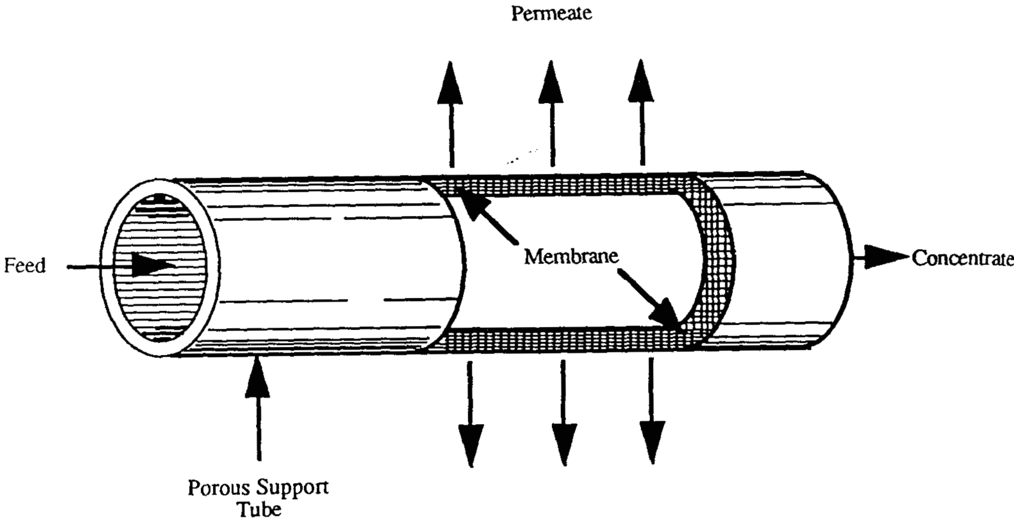


FIGURE 3. Tubular reverse osmosis module. (From McArdle, J. L., Arozarena, M. M., and Gallagher, W. E., *A Handbook on Treatment of Hazardous Waste Leachate,* EPA/600/8-87/006 [PB87-152328], U.S. Environmental Protection Agency, Cincinnati, 1987, 62. With permission.)

1. Provide adequate structural support so that the fragile membrane can withstand high pressures (200 to 1500 $lb_f/in.^2$ or 1.4 to 10.3 MPa)
2. Minimize the buildup of salt and fouling on the membrane surface
3. Have a high membrane surface-to-volume ratio to minimize space requirements and capital costs
4. Allow for easy cleaning or replacement of membranes in the event that fouling becomes a problem
5. Contain membranes that will have a long lifetime and low replacement cost

There are four types of module designs commonly used: (1) tubular, (2) hollow fiber, (3) spiral wound, and (4) plate and frame. Each of these designs is discussed next.

### *1. Tubular Modules*

Tubular modules are the simplest reverse osmosis module design, as illustrated in Figure 3. The membrane is either inserted into or coated onto the surface of a porous tube that is made of ceramic, carbon, or porous plastic and that has an inside diameter of $^1/_8$ to 1 in. (0.32 to 2.54 cm).[35] A module is typically formed by connecting a number of tubes in series or parallel.[12] As pressurized feedwater is introduced into the module, product water permeates through the membrane and the porous tube and is collected on the outside. The reject stream exits on the opposite end of the tube.

During the 1960s, tubular modules were popular for chemical separation and processing of food and pharmaceuticals. However, the low packing density of these units (about 100 $ft^2/ft^3$ or 328 $m^2/m^3$) made them uneconomical for large-scale use.[4] Although tubular designs are still commercially available, they are usually only used in specialized, low-volume applications.[3] One of their advantages is that they can be used to treat extremely turbid feedstreams.[15] In addition, tubular units use a fluid velocity of 3 to 4 ft/sec (0.9 to 1.2 m/sec) to maintain turbulence, thus preventing the buildup of dissolved salts at the membrane surface.[4]

### *2. Hollow Fiber Modules*

An example of a hollow fiber module, the DuPont Permasep module, is shown in Figure 4. The membranes used in this module are hair-like, hollow fibers made of aromatic po-

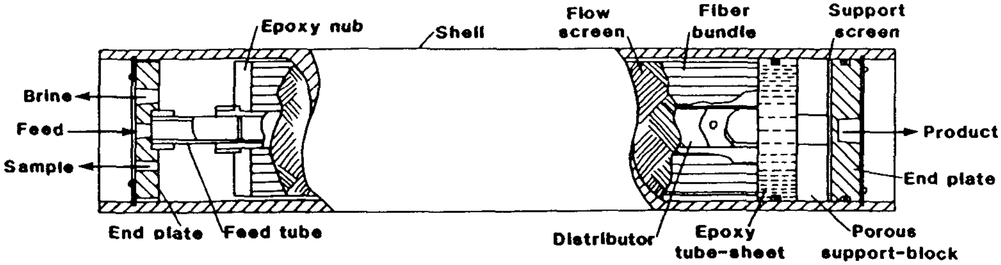


FIGURE 4. Cross-section of a hollow fiber reverse osmosis module. (From Applegate, L. E., *Chem. Eng.*, 91, 70, 1984. With permission.)

lyamide (discussed earlier). Up to 4.5 million of these fibers are bundled together.[8] The fiber bundles are then wrapped around a support frame, and one end of the bundle is potted in epoxy (keeping the ends of the fibers open) to form a tubesheet. The other end of the fiber bundle is sealed in epoxy to create an epoxy nub, which prevents short-circuiting of the feed to the brine outlet. The membrane bundle is then placed in a pressure vessel up to 4 ft (1.2 m) long and 4 to 10 in. (10.2 to 25.4 cm) in diameter.[8]

Pressurized feedwater enters the module through a central porous distributor that extends throughout the entire module. The feed passes through the wall of the distributor and flows radially through the fiber bundle toward the wall of the permeator. During this process, the product permeates radially inward through the membrane fibers. The purified water flows through the bore of each fiber to the tubesheet for discharge from the module at the end of the module opposite the feed inlet. Meanwhile, the concentrate is collected by a flow screen on the perimeter of the bundle. This flow screen conducts the concentrate to a discharge port located at the same end of the module as the feed inlet port.

Productivity of hollow fiber modules ranges from 3 to 6 gallons of product per feet$^2$ of membrane (0.12 to 0.24 $m^3/m^2$) and 10,400 to 13,200 gal/ft$^3$ of element (1390 to 1764 $m^3/m^3$).[28] The packing density is high (5000 $ft^2/ft^3$ or 16,400 $m^2/m^3$) and the modules can withstand relatively high differential pressures (600 to 1000 $lb_f/in.^2$ or 4.1 to 6.9 MPa).[4,27] Hollow fiber modules are also readily cleaned by reversing the flow through the membranes (i.e., backwashing).[5]

The major disadvantages of hollow fiber modules are that they are susceptible to fouling, difficult to clean due to the small spacing between fibers in the bundle, and the flow per square foot of membrane area is lower than in other membrane configurations.[4,36] Accordingly, feed streams with high suspended solids or high viscosity must usually be pretreated prior to treatment with hollow fiber modules.

### a. Tube Side Feed Flow Design

In addition to the feed flow configuration described above, it is also possible to bundle the membrane fibers in a straight fashion to allow feed flow on the inside of the fibers (similar to a typical heat exchanger). The feed flows into the bore of the hollow fibers at one end of the module. As the feed flows through the fibers, the product continually permeates radially outward through the fiber walls. The concentrate, which cannot escape the bore of the fiber, is collected at the other end of the module.

Hollow fiber modules in this configuration have not been used in the past. However, Bend Research, Inc. is currently developing hollow fiber modules utilizing this tube-side feed flow design. The major advantage of this design is that a high linear flow velocity across the entire surface area of the membrane may be used to reduce fouling caused by concentration polarization. The modules have been shown to reject more than 99.5% nickel from nickel-plating rinsewaters. No irreversible fouling was exhibited over 200 days of operation.[37]

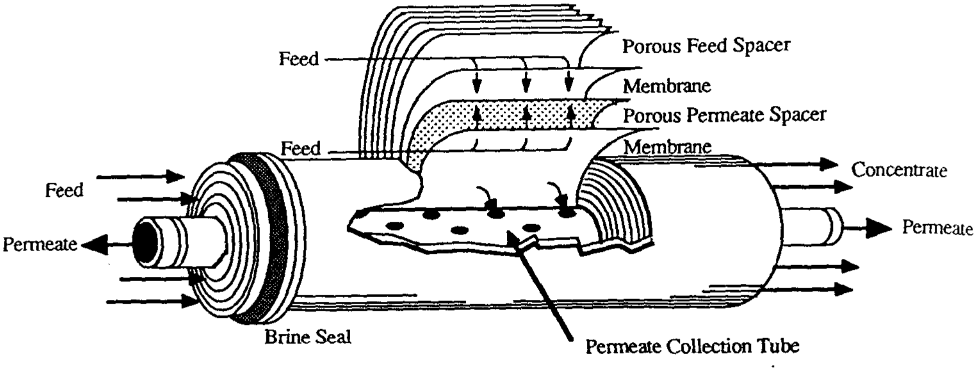


FIGURE 5. Spiral wound reverse osmosis module. (From McArdle, J. L., Arozarena, M. M., and Gallagher, W. E., *A Handbook on Treatment of Hazardous Waste Leachate,* EPA/600/8-87/006 [PB87-152328], U.S. Environmental Protection Agency, Cincinnati, 1987, 62. With permission.)

### *3. Spiral-Wound Modules*

Spiral-wound membrane modules are made up of two sheets of semipermeable membrane separated by a permeate carrier material (such as nylon or dacron). Typically, cellulose acetate or thin-film composite membranes are used. The membrane sandwich is sealed on three sides and the fourth open side is attached to a perforated, plastic collection tube. Before the membrane is wrapped around the tube, a sheet of plastic netting (porous feed spacer) is placed adjacent to the membrane. The netting induces turbulence in the feed channel and consequently reduces concentration polarization. A typical spiral wound module, shown in Figure 5, is typically 4 in. (10.2 cm) or 8 in. (20.3 cm) in diameter and 40 in. (102 cm) long.[8]

After construction, the spiral-wound membrane is inserted into a pressure vessel made of stainless steel or filament-wound glass-reinforced epoxy.[38] In order to operate a spiral wound system economically, up to six spiral-wound cartridges may be connected in series within a pressure vessel, which may be up to 22 ft (6.7 m) long.[8] Feed is introduced at one end of the pressure vessel and flows axially through the mesh spacer to the opposite end of the shell. Permeate is removed from the perforated tube.

Product recovery per spiral-wound cartridge ranges from 5 to 15% of the feed flow rate. Pressure drops from feed to reject are approximately 10 $lb_f/in.^2$ (69 kPa) per cartridge and product side pressure drops are from 30 to 40 $lb_f/in.^2$ (206 to 276 kPa).[36]

Spiral wound modules have been popular because they resist scaling and fouling.[36] Other advantages include high packing density (about 300 $ft^2/ft^3$ or 984 $m^2/m^3$), low manufacturing cost, and relative ease of cleaning (both chemically and hydraulically).[4,15]

The major drawback of spiral-wound modules is that turbid feedwaters must be pretreated to prevent clogging of the small feed flow passages.[36]

### *4. Plate and Frame Modules*

Plate and frame reverse osmosis modules were developed by Aerojet General Corporation in the 1960s.[39] The original plate and frame unit, which was based on a filter-press type design, had several drawbacks (e.g., it was difficult to change membranes and excessive fouling was experienced).[30,36] For these reasons, its development was not pursued in the U.S. Development of the plate and frame technology was continued in Europe, however, by the Danish Sugar Corporation.[40]

Current plate and frame modules (Figure 6) utilize membranes attached to both sides of a rigid plate made of plastic, porous fiberglass, or reinforced porous paper.[15] The flat surfaces of the plates contain grooved channels through which the permeate flows after passing

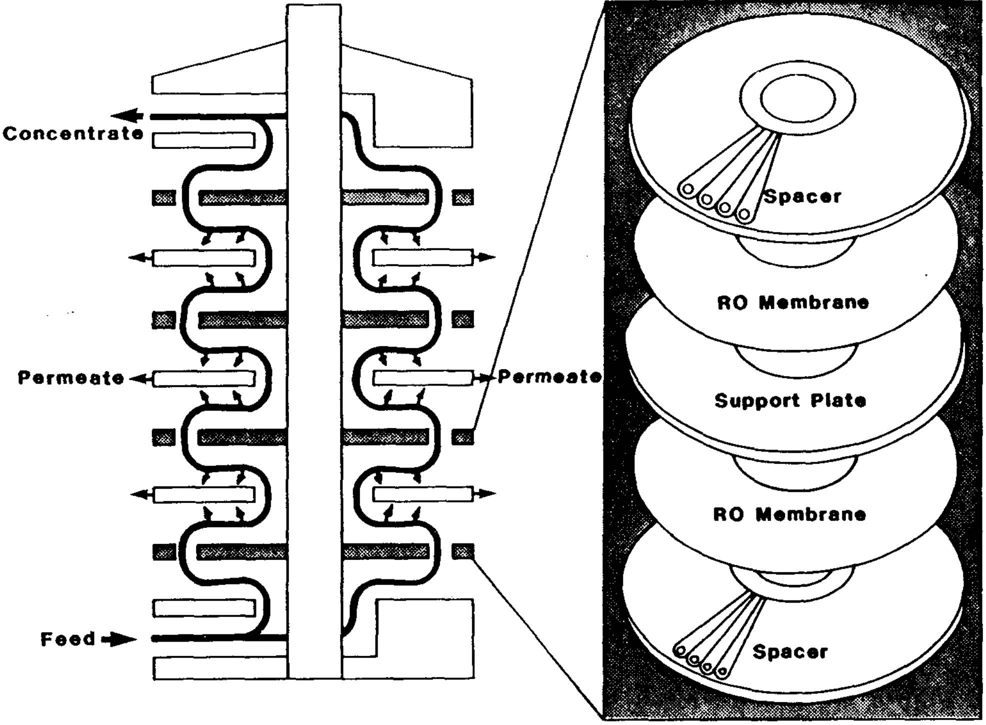


FIGURE 6. Plate and frame reverse osmosis module. (From Advertising brochures, DDS Division, Niro Atomizer, Hudson, Wis. With permission.)

through the membrane. In a typical plate and frame unit, circular spacers, membranes, and support plates are assembled around a hollow central bolt through which the feed is fed via radial ports at pressures from 220 to 1015 $lb_f/in.^2$ (1.5 to 7.0 MPa). As the feed flows through the unit, the spacers divert flow radially across the face of an adjacent membrane. As a result of this contact, water passes through the membrane and is collected in the porous media. Permeate is collected at the outer edge of the support plates.[3]

## E. General Trends on Removal of Contaminants By Reverse Osmosis

Many laboratory studies have been performed to determine the effectiveness of reverse osmosis for the removal of inorganics and organics from water. Highlights of research results that may have some bearing on the treatment of hazardous wastes are presented below.

### *1. Removal of Inorganics*

There is a tremendous amount of data indicating that reverse osmosis is an effective method of removing inorganics from water.[42] It has been found that the rejection of ionized species by reverse osmosis increases as the charge on the ion increases; salts with monovalent ions show poorer rejection than those containing divalent or trivalent anions or cations.[43]

### *2. Removal of Organics*

The degree of organic rejection by reverse osmosis membranes depends on several factors including molecular size, ion charge, solubility of the compound in water and in organic solvents, shape of the molecule, and type of membrane. Nonpolar membranes perform better for treatment of low molecular weight polar organics. For high molecular weight and/or less polar organic compounds, the membrane material is not as important. Cellulose acetate membranes show the least overall rejection of organics, while composite membranes made of polyamide and polyurea are much more effective in limiting molecular penetration of organics due to their highly cross-linked surface structure.[44]

Low molecular weight nonelectrolytes and nonpolar water soluble species with hydrogen bonding capabilities (e.g., alcohols, aldehydes, acids, and amines) are not effectively rejected and tend to pass through the membrane. As the organic molecule becomes larger, more sterically complex, and/or polyfunctional, reverse osmosis membrane rejection increases. Compounds with vapor pressures greater than water are poorly rejected by reverse osmosis membranes and volatile organics are not effectively removed.[44]

Rejections for hydrocarbons and oxygenated organic compounds are discussed in detail below.

### *a. Hydrocarbons*

Rejection of hydrocarbons by cellulose acetate membranes appears to increase with decreasing solubility in water.[45] Compounds with solubilities of less than approximately 100 mg/ℓ (such as polycyclic aromatic hydrocarbons) typically have rejections greater than 90%.[12,46]

For hydrocarbons of equal solubility, rejection decreases in the following order:[12]

$$\text{aromatics} > \text{cyclic compounds} > \text{chain compounds}$$

Benzene has a relatively high solubility and a moderate rejection of about 75% using cellulose acetate membranes.[47] Chain hydrocarbons of the same solubility have lower rejections (approximately 40%).[12] Rejections of toluene and ethylbenzene via cellulose acetate membranes are 72 and 78%, respectively.[47] Reverse osmosis is ineffective for removing trihalomethanes and other halogenated aliphatics.[48,49]

### *b. Oxygenated Compounds*

The degree of ionization is very important in determining the rejection characteristics of a compound. Generally, rejection increases in the pH range over which the species changes from mainly dissolved molecules to mainly ions.[12]

The rejection of nonionizable compounds (such as alcohols) appears to depend mainly on molecular size. Light found that removal efficiencies were high for high molecular weight chemicals (e.g., malathion) and low for small polar chemicals (e.g., formaldehyde and ethanol).[46] Rejections of alcohols by composite membranes range from about 40% for methanol (the smallest alcohol with a molecular mass of 32) to greater than 90% for alcohols greater than propanol (molecular mass 60).[12] (Equivalent rejections for cellulose acetate membranes are 1 to 20%.[50])

## F. Reverse Osmosis Treatment of Hazardous Wastes

### *1. Metal Finishing/Electroplating Waste Water*

One of the major applications of reverse osmosis to hazardous wastes has been the treatment of metal finishing/electroplating rinse waters.[10,51] These wastes are amenable to reverse osmosis for several reasons:[3]

1. Existing reverse osmosis membranes exhibit high rejections for the metallic salts generated during plating operations.
2. The metals in plating waste streams have a high economic value when reused.
3. Conventional treatment and disposal of heavy metal waste streams is expensive and may produce a hazardous sludge.

A typical electroplating operation with a reverse osmosis recovery system is shown in Figure 7. Following immersion in the plating bath, metal parts are passed through a series

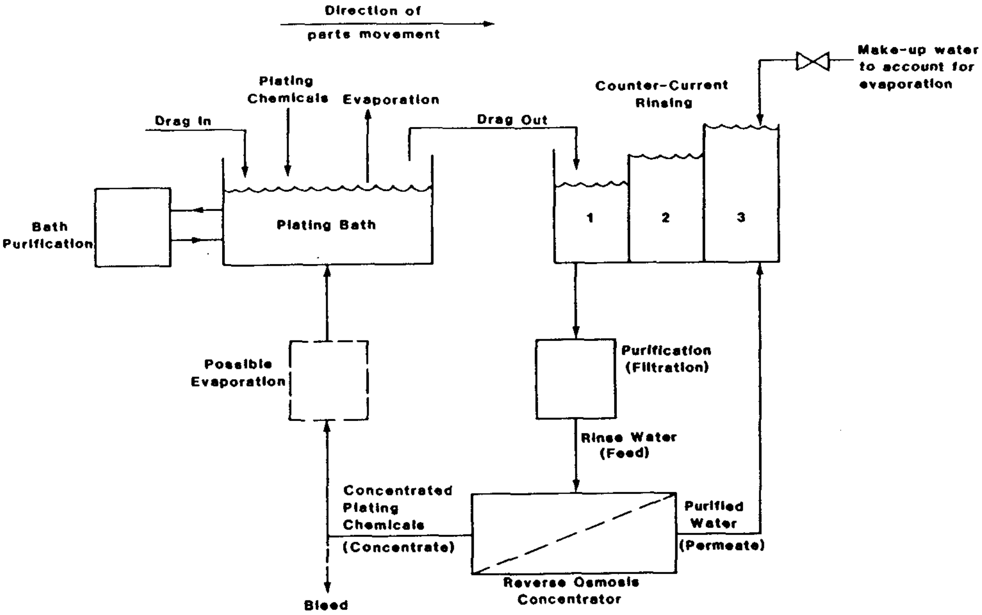


FIGURE 7. Basic flow diagram for a reverse osmosis system treating electroplating rinse water. (From Donnelly, R. G., Goldsmith, R. L., McNulty, K. J., Grant, D. C., and Tan, M., *Treatment of Electroplating Wastes by Reverse Osmosis*, EPA/600/2-76/261 [PB 265393], U.S. Environmental Protection Agency, Cincinnati, 1976, 7. With permission.)

of rinse tanks where the excess plating chemicals are rinsed off. During this process, plating chemicals are "dragged out" into the rinse tanks, which are typically operated in series with the flow of rinse water being countercurrent to the direction of parts movement. In the absence of reverse osmosis recovery, the rinse water from the first tank would typically be routed to disposal. When reverse osmosis is used, the most concentrated rinse water is fed to a reverse osmosis unit. The concentrate from the module is returned to the plating bath, and the permeate is reused in the final rinse tank.

A summary of current reverse osmosis installations that are being used to recover nickel, copper, zinc, brass, and hexavalent chromium from metal plating rinse waters is presented in Table 3. Cellulose acetate, polyamide, and thin-film composite membranes have been used to treat these wastes. The type of membrane required depends on the waste treated; no one membrane can handle all types of electroplating wastes.[51] To date, the only practical configurations for most reverse osmosis applications have been hollow fiber and spiral wound modules. Pretreatment (e.g., a 5 μm ultrafilter) is typically required.[53]

In addition to the applications summarized in Table 3, Thorsen reports use of a reverse osmosis system to recover phosphoric acid from rinse water produced during an aluminum product electrolytic polishing process. During this process, the products are dipped into a polishing bath of concentrated acid and are then rinsed with clean water in subsequent rinse tanks. As a result, acid and metal dragouts are carried over to the rinse water. Reverse osmosis treatment of the rinse waters (pH $< 1.0$) allows the permeate to be recirculated as rinse water. The concentrated acid is reused in the polishing bath. Total acid recovery was 96 to 98% during preliminary tests. Membrane life was expected to be approximately 2000 hours.[54]

Depending on the operating conditions of the plating bath, a zero waste discharge situation may be possible. The feasibility of a closed-loop, zero discharge system depends mainly on the bath temperature, which determines the water evaporation rate. In order to achieve zero

## Table 3
## CHARACTERISTICS OF REVERSE OSMOSIS INSTALLATIONS USED TO TREAT METAL FINISHING RINSE WATERS

| Plating bath | Membranes used | Recovery efficiency | Average membrane life | Other |
|---|---|---|---|---|
| Nickel | Cellulose acetate | 90—97% | 2 years | Payback (based on value of plating salts recovered) averages 18 months; due to the elevated bath temperature (and therefore the high evaporation rate), complete recycling of the concentrate and permeate streams is generally possible |
| Copper sulfate | Hollow fiber polyamide cellulose triacetate and spiral wound thin film composites | NA | 1—3 years | The low temperature of the bath allows only a small portion of the concentrate to be directly reused |
| Copper cyanide (printed circuit board plating) | Polyamide hollow fiber module | 90% | 3 years | Feed rate is 210 gal/hr (795 ℓ/min); 1-μm filter cartridge followed by activated carbon is used for pretreatment; portion of concentrate is recycled to plating bath; remainder is sent to waste treatment system; all of the permeate is reused as rinsewater |
| Copper plating of leaded brass medical devices | Polyamide hollow fiber module | 93% | >4 years | Pretreatment includes a 1.2-μm filter followed by 45-μm filters; about $^1/_2$ of concentrate is recycled to plating bath with the remainder sent to waste treatment system; all of the permeate is reused as rinse water |
| Zinc sulfate | Spiral wound thin film composite | 87.5% | NA | Feed rate is 45 gal/hr (2.8 ℓ/min); concentrate volume is further reduced via evaporation (operating at a 90% recovery rate) prior to return to the bath |
| Brass cyanide | Polyamide and cellulose triacetate hollow fiber modules | 90% | 3—4 years | Feed rate is approximately 60 gal/hr (3.8 ℓ/min). Pretreatment is with 1-μm filter cartridges (polyamide modules) and 3-μm filter cartridges (cellulose triacetate modules) |
| Hexavalent chromium | Spiral wound thin film composite | NA | NA | 5-μm filter cartridge used for pretreatment |

*Note:* NA = not available.

Adapted from Cartwright, P., *Plating Surf. Finish.*, 71, 62, 1984.

discharge, water evaporation from the bath must offset the inflow of permeate from the reverse osmosis system. This is usually the case if the bath temperature is above 130°F (54°F).[3] Rinses from Watts nickel, bright nickel, and nickel sulfamate processes can be treated successfully in a zero discharge system; however, duplex nickel (a semibright nickel) rinse waters cannot.[55] If the bath temperature is not high enough to allow zero discharge, evaporators may be used to concentrate the permeate to bath strength.

### 2. *Treatment of Hazardous Leachate*

Experimental investigations suggest that reverse osmosis may be used successfully to treat hazardous waste leachate. During pilot-scale tests, Rickabaugh et al. found that a spiral wound, polyamide, thin-film composite membrane was superior to a cellulose acetate, spiral wound membrane for removal of low concentrations (ppb range) of chlorinated hydrocarbons and pesticides from leachate.[56] Rejection of contaminants (i.e., 1,3-DCB; 1,2-DCB; 1,3,5-TCB; 1,2,3-TCB; hexachlorobutadiene; hexachlorobenzene; heptachlor; heptachlor epoxide; dieldrin; and endrin) was essentially 100%; concentrations of all compounds in the permeate stream were below detection limits (0.1 to 1.3 ppb, depending on the contaminant). For each pass, approximately 44% of the original volume of leachate was recovered and could be discharged. After three passes, this represented an 83% reduction of the leachate, leaving only 17% requiring disposal.

Pilot plant studies treating hazardous waste leachates with cellulose acetate tubular membranes obtained rejections of dissolved organics (as measured by total organic carbon [TOC] and chemical oxygen demand [COD]) in excess of 50%.[57] These rejections were achieved while treating leachates with average initial concentrations of 8480 mg/ℓ and 17,200 mg/ℓ TOC (26,400 mg/ℓ and 33,100 mg/ℓ COD, respectively). The leachates contained high concentrations of solvents (e.g., benzene, toluene, acetone, and methylene chloride), phenols, amines, chlorinated aromatics, polynuclear aromatics, and pesticides. Pretreatment consisted of lime coagulation followed by pH adjustment.

Chian and DeWalle demonstrated that reverse osmosis can effectively treat sanitary landfill leachate.[58] High rejection of TDS (85 to 99%) was achieved with both cellulose acetate and noncellulose acetate membranes.

Environment Canada has obtained encouraging results when treating landfill leachate containing dichloromethane, acetone, 1,1-dichloroethene, and chloroform with a mobile reverse osmosis unit utilizing spiral wound membranes.[59]

The efficiency of reverse osmosis for the treatment of leachates will depend on the membrane material, the module configuration, and the membrane manufacturer.[2] Whittaker simultaneously tested four thin-film composite, spiral wound membranes made by different manufacturers on landfill leachate. Major differences were reported in the performance of the membranes, particularly with regard to their ability to remove low-molecular weight organics and their susceptibility to fouling.[60]

### 3. *Treatment of Contaminated Ground Water*

Reverse osmosis efficiencies for the treatment of organic and radioactive compounds in ground water using thin film composite membranes are summarized in Table 4.

High percentages of 15 major pesticides were removed from aqueous industrial waste with reverse osmosis.[62] Initial pesticide concentrations ranged from 0.28 to 10.53 ppm. Greater than 99.5% removal of nonpolar pesticides (e.g., chlorinated hydrocarbons and organophosphorous compounds) were reported; removal of more polar pesticides (e.g., randox and atrazine) was less satisfactory. However, it was concluded that a significant fraction of the removal was due to adsorption on the membrane.

Lykins et al. reported 100% removal of aldicarb sulfoxide and aldicarb sulfone from ground water contaminated with agricultural chemicals using hollow fiber, polyamide, re-

### Table 4
### REVERSE OSMOSIS REMOVAL EFFICIENCIES FOR TREATMENT OF ORGANIC AND RADIOACTIVE COMPOUNDS IN GROUND WATER[a]

Excellent Removal Efficiency (70—100%)

| | | |
|---|---|---|
| Carbon tetrachloride | 1,1,1-Trichloroethane | 1,2-Dichloropropane |
| Ethylene dibromide | Trichloroethylene | Chlorobenzene |
| Alachlor | Carbofuran | Radium |
| Uranium | | |

Average Removal Efficiency (30—69%)

| | | |
|---|---|---|
| 1,2-Dichloroethane | o-Dichlorobenzene | |

Poor Removal Efficiency (0—29%)

| | | |
|---|---|---|
| *cis*-1,2-Dichloroethylene | Benzene | Ethylbenzene |

[a] Removal efficiencies were obtained using thin film composite membranes.

From Feige, W. A., Clark, R. M., Lykins, B. W., Jr., and Fronk, C. A., *Treatment of Water from Contaminated Wells*, EPA/600/D-87/011 (PB87146239), U.S. Environmental Protection Agency, Cincinnati, 1987. With permission.

verse osmosis membranes.[63] Removal of 1,2-dichloropropane ranged from 58 to 72%. Rejection of more volatile compounds (e.g., 1,2-dichloropropane) appeared to be more effective with thin film composite membranes rather than hollow fiber polyamide membranes. During full-scale tests, 90% endrin and methoxychlor and 40% lindane were removed from contaminated ground water. (The initial ground water feed contained 0.002 mg/ℓ endrin, 1.0 mg/ℓ methoxychlor, and 0.04 mg/ℓ lindane.)[64] Influent containing 105 μg/ℓ PCBs was also reduced by more than 95% via reverse osmosis.

High removals have been attained for DDT, aldrin, parathion, endrin, chlordane, PCBs, methoxychlor, and malathion. Lindane and related hydrophobic pesticides are not effectively removed by reverse osmosis. Polyamide membranes appear to be more effective than cellulose acetate membranes in removing these compounds.[44]

Reverse osmosis treatment of ground water contaminated with 3.4 to 20.2 pCi/ℓ $^{226}$Ra was demonstrated by Sorg et al.[65] Both hollow fiber and spiral wound cellulose acetate membranes removed 82 to 96% $^{226}$Ra, resulting in a treated water that contained <5 pCi/ℓ.

#### 4. *Environment Canada Mobile Reverse Osmosis Unit*

Environment Canada has been investigating the use of mobile reverse osmosis units for the cleanup of chemical spills, leachates, and waste streams since 1984.[59] The mobile unit, which has a capacity of approximately 528 to 634 gal of permeate per hr (2000 to 2400 ℓ/hr), utilizes 5 to 25 μm prefilters to reduce fouling and may be equipped with spiral wound, tubular, or hollow fiber elements. The unit's capacity for cleanup varies with the membrane used and the types and concentrations of chemicals treated. Rejection efficiencies of four types of spiral wound reverse osmosis membranes on frequently spilled chemicals treated by the Environment Canada mobile unit were reported by Whittaker.[60] These short-term results indicate that reverse osmosis can be used successfully to remove many commonly spilled chemicals, such as benzene (1000 ppm), ferric chloride (550 ppm), formaldehyde (790 ppm), zinc sulfate (640 ppm), ammonium nitrate (790 ppm), and 2,4-D (220 ppm), from aqueous solutions.

Summaries of the mobile reverse osmosis unit's ability to treat wood preservative spills, PCB-contaminated ground water, and pesticide-contaminated runoff are presented below.

### *a. Wood Preservative Spills*

Two wood preservative spills have been successfully remediated with a mobile reverse osmosis unit:[59]

1. A cleanup of over 68,690 gal (260,000 ℓ) of contaminated water containing 100 to 2200 ppm total chlorophenols was accomplished. Initially, feeds of 510 and 1655 ppm total chlorophenols resulted in permeates of 14.5 and 23 ppb, respectively, representing rejections exceeding 99.99%. These rejections dropped somewhat during processing, but remained at 98.9% or better. High fluxes were also experienced. The cleanup lasted approximately 4 weeks.
2. A cleanup of contaminated water containing sodium tetra and penta chlorophenate (3 to 700 ppm chlorophenols) and paraffin waxes was accomplished. During processing of the more highly concentrated solutions, the permeate flow rate dropped dramatically and treatment was halted. The decreased flux was attributed to the presence of paraffin wax in the feed. Further reverse osmosis treatment was attempted by a private contractor who lowered the pH to remove the wax, filtered the solution, raised the pH, and then treated the resulting solution with reverse osmosis. Over 41,480 gal (157,000 ℓ) were treated in this manner; 7930 gal (30,000 ℓ) of concentrated solution were recovered for disposal and 33,550 gal (127,000 ℓ) of permeate were discharged into the sanitary sewer system.

### *b. PCB-Contaminated Ground Water*

Environment Canada's mobile reverse osmosis unit has also been tested on ground water containing approximately 24 ppb PCBs. During initial treatment, concentrate and permeate flux rates dropped steadily due to membrane scaling caused by the high inorganic content of the ground water. The ground water was acidified to a pH of 4.5 to 5.5 (by adding 30% HCl to the feed tank) to alleviate this problem. During the 7-day trial, 11,360 gal (43,000 ℓ) of contaminated ground water were processed, yielding 790 gal (3000 ℓ) of concentrate and 10,570 gal (40,000 ℓ) of permeate with a PCB concentration of less than 0.27 ppb.[59]

### *c. Pesticide-Contaminated Runoff*

Contaminated runoff resulting from a fire at a pesticide warehouse was also treated successfully with a mobile "lab-scale" reverse osmosis unit. During the test, water containing 264 ppb aldicarb, 323 ppb carbofuran, 8867 ppm atrazine, and 1507 ppm butylate was treated. Prior to reverse osmosis treatment, the pesticide-contaminated water was treated with alum to remove suspended solids. The supernatant was fed to the reverse osmosis membranes at a rate of 2.1 to 2.6 gpm (8 to 10 ℓ/min). A volume reduction ratio of 6 to 10:1 resulted, and the concentrate was further treated with a small carbon adsorption system. About 25,100 gal (95,000 ℓ) of contaminated water were treated and reduced to 111 gal (420 ℓ) of spent carbon, 290 gal (1,100 ℓ) of concentrate, and 158 gal (600 ℓ) of precipitated solids and tank-bottom sludge. The reverse osmosis permeate contained 2.9 ppb aldicarb, 8.6 ppb carbofuran, 30.3 ppm atrazine, and 22.9 ppb butylate. (These concentrations were further reduced during activated carbon treatment.)[59]

### *5. Other Applications*

Reverse osmosis may be used to concentrate ferrocyanide, thiosulfate, and silver salts from photographic processing rinse waters, which typically contain 30 ppm silver. Following reverse osmosis treatment, the concentrated silver can be easily recovered by electrolytic treatment.[6]

### Table 5
### TEST PROCEDURES FOR EVALUATING THE FEASIBILITY OF APPLYING MEMBRANE SEPARATION TECHNOLOGIES TO SPECIFIC WASTE STREAMS

| Type of test | Test procedure | Advantages | Disadvantages |
|---|---|---|---|
| Cell test | Crossflow exposure of small pieces of membrane to test solution; effective for quick evaluation of different membrane polymers | Fast, inexpensive, small quantities of test solution required | Cannot be used to determine long-term chemical effects of solution on membrane; does not provide engineering scale-up data; does not indicate optimum membrane configuration; data on fouling effects not provided |
| Applications test | Exposes 30 to 50 gal sample to production-sized membrane mounted in a test apparatus for 1 to 2 hr | Fast; provides scale-up data (flow, element efficiency, osmotic pressure as a function of recovery, and pressure requirements); gives an indication of membrane stability | Long-term chemical and fouling effects not evaluated |
| Pilot test | Test apparatus (such as that used in the applications test) placed in the process operating on a "sidestream" for at least 30 d | Provides the same data as an applications test; long-term membrane fouling and stability data available | Expensive due to monitoring and time required |

Adapted from Cartwright, P. S., *Desalination*, 56, 17, 1985.

The feasibility of using thin film composite reverse osmosis membranes for treatment of oil shale retort water (containing high concentrations of sulfide, ammonia, chloride, and low to moderate concentrations of phenols, hydrocarbons, polyaromatics, organic acids, etc.) has been demonstrated.[33]

Reverse osmosis has been used to recover up to 90% of the water from textile effluents. The permeate may be reused in scouring, bleaching, dyeing, and finishing processes.[12]

### G. Test Procedures for Evaluation of Specific Waste Streams

The feasibility of using reverse osmosis to treat a specific waste stream is dependent on several variables, including membrane type, concentration of dissolved solids, temperature of the feed solution, and applied pressure. Since the composition of each waste stream is different, it is impossible to predict the performance of reverse osmosis treatment without performing initial tests on the waste stream.[14] Testing will also determine which membrane material is chemically compatible with the treated waste stream. The three types of test procedures available for determining the feasibility of reverse osmosis treatment (i.e., cell tests, applications tests, and pilot tests) are summarized in Table 5.[6] The advantages and disadvantages of each test are also provided.

McCoy and Associates, Inc. has compiled a list of manufacturers of membrane separation products suitable for hazardous waste management applications.[3]

## IV. ULTRAFILTRATION

Ultrafiltration is similar to reverse osmosis in that it is a pressure-driven membrane separation technology. However, ultrafiltration systems operate at lower pressures than reverse osmosis units and remove only high molecular weight compounds. Unlike reverse osmosis, ultrafiltration is not capable of removing ionic compounds.

In ultrafiltration systems, the semipermeable membrane retains materials based solely on size, shape, and molecule flexibility.[4] As a feed solution is pumped through a membrane module at pressures typically between 10 to 100 lb$_f$/in.$^2$ (69 to 690 kPa), the membrane acts as a sieve to retain dissolved and suspended nonionic materials that are physically too large to pass through its pores.[8] The retained materials (concentrate) exit the module separately from the purified solvent (permeate). In theory, ultrafiltration is like ordinary filtration except that very small particles (10 to 100 Å) are retained by the membrane.[10,12]

### A. Ultrafiltration Performance Factors

The primary measure of ultrafiltration membrane performance is flux rate (i.e., the rate of flow through an ultrafiltration membrane).[66] Flux can be calculated using the following equation:[8]

$$Q_w = (KA/t)\Delta P \tag{6}$$

where $Q_w$ = flow rate through the membrane; K = membrane permeability constant; A = membrane area; t = membrane thickness; and $\Delta P$ = hydraulic pressure differential across the membrane.

Isooka et al. suggest that there is a correlation between the viscosity of industrial solvent waste streams and ultrafiltration membrane flux.[67] Generally, when the viscosity is greater than 30 to 40 cp, the flux rate falls to unacceptably low values.

### B. Concentration Polarization and Fouling

Like reverse osmosis, ultrafiltration performance may be reduced due to concentration polarization, fouling, and other factors.[8] In fact, concentration polarization is more of a problem in ultrafiltration systems than in reverse osmosis systems. This is due to the nature of the solutions treated by ultrafiltration; the technology is often used to separate organic components from water. These organic materials have smaller diffusion constants, which limit diffusion of materials retained by the membrane back into the liquid.[3]

The effects of concentration polarization may be minimized by:[68]

1. Operating at higher feed velocities since high velocity turbulent flow shears off some of the polarization gel layer;
2. Increasing treatment temperature; and/or
3. Choosing a membrane module design that is not susceptible to concentration polarization and fouling. (Further details on the fouling potential of specific ultrafiltration membrane modules are provided later.)

The nature and causes of ultrafiltration membrane fouling and methods for controlling this problem have been described by Fane and Fell.[69]

When membrane fouling is expected, some method of chemical cleaning is usually used in conjunction with mechanical cleaning, flushing, or backwashing. If strong chemical agents are to be used, it is important to select membrane materials that will withstand repeated cleaning. For example, polysulfone and zirconium (IV) oxide can tolerate high temperatures and strong chemicals over a wide pH range.[4]

### C. Ultrafiltration Membranes

Ultrafiltration membranes have an asymmetric structure consisting of an extremely thin surface layer (0.1 to 1.0 μm thick) supported by a thicker spongy substructure about 100

Table 6
POLYMERS USED TO MANUFACTURE ULTRAFILTRATION MEMBRANES

| Polymer | Molecular weight cutoff range | pH limits | Maximum operating temperature (°C) | Cl resistance | Organic solvent resistance |
|---|---|---|---|---|---|
| Cellulose acetate | 1,000—50,000 | 3.5—7 | 35 | Good | Poor |
| Polysulfone | 5,000—50,000 | 0—14 | 100 | Good | Fair |
| Aromatic polyamides | 1,000—50,000 | 2—12 | 80 | Poor | Fair |
| Polyacrylonitrile-poly-(vinyl chloride) copolymers | 30,000—100,000 | 2—12 | 50 | Fair | Fair |

From Strathmann, H., *Synthetic Membrane Processes — Fundamentals and Water Applications,* Belfort, G., Ed., Academic Press, Orlando, Fla., 1984, 346. With permission.

μm thick.[3,70] The retention capability of these membranes is described in terms of molecular weight cutoff (i.e., the molecular weight of the solute that is too large to pass through the pores). Commercially available membranes are capable of removing molecules with molecular weights between 500 and 1 million.[3] It is important to keep in mind that the term "molecular weight cutoff" tends to be misleading since solute passage is determined not only by a molecule's size, but by its shape and charge distribution as well.[4]

Ultrafiltration membranes are made from a wider selection of polymers than reverse osmosis membranes.[51] The most widely used membrane materials are cellulose acetate, polysulfones, various aromatic polyamides, and polyacrylonitrile-poly(vinyl chloride) copolymers.[71] The characteristics of these membranes are summarized in Table 6. The kind of ultrafiltration membrane used will depend on the type of waste to be treated.

## D. Module Designs

For the successful application of ultrafiltration, the design of the module used to contain the membrane is as important as the selection of the proper membrane material.[71] Several types of ultrafiltration membrane module designs are available: (1) tubular, (2) hollow fiber, (3) spiral wound, and (4) plate and frame. Table 7 compares the characteristics of these module configurations.

### *1. Tubular Ultrafiltration Modules*

The tubular membrane module was first developed for use in reverse osmosis systems (see Figure 3). Today, the design is not used extensively for reverse osmosis due to high capital and operating costs. However, it is still widely used in ultrafiltration applications because it is capable of treating solutions with high suspended solids and is easily cleaned.[71] In addition, high flow velocities may be obtained to create turbulent conditions and consequently decrease fouling.[4] Disadvantages include high capital and operating costs and small membrane surface per unit volume.[3]

### *2. Hollow Fiber Ultrafiltration Modules*

Ultrafiltration hollow fiber modules differ completely in design and operation from reverse osmosis hollow fiber units.[51] In ultrafiltration, the membrane skin is formed on the inside of the hollow fiber so that feedwater passes through the bore and product water permeates outward through the support structure. In reverse osmosis, the membrane skin is on the outside of the hollow fiber and product water flows into the fiber bore.[2]

A typical ultrafiltration hollow fiber module is made of acrylic copolymer and has a 0.1-μm skin on the inside supported by a spongy outer structure.[8] Inside diameters of the fibers

Table 7
CHARACTERISTICS OF ULTRAFILTRATION MEMBRANE MODULE CONFIGURATIONS

| Module type | Membrane surface per module ($m^2/m^3$) | Capital cost | Operating cost | Flow control | Ease of cleaning in place |
|---|---|---|---|---|---|
| Tubular | 25—50 | High | High | Good | Good |
| Plate and frame | 400—600 | High | Low | Fair | Poor |
| Spiral wound | 800—1,000 | Very low | Low | Poor | Poor |
| Hollow fiber | 600—1,200 | Low | Low | Good | Fair |

From Strathmann, H., *Synthetic Membrane Processes — Fundamentals and Water Applications*, Belfort, G., Ed., Academic Press, Orlando, Fla., 1984, 349. With permission.

range from 500 μm (low fouling situations) to 1100 μm (high fouling applications), about 10 to 30 times larger than reverse osmosis hollow fibers.[12]

A schematic design of an ultrafiltration hollow fiber module is presented in Figure 8. As shown, the fibers are aligned in a parallel fashion and potted in epoxy on either end inside a low-pressure vessel. The vessel is approximately 43 in. (109 cm) long and 3 in. (7.6 cm) in diameter. During operation, the feed flows down the center of the fibers. The filtrate, consisting of low molecular weight solutes and water, permeates the wall of the fibers and is removed via a product port. The concentrate continues to flow through the fibers and is removed at the other end of the vessel.[8]

The advantages of the hollow fiber module are that it is compact with a very good membrane surface to volume ratio, allows good feed flow control, and is economical. Unfortunately, the design is very susceptible to plugging by particulates and is difficult to clean. Therefore, pretreatment of the feed solution is always necessary.[71]

### 3. *Spiral Wound Ultrafiltration Modules*

The design of a spiral wound ultrafiltration module is similar to that of the reverse-osmosis spiral wound module (Figure 5). Due to its greater membrane area, the module can treat large volumes more economically than the tubular module.[8] However, it is more vulnerable to fouling, and severe membrane fouling occurs even with solutions containing only moderate concentrations of suspended solids.[4,71] Therefore, the use of the spiral wound membrane module in ultrafiltration is limited.[71] Also, it cannot be cleaned mechanically; chemical cleaning and flushing must be used.[8]

### 4. *Plate and Frame Ultrafiltration Modules*

As shown in Figure 9, ultrafiltration plate and frame modules consist of membrane-covered support plates stacked horizontally in a frame apparatus. When the plates are hydraulically compressed, holes in the membrane-covered plates form feed/concentrate flow channels within the module. As the feed flows between the membrane-covered plates, permeate exits via the support plates and is collected at the top of the module. The remaining liquid continues to flow through the module for further treatment. Concentrate leaves the module end opposite the feed intake. Internal flow within the module may be arranged in a combination of parallel and series flow patterns by using section plates. Plate and frame modules typically operate at pressures up to 145 $lb_f/in.^2$ (999 kPa).[3]

Plate and frame modules provide a large membrane surface to volume ratio. In addition, they generally have lower capital and operating costs than tubular modules. On the other hand, the feed flow channels are susceptible to plugging, especially when solutions containing

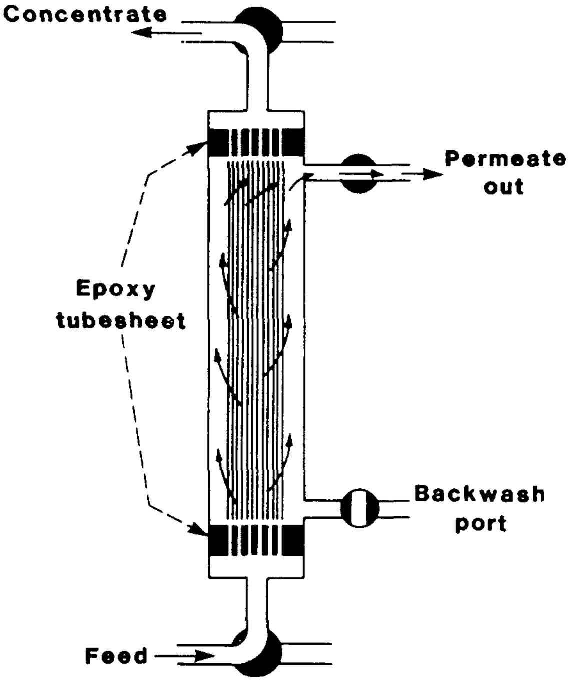


FIGURE 8. Hollow fiber ultrafiltration module. (From Applegate, L. E., *Chem. Eng.*, 91, 86, 1984. With permission.)

high suspended solids are treated. It is usually possible to dismantle and mechanically clean the membranes, but it is a time-consuming process.[71]

### E. Applications of Ultrafiltration

Ultrafiltration is currently being used on a commercial scale to

1. Concentrate paint wastes
2. Concentrate oily wastes from metal finishing, can forming, aluminum and steel coil cleaning, and metal machining and rolling rinse waters
3. Remove toxic metals from metal finishing waste water
4. Treat rinse waters from alkaline metal cleaning baths
5. Treat industrial laundry waste waters
6. Concentrate solvent/ink wastes generated during printing operations

These applications are described in the following discussion. (Although it is not commercially viable yet, the treatment of hazardous waste leachates is also discussed.)

#### *1. Treatment of Paint Wastes*

Ultrafiltration has been used to successfully recover electrophoretic paints from rinse waters generated in the automobile and household appliance industries. These wastes are generated from an electrophoretic coating (electropainting) process, during which a paint film is applied to a metallic surface by passing an electric current through a water bath. When the painted products emerge from the electropainting tank, they drag out excess paint which is removed by rinsing with water. The rinse waters contain 1 to 2% paint, which can be recovered for reuse in the process via ultrafiltration; the purified water is also recycled

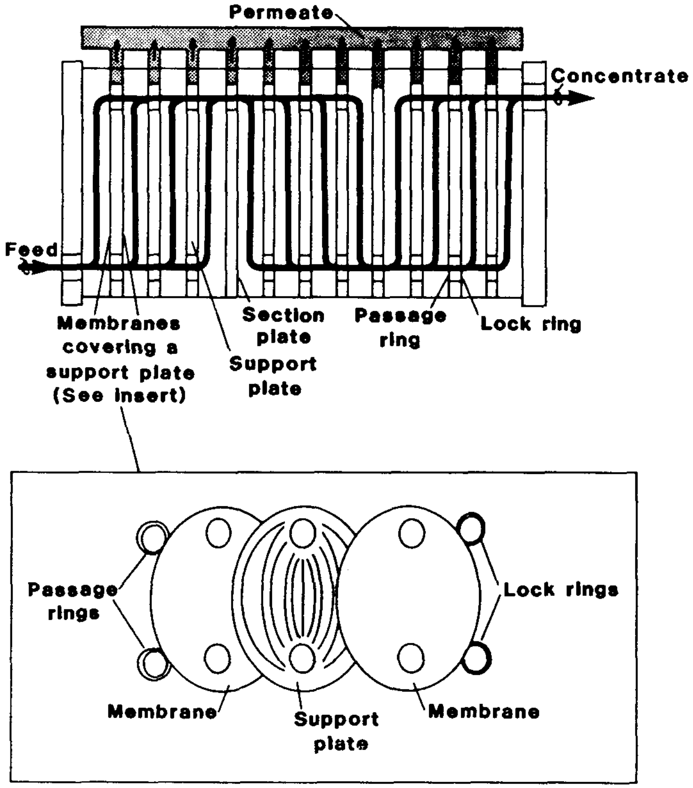


FIGURE 9. Plate and frame ultrafiltration module. (From Advertising brochures, DDS Division, Niro Atomizer, Hudson, Wis. With permission.)

this manner. Typically, tubular modules with cellulose acetate membranes are used in these applications. The average membrane life is more than 2 years.[71]

Solvent/paint waste streams from automated paint spraying operations may also be treated using ultrafiltration. These types of wastes are typically generated when the paint color is changed and the lines are cleaned with paint solvent to flush out the old paint. An automobile manufacturing plant, which installed an ultrafiltration system to recycle paint cleaning solvent, reported a payback period of only 5.3 months due to savings in waste disposal and fresh solvent costs.[67] However, low fluxes were encountered because paint solutions typically contain high levels of dissolved polymers which form a gummy, gel-like layer on the membrane surface. This layer is difficult to hydrodynamically remove and also has a low permeability.

### 2. *Recovery of Oily Wastes*

Ultrafiltration has proved to be a viable method for the treatment of emulsified oils used as coolants and lubricants in machining operations. Waste oils (about 3 to 5% oil) can typically be concentrated so that the oil can be directly reused in the process, and the permeate can be reused as a rinsing solution. If desired, the oil emulsion may be concentrated further with ultrafiltration (up to 40 to 50%) so that it can be incinerated. Fluxes are usually between 20 and 30 gal/ft$^2$/day (0.8 and 1.2 m$^3$/m$^2$/day) with permeate concentrations less than 250 mg/$\ell$.[12] This process is widely used in metal processing plants, particularly automobile plants and tin can manufacturers.[71]

According to Cartwright, ultrafiltration systems processing oily wastes are currently operating on waste water flows from 300 to 100,000 gal/day (1140 to 379,000 ℓ/day).[72] Operating pressures are usually between 50 and 100 $lb_f$/in.$^2$ (0.34 and 0.69 MPa). A survey of over 200 operating systems indicated that operating costs can range from $2.00 to $7.60 per thousand gallons of waste treated ($0.53 to $2.01 per meter$^3$). Membrane modules last $1^1/_2$ to 3 years before replacement is necessary.[72]

Use of a combined ultrafiltration/reverse osmosis to treat oily wastes from an aluminum rolling process was described by Sonksen et al.[66] During the rolling process, an oil-water emulsion is used as a coolant for the rolls and metal, a lubricant to decrease horsepower losses due to friction, and a cleaning solution. The resulting wastes have an oil concentration varying from 0.5 to 5%. In this treatment scheme, ultrafiltration was used to remove oil and suspended materials from oily wastes (100,000 gal/day or 378,500 ℓ/day) prior to reverse osmosis polishing. The end product was an almost deionized quality water. The most significant problem encountered was rapid, frequent fouling of the tubular ultrafiltration membranes; the membranes had to be cleaned every day.

Paulson et al. described a combined ultrafiltration/reverse osmosis system used to concentrate oily rinse waters generated by an aluminum can manufacturer.[73] In this system, the rinse water is filtered prior to ultrafiltration to remove metal fines. Following ultrafiltration, the concentrate is used as a fuel and the permeate is sent to a reverse osmosis unit for further concentration. The reverse osmosis permeate is reused in the process as rinse water and the concentrate (10% of the total waste stream) is sent offsite for disposal. The entire system is designed to handle 20 gal/min on a 20 hr/day basis. The total installed cost of the waste treatment system was under $300,000. A payback period of less than 1 year was reported due to over $400,000 per year in disposal cost savings. The operating cost for the entire system is $0.005 per gallon ($0.001 per liter).

### 3. *Electroplating Waste Waters*

Ultrafiltration is a proven technology in the electroplating industry.[51] An example of a chemical treatment/ultrafiltration system used to pretreat metal finishing waste water prior to discharge to the municipal sewer was described by Roush.[74] The most common contaminants in the waste water were copper and chromium.

The continuous flow treatment process includes: (1) chemical reduction with sodium metabisulfite ($Na_2S_2O_5$) to reduce hexavalent chromium to the trivalent state, (2) addition of NaOH to precipitate metal hydroxides, (3) addition of 5% dithiocarbamate solution to precipitate any remaining soluble complexed metals, and (4) ultrafiltration using tubular membrane modules. During a 22-day test period, approximately 93,000 gal (352,000 ℓ) of waste water were treated with average influent concentrations of 83.0 ppm copper and 43.8 ppm chromium. The ultrafiltration permeate contained an average of 0.7 ppm chromium (99.1% removal) and 0.2 ppm copper (99.6% removal). Membrane fouling by gelatinous metal hydroxide precipitates made it difficult to maintain the recommended permeate flow rate of 5 to 6 gal/min (19 to 23 ℓ/min). Cleaning the membranes with sodium hypochlorite increased the flow rate temporarily. The cost of treatment was about $47 per 1000 gal of metal finishing waste water ($12.40 per meter$^3$).[74]

### 4. *Treatment of Rinse Waters From Alkaline Metal Cleaning Baths*

Strathmann reports that rinse waters containing dragout from alkaline baths used to clean greasy or dirty metal parts may be treated with ultrafiltration to concentrate the impurities (e.g., mineral oil and grease) for disposal while recovering the water for reuse.[71] In these situations, polyamide or polysulfone membranes are usually used because they can withstand the elevated temperatures and strong alkaline conditions present in these rinse waters.

### 5. *Industrial Laundry Waste Waters*

via a combined activated carbon/ultrafiltration treatment system preceded by lime coagulation/flocculation and settling.[75] A full-scale system achieved high flux rates (300 to 400 gal/ft$^2$/day; 12 to 16 m$^3$/m$^2$/day) at a relatively low pumping pressure of 40 lb/in.$^2$ (276 kPa). Reductions in suspended solids and freon-extractable oils and greases were >90%. Satisfactory removal of metals and organics was also obtained.

### 6. *Printing Wastes*

During printing operations, solvent wastes containing ink are generated. Ultrafiltration can be used to achieve clean separation of the solvent from ink and other contaminants. The flux rates obtained during treatment of these wastes are usually quite high due to the nonfouling nature of the ink pigments (i.e., they contain relatively little dissolved polymer). For this application, tubular modules with polyamide membranes have been used.[67]

### 7. *Hazardous Leachates*

Ultrafiltration has not yet been applied to the full-scale treatment of hazardous waste leachate. However, as membranes exhibiting greater productivity and chemical resistance are developed, ultrafiltration will probably become a more viable alternative for leachate treatment.[2]

During lab-scale investigations, Syzdek and Ahlert treated hazardous waste leachate (14,000 to 17,000 mg/ℓ TOC and 16,500 to 20,000 mg/ℓ TDS) with membranes have molecular weight cutoffs of 2000, 10,000, 30,000, 50,000, 100,000, and 300,000.[76] With the exception of the 50,000 and 300,000 molecular weight membranes, flux remained constant. The rapid flux decrease experienced with the two membranes was associated with fouling caused by high molecular weight suspended and colloidal matter.

## V. ELECTRODIALYSIS

Instead of driving pure water through a membrane and leaving contaminants behind, as in the case of reverse osmosis and ultrafiltration, electrodialysis is a process in which ions are selectively transported through semipermeable membranes from one solution to another under the influence of a direct current electrical field. A schematic diagram of a typical electrodialysis cell is shown in Figure 10. As shown, membranes selective to cations (such as sodium, calcium, and magnesium) are alternated with membranes selective to anions (such as chloride, sulfate, and bicarbonate). This multicompartment electrodialysis process using ion-selective membranes was suggested by Meyer and Strauss in 1940.[77] In this design, when a direct current is applied to the electrodes, all cations (positively charged ions) migrate towards the cathode. They are able to penetrate the cation-selective membranes, but not the anion-selective membranes. In a similar fashion, all anions (negatively charged ions) migrating towards the anode can pass through the anion-permeable membranes, but not the cation-permeable membranes. As a result, alternate compartments are formed in which the ionic concentration is greater or less than the concentration in the feed solution. By manifolding the appropriate compartments, product water (low electrolyte concentration) and brine (high electrolyte concentration) are collected.

### A. Electrodialysis Membranes

The first electrodialysis membranes that had high ion selectivity, low electrical resistance, adequate mechanical strength, and good chemical stability were developed in 1950.[78] Until that time, the membranes utilized for electrodialysis research (e.g., parchment, clay, and cellophane) had not been commercially feasible.[5] Modern electrodialysis membranes are porous, sheet-like, structural matrixes made of synthetic ion exchange resins. They look like a sheet of plastic which is usually yellow to brown in color.[79] Cation-permeable mem-

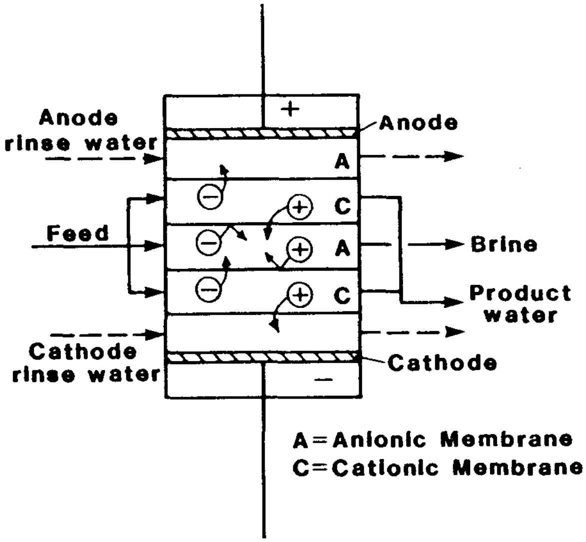


FIGURE 10. A typical electrodialysis cell. (From McCoy and Associates, *The Hazardous Waste Consultant,* 3, 4, 1985. With permission.)

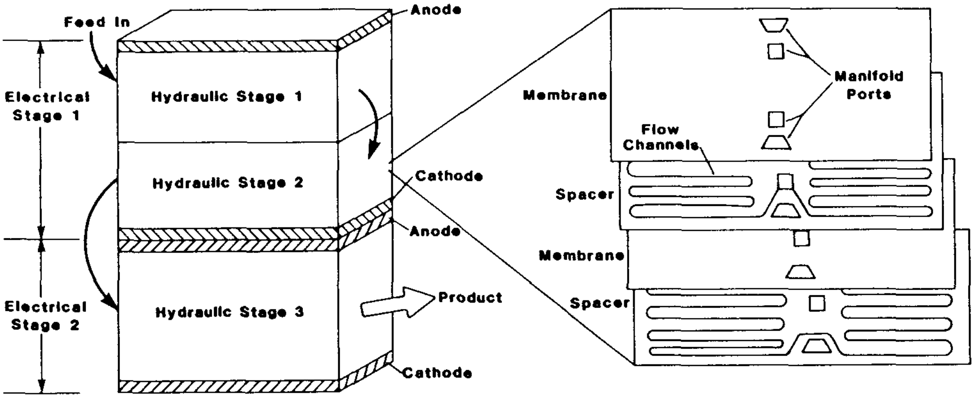


FIGURE 11. An electrodialysis stack. (From McCoy and Associates, *The Hazardous Waste Consultant,* 3, 4, 1985. With permission.)

branes are typically made of cross-linked polystyrene containing sulfonate groups ($-SO_3$). Anion-permeable membranes usually consist of cross-linked polystyrene containing quaternary ammonium groups ($-NR_3+$).[8]

Commercial ion-selective membranes are between 0.15 and 0.6 mm thick and have electrical resistances that range from 3 to 20 $\Omega/cm^2$ (at room temperature in equilibrium with 0.5 N sodium chloride solutions). Electrical resistance is higher in more dilute solutions. It also decreases with increasing temperature at a rate of about 1.8% per degree Celsius.[80]

## B. Design of an Electrodialysis Stack

As shown in Figure 11, electrodialysis units (called stacks) may contain hundreds of electrodialysis cells placed between the electrodes, resulting in hundreds of feed/product streams and brine streams.[8] The number of cells required will depend on the electrodialysis capacity required, the uniformity of flow distribution among the compartments of the same

The membrane sheets in a stack are separated from each other by spacer gaskets that form compartments through which fluids can pass. The spacers also promote turbulence and thus reduce membrane fouling. Internal manifolds distribute the feed to the proper compartment and remove the product and brine streams.[8]

There are two basic spacer designs: (1) tortuous path and (2) sheet flow.[81] The tortuous path configuration has been developed to provide greater turbulence and better control of flow patterns. In this design, feedwater is forced to flow in a zig-zag pattern along the membrane surface, thus creating increased turbidity to prevent fouling.[4] Sheet flow configurations are operated at lower flow velocities and are designed to provide a fairly even flow distribution.[4,79]

It is usually not feasible to operate an electrodialysis unit so that the desired change in salt concentration is obtained in one pass through the stack. A single pass through an electrodialysis cell will typically remove 30 to 50% of the salt.[79] If a greater degree of salt removal is desired, the feed must be routed through a second stage in series.[3] Three common modes of operation include:[79]

1. Continuous operation — the output from one stage is fed directly to the inlet of the next stage until the desired concentration is obtained.
2. Batch operation — the product is recycled to a feed reservoir, which is periodically treated to the required concentration.
3. Feed-and-bleed operation — the output of the unit is recycled directly to the inlet in such a flow ratio that a product of desired quality is obtained at the outlet of the unit.

Electrodialysis plants typically operate at 50 to 90% conversion (i.e., 50 to 90% of the feed stream is recovered as product water). They can operate over a broad pH (1 to 13) and temperature range (up to 109°F; 43°C). As the temperature increases, the electrical resistance and consequently the power consumption decreases. The pressure of the feed and brine streams ranges from 40 to 60 $lb_f/in.^2$ (276 to 413 kPa).[8]

Applegate and Reynolds describe equations that may be used to calculate electrodialysis performance variables (e.g., energy consumption, electric current requirements, and membrane area requirements).[8,11]

## C. Fouling of Electrodialysis Membranes

Electrodialysis membranes are susceptible to fouling by calcium carbonate; barium, calcium, and strontium sulfates; iron (+3) oxides; manganese dioxide; colloids; microorganisms; and organic chemicals.[3,81] Fouling (apparently caused by the local pH shift that occurs on the brine side of the membrane) increases the voltage drop across the stack and consequently increases energy consumption.[5] When the increased voltage drop reaches a certain point, the stack must be taken apart so that the membranes can be mechanically cleaned. Scaling and fouling may be reduced via pretreatment (e.g., coagulation, settling, filtration, and activated carbon adsorption) and/or by the addition of a small amount of acid to the feed stream. Organic fouling may be reduced by cleaning the membranes with an enzyme detergent solution.[11]

## D. Electrodialysis-Reversal Process

Around 1970, the electrodialysis-reversal process (EDR) was developed to overcome fouling and membrane scaling problems associated with the conventional electrodialysis process.[80,82] During EDR, the polarity of the electrodes is periodically reversed (i.e., the cathode becomes the anode and vice versa) to redissolve deposits that are present on the membrane.[8] Consequently, membranes that can function in either the anion or cation selective mode must be used.

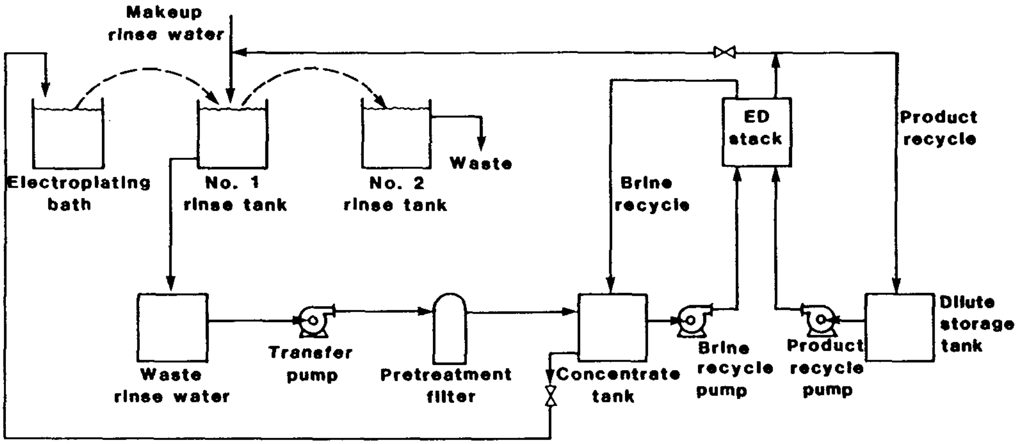


FIGURE 12. Electrodialysis system for treating electroplating rinse water. (From Applegate, L. E., *Chem. Eng.*, 91, 83, 1984. With permission.)

The EDR process differs from conventional electrodialysis in the following ways:[8]

1. The direction of the direct current field is reversed up to 3 to 4 times per hour by switching the polarity of the electrodes. This immediately begins converting the feed/product stream to the brine stream, and vice versa, by reversing the flow direction of the ions. In this fashion, any buildup of precipitated salts is dissolved and carried away when the cycle reverses.
2. Automatic valves change the feed/product stream to the brine compartments and switch the brine stream discharge to the feed/product compartments.
3. For approximately 1 to 2 min, both streams are automatically diverted as waste due to their high salinity. When the desired product conductivity is obtained, the product stream is automatically diverted to product storage.

This process disperses polarization films, reduces slime and colloid fouling, and flushes scaling deposits out of the electrodialysis system.[8] To be effective, the polarity reversal has to be frequent enough to avoid the accumulation of heavy scale, and it must be supplemented with regular chemical cleaning.[81] Because of the overall increased performance characteristics of the EDR process, nearly all new installations utilize this technology.[3,8,80]

### E. Electrodialysis Treatment of Hazardous Wastes

Since electrodialysis is only capable of removing ionic species, its greatest potential market is probably the metal finishing/electroplating industry.[3] Figure 12 is a flow diagram of an electrodialysis system used to treat rinse water from a nickel galvanization process. Nickel-contaminated rinse water from the No. 1 rinse tank is pumped through a pretreatment filter. (If organic electrolytes are used in the plating bath, an activated carbon filter is necessary to prevent membrane fouling. Otherwise, a normal prefilter can be used). The brine leaving the electrodialysis stack is recycled to the feed until the desired concentration of nickel in the concentrate is obtained. Chemicals from the concentrate tank are recycled to the plating bath and product water is recycled to the rinse tanks. Overall conversion is usually around 90%. Nickel salt concentrations in the feed, concentrate, and product streams during operation of this system are 14,280 mg/ℓ, 163,100 mg/ℓ, and 1309 mg/ℓ, respectively.[83]

EDR has been used to remove and concentrate over 99% nickel from Watts nickel plating rinse water.[84] Based on a capital cost of $50,000 and an annual savings of $29,100, the paypack on the treatment system was estimated at 1.9 years. Silver cyanide from a silver plating operation has also been recovered using EDR.[84] During treatment of rinse water containing 250 mg/ℓ AgCN at a feed rate of 2.3 gal/min (8.7 ℓ/min), the system recovers 4.15 oz of AgCN per hour. Payback was less than 8 months due to the recovery of over $80,000 worth of AgCN per year. EDR has also been successfully applied in the recovery of cadmium, copper, silver, and zinc.[84] Itoi reported test results of electrodialysis treatment of cyanide galvanization rinse waters containing 120,000 mg/ℓ CuCN and 135,000 mg/ℓ NaCN.[83] First stage permeate contained 520 ppm cyanide, and the concentrate contained 36,000 ppm cyanide.

Electrodialysis can be used to recover hydrochloric and sulfuric acid from acidic waste waters generated by the iron and steel industry.[85] It is believed that electrodialysis treatment allowing reuse of the acids is less expensive than conventional neutralization treatment techniques.

## VI. ECONOMICS OF REVERSE OSMOSIS, ULTRAFILTRATION, AND ELECTRODIALYSIS

The economic feasibility of membrane separation is one of the major factors that determines whether these technologies will be applied in hazardous waste treatment applications. Although costs depend on site-specific conditions, the following factors should be taken into account when performing an economic analysis of membrane separation processes:

1. Major capital costs include the cost of the membrane modules and the pumps.[12] However, the cost of piping, instrumentation, pretreatment, and storage facilities also need to be considered.[3]
2. The major operating expense is membrane replacement.[12] Therefore, the lifetime of the membranes will have a significant impact on the economic feasibility. Other operating expenses that must be considered include the costs of: power to run the pumps, labor for operations and maintenance, replacement filtration cartridges and pretreatment chemicals, and membrane cleaning chemicals.[3]
3. Savings experienced as a result of membrane separation treatment of waste streams include savings of chemicals recycled to the process, energy savings for the thermal energy content of recycled streams, savings for makeup water and associated sewer charges, and credits for reduced waste treatment and disposal costs.[3,51]
4. The cost of a membrane separation system is dependent on the type and quantity of waste treated and the level of pretreatment necessary.[10] Overall, a higher feed TDS concentration will require a more complex and expensive plant than will be required for a more dilute feed stream.[86]

### A. Reverse Osmosis

Capital costs of reverse osmosis systems range from approximately $0.50 to $4 per gallon per day of purified water ($0.13 to $1.06 per liter per day), depending on the volume of waste to be treated. Total operating costs range from $1 to $5 per 1000 gal ($0.26 to $1.32 per meter$^3$).[10] Reverse osmosis membrane replacement costs are between $3.72 to $7.90 per feet$^2$ ($40 to $85 per meter$^2$).[12]

The economic feasibility of removing certain metals from electroplating rinse waters with reverse osmosis has been evaluated by Franklin Associates, Ltd.[87] A summary of the economic analysis for recovery of cadmium, copper, chromium, nickel, and zinc is presented in Table 8. These cost calculations indicate that reverse osmosis is economically favorable for cadmium, chromium, and nickel recovery, but is unfavorable for copper recovery. Reverse osmosis is not considered feasible for treatment of zinc plating rinse waters due to

Table 8
ECONOMIC COMPARISON OF MEMBRANE SEPARATION TECHNOLOGIES FOR TREATMENT OF HEAVY METALS

| Technology | Metal recovered | Capital cost | Annualized capital cost[a] | Annual operating and maintenance costs[b] | Annual metal savings | Total annual cost[c] | Annual disposal cost w/o recovery[d] |
|---|---|---|---|---|---|---|---|
| Electrodialysis (90% metal recovery) | Cadmium | $101,500 | $17,235 | $13,311 | $35,915 | $ −5,369 | $3,118 |
| | Copper | 101,500 | 17,235 | 12,181 | 7,487 | +21,929 | 1,156 |
| | Chromium | 101,500 | 17,235 | 12,346 | 17,303 | +12,278 | 1,442 |
| | Nickel | 101,500 | 17,235 | 12,727 | 69,697 | −39,735 | 2,105 |
| | Zinc | 101,500 | 17,235 | 19,147 | 55,892 | −19,510 | 13,250 |
| Reverse osmosis (95% metal recovery) | Cadmium | 26,000 | 4,415 | 12,938 | 37,909 | −20,556 | 3,118 |
| | Copper | 26,000 | 4,415 | 10,228 | 7,903 | +6,740 | 1,156 |
| | Chromium | 26,000 | 4,415 | 10,963 | 18,264 | −2,886 | 1,442 |
| | Nickel | 26,000 | 4,415 | 8,327 | 73,571 | −60,829 | 2,105 |

*Note:* Assumptions: All metals in the liquid waste (e.g., rinse water) are soluble; metal concentration is 0.5 ounce per gallon (2800 ppm); and flow rate is 4 to 7 gal/min. Amount and value of metals in liquid wastes are as follows: Cu, 12,324 lb/year, $0.675/lb; Cd, 33,254 lb/year, $1.20/lb; Cr, 15,380 lb/year, $1.25/lb; Ni, 22,447 lb/year, $3.45/lb; and Zn, 141,331 lb/year, $0.44/lb.

[a] Annualized over 10 years @ 11% interest.

[b] Includes allowance for equipment insurance @ 1% of capital. Electricity costs are $0.06/kilowatt hour.

[c] Annualized capital cost plus annual operating and maintenance costs minus annual metal savings equals total annual cost.

[d] Cost for secure landfill disposal (including collection and transportation) is $75 per cubic yard.

Adapted from Franklin Associates, Ltd., Update of Waste Management Technologies/Economics for Wastes Generated by Electroplating and Electric Arc Furnace Processes, Prairie Village, Kan., 1986. With permission.

poor economics and plating bath heating requirements. The assumptions used in this analysis are as follows: (1) 95% of the metal in the rinse water is recovered, (2) membrane lifetimes are 1 to 2 years, (3) membrane replacement and installation costs are about $7000, (4) operating costs consist mainly of the cost of the electricity needed to run a 15 hp pump, and (5) membrane cleaning costs are minimal, but cleaning needs to be performed once a month.

Reverse osmosis costs for treatment of hazardous leachates have been estimated by McArdle et al.[2] The capital costs for 25 to 100 gal/m (95 to 379 ℓ/min) streams range from $69,000 to $235,000, based on the cost of packaged systems (including motor pump unit, reverse osmosis filter cartridges and housings, pressure gauges, and control modules). The estimated annual operating and maintenance costs range from $30,000 to $76,000. Replacement modules and concentrate disposal account for about 8 and 20% of these costs, respectively.

## B. Ultrafiltration

It is 20 to 50% more expensive to replace ultrafiltration membranes than reverse osmosis membranes; ultrafiltration pricing seems to be based on higher flux rates.[12]

McArdle et al. have compiled estimated costs for the treatment of hazardous waste leachate streams as follows.[2] Capital costs for ultrafiltration of 25 to 100 gal/m (95 to 379 ℓ/min) leachate range from $55,000 to $134,000 (based on the cost of a packaged system). The annual operating and maintenance costs are between $32,000 and $93,000. Replacement modules account for about 31% of these costs, while disposal of treatment residuals accounts for 6%.

## Table 9
## ECONOMICS OF MEMBRANE SEPARATION TREATMENT VS. LAND DISPOSAL FOR ELECTROPLATING RINSE WATERS

| Technology | Waste stream | Recovery/ treatment cost | Land disposal cost[a] |
|---|---|---|---|
| Electrodialysis | Nickel plating rinse water | −$1,574/ton | +$75/ton |
| | Cadmium plating rinse water | −$144/ton | +$75/ton |
| | Zinc plating rinse water | −$123/ton | +$75/ton |
| Reverse osmosis | Copper plating rinse water | +$461/ton | +$75/ton |
| | Nickel plating rinse water | −$2,282/ton | +$75/ton |
| | Cadmium plating rinse water | −$521/ton | +$75/ton |
| | Chromium plating rinse water | −$158/ton | +$75/ton |

[a] Includes collection, transportation, and disposal costs.

Adapted from Franklin Associates, Ltd., Update of Waste Management Technologies/Economics for Wastes Generated by Electroplating and Electric Arc Furnace Processes, Prairie Village, Kan., 1986.

### C. Electrodialysis

The cost of electrodialysis plants depends primarily on processing temperature, feedwater salinity and ionic composition, and the amount of pretreatment required.[8] In general, membrane area requirements and energy consumption increase with increases in TDS concentrations (i.e., the amount of salt to be removed).[11]

According to Franklin Associates, electrodialysis recovery systems are technically capable of recovering cadmium, copper, chromium, nickel, and zinc.[87] However, as shown in Table 8, recovery of only cadmium, nickel, and zinc appears to be economically feasible; recovery of copper and chromium does not seem to be cost effective. The assumptions used in this analysis include: (1) 90% recovery of metal from the rinse water would require approximately 125 cell pairs, (2) replacement and installation costs are $80 per cell pair, (3) the cells have a lifetime of about 2 years, (4) energy consumption is 1 kWh of electricity per pound of recovered metal (2.2 kWh/kg) or $0.06 per pound of recovered metal ($0.13 per kilogram), and (5) the current density is 5 A/ft$^2$ (53.8 A/m$^2$) with an efficiency of 70%.

### D. Membrane Separation Costs vs. Land Disposal Costs

A comparison of reverse osmosis and electrodialysis costs and land disposal costs is presented in Table 9. Costs (or savings) are presented in terms of dollars per ton of waste that would not require hazardous waste land disposal if the membrane separation process were implemented. This information suggests that electrodialysis recovery of cadmium, nickel, and zinc and reverse osmosis recovery of nickel, cadmium, and chromium are less costly than land disposal.[87]

## VII. INNOVATIVE MEMBRANE SEPARATION TECHNOLOGIES

This section is devoted to three innovative membrane separation technologies that have recently been developed: (1) micellar-enhanced ultrafiltration, (2) the Aquatech electrodialysis process, and (3) liquid membranes. These technologies are not commercially available yet, but they may be worth watching in the future.

### A. Micellar-Enhanced Ultrafiltration

Standard ultrafiltration membranes are not capable of rejecting molecules with a molecular weight below about 300.[5] However, the Institute for Applied Surfactant Research at the University of Oklahoma has recently discovered that the addition of surfactants enhances ultrafiltration of waste waters containing low molecular weight organics and heavy metals.[88] This process is called "micellar-enhanced ultrafiltration".

During micellar-enhanced ultrafiltration, surfactants (which form spherical or cylindrical aggregates of 20 to 200 molecules called micelles) combine with organics and heavy metals to form an aggregate that is large enough to be rejected by an ultrafiltration membrane. Some surfactant generally leaks through the membrane, but the concentration is usually very low (<100 ppm); these residual surfactants are usually not a problem because they are generally nontoxic and biodegradable. Studies performed on micellar-enhanced ultrafiltration at the Univeristy of Oklahoma have demonstrated >99% rejection of copper, zinc, and 4-tert-butylphenol; >97% rejection of cresol; and 71 to 98.8% rejection of low molecular weight n-alcohols.[88]

This process has not yet been applied on a commercial scale. However, only minor modifications to existing ultrafiltration systems would be required to implement this technology.[88]

### B. Aquatech Electrodialysis Process

Aquatech Systems has developed an electrodialytic process which allows recovery of aqueous salt streams containing acids or neutralized acid by-products from manufacturing processes. The electrically driven process uses ion exchange membranes to separate and concentrate the acid and base constituents of waste streams so that they may be recycled. Some of the waste streams that have been recovered via this technology include stainless steel pickle liquor and spent aluminum pot linings.[89]

A schematic diagram of the Aquatech process is presented in Figure 13. The key component of the technology is a bipolar membrane composed of two distinct layers that are selective to ions of opposite charges. The membrane splits water molecules into hydrogen and hydroxyl ions that combine with oppositely charged salt ions to form an acid and a base. The steps of the treatment process are as follows:[89]

1. When an aqueous salt solution enters the system, it is divided into its negative ($X^-$) and positive ($M^+$) components; the anionic membrane allows only negative salt ions to pass through it, while the cationic membrane selectively passes positive salt ions.
2. Under an electrical current, water diffuses into the bipolar membrane interface where it dissociates to hydrogen ($H^+$) and hydroxyl ($OH^-$) ions.
3. The $H^+$ ions then pass back through the bipolar membrane's positive layer and combine with the anionic salt ions ($X^-$) to form HX. Meanwhile, the $OH^-$ ions pass back through the bipolar membrane's negative layer to combine with the cationic salt ions ($M^+$) and form MOH.

Each cell is typically about 4 mm thick. As many as 200 cells are combined to form a single 20 × 40-in. (51 × 102 cm) stack, which requires only two electrodes. Feedstreams are recirculated through the stack until desired concentration levels are reached.[90]

A schematic diagram of the treatment of stainless steel pickle liquor with the Aquatech process is shown in Figure 14. The acid stream is first neutralized with potassium hydroxide (KOH) to form a potassium fluoride/nitrate solution. The treated waste is then dewatered in a filter press. The filter cake, containing metal hydroxides, can be dried and returned to the steel smelter, while the filtrate (containing soluble fluoride and nitrate salts) proceeds to the Aquatech stack for recovery. The dilute salt solution that exits from the Aquatech unit is further treated using conventional electrodialysis. The concentrate from the electrodialysis process is returned to the Aquatech salt loop while the dilute solution, containing 0.02 to 0.04 N salt, is used for washing the filter cake.[91]

After regeneration, a 3-*M* stream of mixed hydrofluoric/nitric acid is produced, in addition

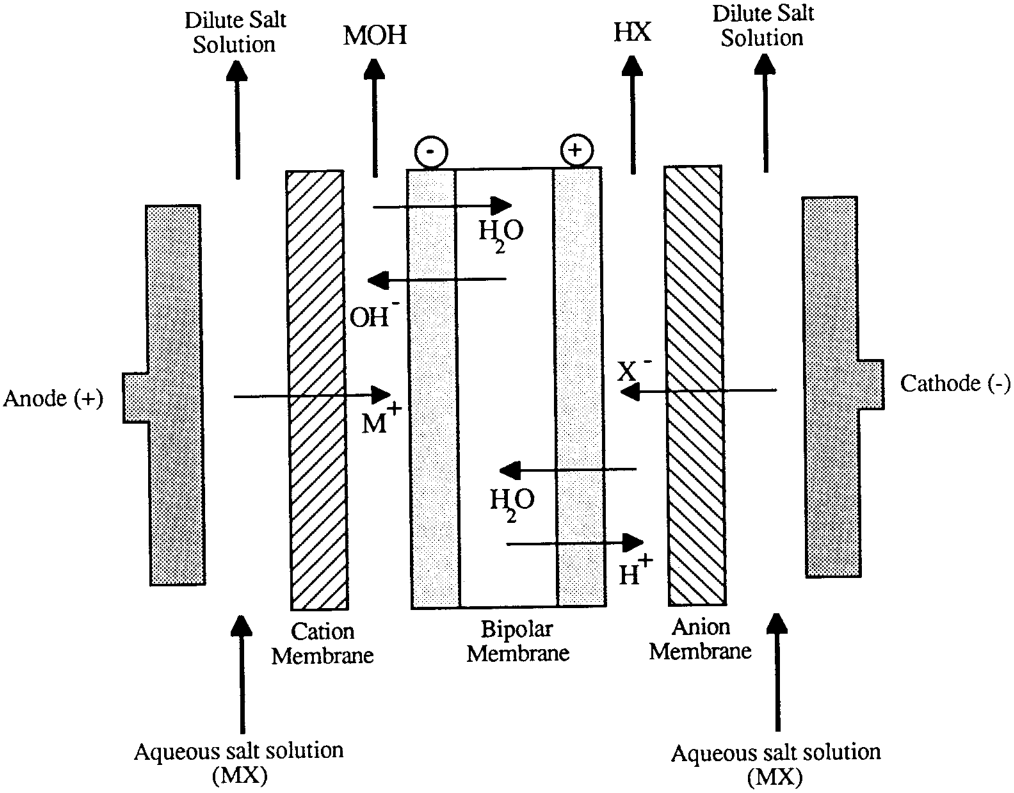


FIGURE 13. Aquatech electrodialysis cell. (Adapted from Aquatech Systems, advertising brochure, Mt. Bethel, N.J., 1985. With permission.)

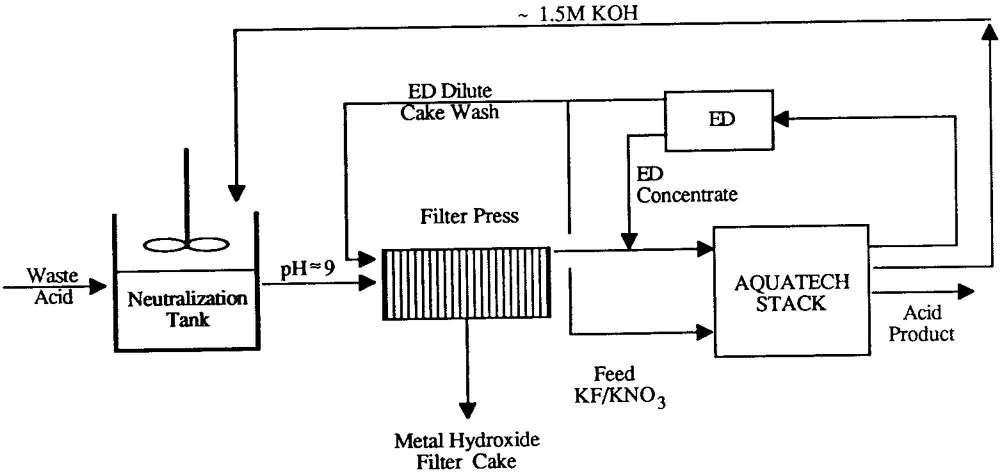


FIGURE 14. Aquatech stainless steel pickle liquor recovery process. (From Mani, K. N., Chlanda, F. P., and Byszewski, C. H., Aquatech Membrane Technology for Recovery of Acid/Base Values from Salt Streams, Aquatech Systems, Mt. Bethel, N.J. With permission.)

to a 2-*M* potassium hydroxide solution. Both the acids may be recycled back to the pickling process, and the potassium hydroxide can be reused in the waste-acid neutralization step.[90] During pilot testing of the process, 93 to 99% recovery of HF, $HNO_3$, and KOH resulted.[91]

The cost of a 1.5 million gal/year (5.7 million ℓ/year) Aquatech plant for treatment of spent pickle liquor is estimated to be about $1.8 million and annual operating costs are $815,000. Annual savings, when compared to neutralization and land disposal of resulting sludges, are on the order of $450,000.[91]

### C. Liquid Membranes

Liquid membranes, which were developed by Li in 1968, are thin liquid films that act as a diffusional barrier between the phase containing the species to be removed and the concentrate stream.[92,93] They differ from conventional membrane processes such as reverse osmosis and ultrafiltration in that the species to be removed and not the solvent permeates the membrane.[93] Liquid membranes are also unlike their solid counterparts because they separate by chemistry rather than size. Therefore, the important feature of the fluid to be separated is not its molecular size, but its relative solubility in the membrane.[94]

Two types of liquid membranes exist: (1) immobilized liquid membranes that are supported by a solid structure and (2) emulsions. Immobilized liquid membranes consist of a liquid, water-immiscible organic complexing agent that is immobilized and held by capillary forces within the pores of a microporous membrane, such as a spiral wound or hollow fiber sheet.[93,94] Transport through the liquid membrane is usually enhanced by a chemical reagent which reacts or interacts with the species to be removed.[93] One type of transport, coupled transport, is discussed in detail in the next section.

Emulsion liquid membranes are formed by dispersing an emulsion of two immiscible phases (such as a caustic soda solution and a hydrocarbon solvent-surfactant solution) in a third phase (such as an aqueous solution containing the material to be recovered). Small emulsion globules (approximately 1 to 5 mm in diameter) are formed and distribute themselves in the third phase. These globules, in turn, contain many small "encapsulated" aqueous reagent droplets that have diameters from 1 to 10 μm. The liquid membrane, which is the emulsion between the encapsulated droplets and the third phase, usually contains additives, surfactants, and a base material that is a solvent for all of the other ingredients.[12]

The mixture is agitated in a mixer to maintain good dispersion of the emulsion globules in the waste water. Weakly dissociated organic acids or bases permeate across the liquid membrane into the encapsulated droplets. The droplets contain reagents which enhance the permeation rate and neutralize the weak acids or bases. Neutralization converts the acids or bases into salts which are highly dissociated. The insoluble liquid membrane acts as a barrier to the ionic components and prevents them from permeating back into the waste water solution. Therefore, the ionized salts remain trapped within the encapsulated droplets. When the desired degree of treatment has been obtained, mixing is halted and the emulsion globules coalesce, forming an emulsion layer that can be easily separated from the waste water. The highly concentrated ionized salt solution can then be separated from the oil emulsion.[12]

Emulsion liquid membranes have been used to extract inorganics from aqueous solutions.[95] Bench-scale results indicate that they are suitable for selective recovery of metals from solutions which contain very low metal concentrations.[96] Some data is also available on the removal of organics from waste water.[97,98] However, this technology is still in the experimental stage and further development is required before it can be considered to be commercially feasible.[93]

#### *1. Coupled Transport*

Coupled transport is a new liquid membrane process that is well suited to the recovery of metal-containing waste streams such as electroplating rinse waters. During this process, the flow of the metal is coupled to the flow of some second species, typically hydrogen. Under the right conditions, the flow of this second species can force the metal ions to flow against their own concentration gradient, allowing them to be removed from the dilute waste stream to a more concentrated solution.

Coupled transport membranes are typically immobilized liquid membranes in which a liquid, water-immiscible metal-ion-complexing agent is contained within a microporous membrane. The complexing agent is specific for the metal to be removed.[99] During coupled transport, the agent picks up metal ions from a dilute solution on one side of the membrane, transports them across the membrane as neutral complexes, and releases them to the concentrated solution on the opposite side of the membrane. The free complexing agent then diffuses back across the membrane where it picks up more of the metal. In this manner, the complexing agent shuttles metal ions across the membrane.

The coupled species is usually the hydrogen ion. This ion can either cross the membrane in the same direction as the metal ion (''cotransport'') or opposite to the metal ion flow (''countertransport''). In order to maintain electroneutrality across the membrane, the hydrogen ion must move in the same direction as the metal ion if the metal is present in anionic form (e.g., chromium as chromate ion). Conversely, for removal of free metal ions (e.g., copper and nickel), the flow of hydrogen ions must be counter to the flow of metal ions.[99] A schematic diagram illustrating both cotransport and countertransport is presented in Figure 15.

Under cotransport conditions, the anionic form of the metal in the acidic feed stream combines with hydrogen ions and the complexing agent to form a complex. This complex diffuses down its concentration gradient to the opposite side of the membrane where it dissociates due to the higher pH of the product stream. The metal and hydrogen ions are then released to the aqueous phase, and the complexing agent diffuses back to the feed side of the membrane.[99]

During countertransport, the cationic metal ion in the feed stream combines with the complexing agent and diffuses across the membrane. Due to lower pH conditions present on the product side of the membrane, an excess hydrogen ion displaces the metal from the complex and releases the metal cation into the product stream.[93] The complex containing the hydrogen ion diffuses back to the feed side of the membrane.

### *a. Application of Coupled Transport*

During the past 9 years, the coupled transport process has been applied on a prototype basis for removal and recovery of aluminum, cobalt, copper, chromium, iron, nickel, and uranium from waste waters.[93,100-104] Copper and chromium recovery have been especially successful.[93] Baker et al. reported transport rates on the order of 3 $\mu g/cm^2/min$ for copper separation.[104]

Bend Research, Inc. is currently developing a new membrane separation process utilizing a coupled transport membrane.[105] The technology is being tested on electroplating rinse waters to concentrate metals and produce reusable rinse water. Preliminary results indicate that the economics of coupled transport treatment compare favorably with that of conventional waste treatment techniques.

### *b. Sludge Reclamation Process*

Bend Research has also developed a sludge reclamation process that is based on the use of coupled transport membranes.[106] This scheme, which is shown in Figure 16, is capable of selectively removing and concentrating a specific metal ion from a sludge containing a mixture of metals. The process relies upon coupled transport processes for the concentration of copper and chromium, a membrane-contactor process for zinc removal, and precipitation for nickel removal. It is reported that this process will be able to economically reduce the

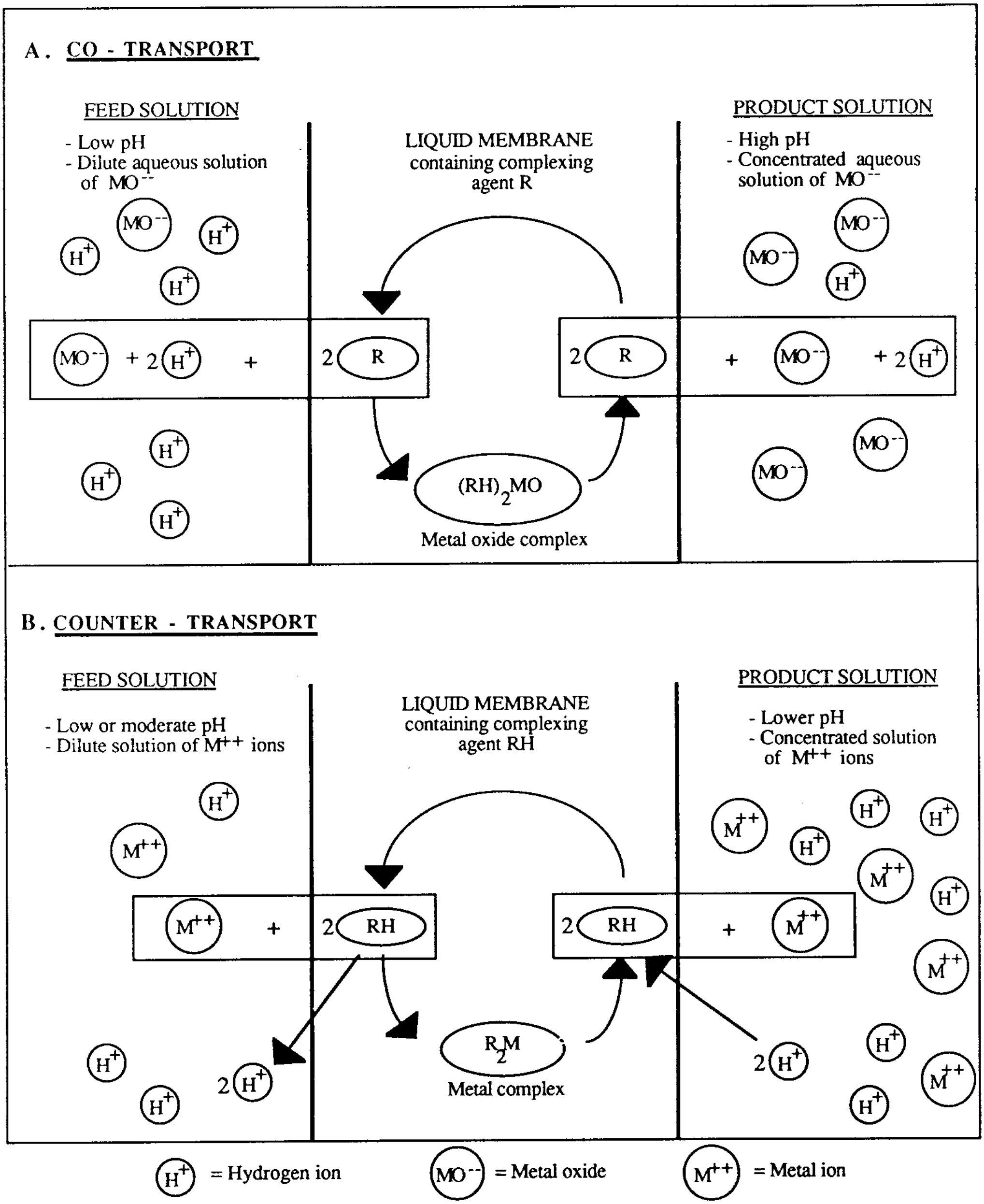
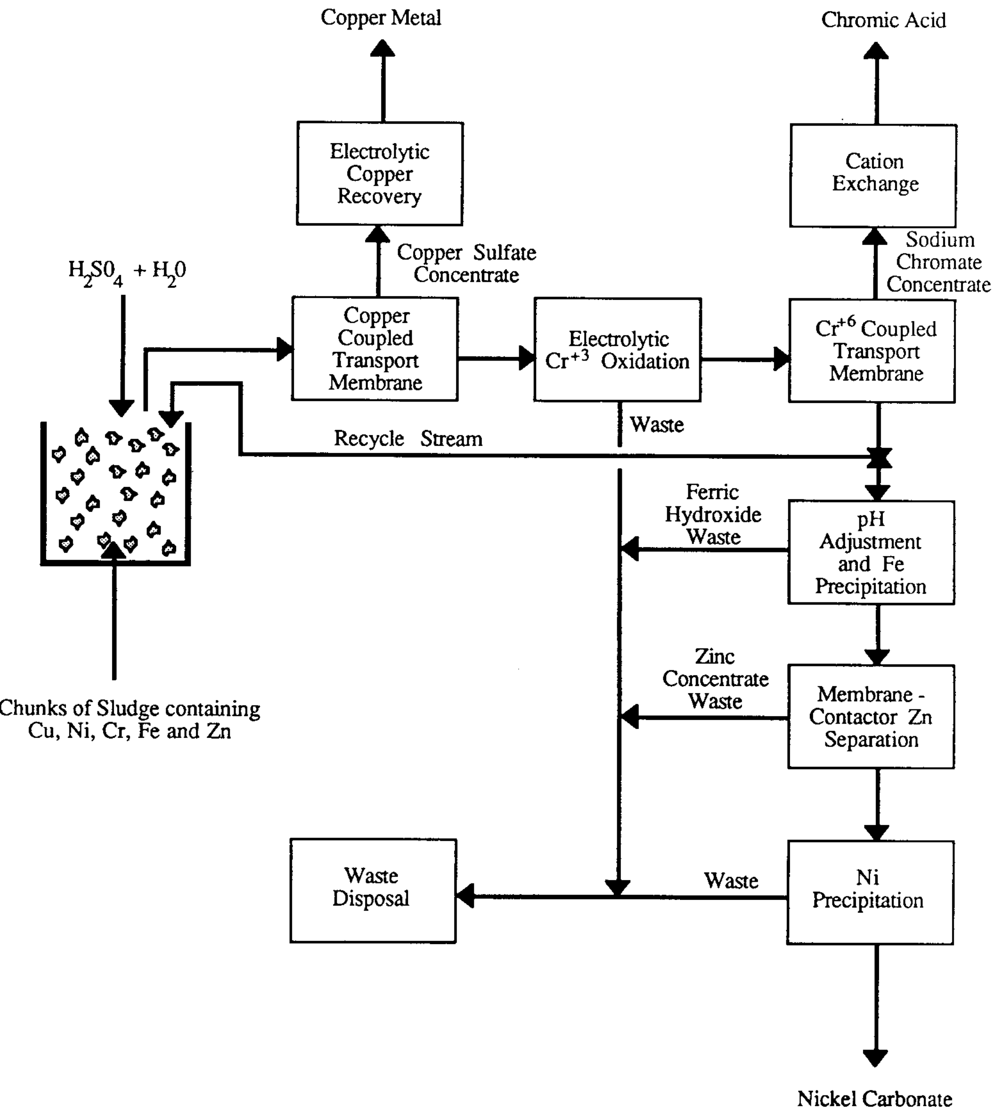


FIGURE 15. Schematic diagram of cotransport and countertransport mechanisms.

volume and toxicity of hazardous sludges to 10% of their original values. The waste products are iron hydroxide, zinc sulfate, and various nontoxic sodium salts that remain in solution after nickel recovery. During tests on metal plating sludges, at least 99% of copper, chromium, and nickel were recovered in purities of 97% or greater.

## VIII. NEED FOR FURTHER DEVELOPMENT

Fouling of membrane surfaces is one of the major practical limitations on the use of reverse osmosis and ultrafiltration for the treatment of hazardous wastes. Consequently, the



IGURE 16. Bend Research's electroplating sludge reclamation process using coupled transport membranes. From Bend Research, Inc., Technology Summary: Sludge Reclamation Using Coupled Transport Membranes, end, Ore. With permission.)

evelopment of fouling-resistant membranes that can be easily cleaned is necessary. Memrane materials also need to be developed that will reject small, unionized organics and ithstand higher operating temperatures (149°F or 65°C and higher).[12]

## REFERENCES

1. **Belfort, G.,** Membrane methods in water and wastewater treatment: an overview, in *Synthetic Membrane Processes: Fundamentals and Water Applications,* Belfort, G., Ed., Academic Press, Orlando, Fla., 1984, chap. 2.
2. **McArdle, J. L., Arozarena, M. M., and Gallagher, W. E.,** *A Handbook on Treatment of Hazardous Waste Leachate,* EPA/600/8-87/006 (PB87-152328), U.S. Environmental Protection Agency, Cincinnati, 1987.

3. McCoy and Associates. Membrane separation technology: applications to waste reduction and recycling, *The Hazardous Waste Consultant,* 3, 4, 1985.
4. **Tang, D. T. L., Boroughs, R. D., and Chu, T. J.,** Application of membrane technology, *Ind. Water Eng.,* 18, 1981.
5. **Lonsdale, H. K.,** The growth of membrane technology, *J. Membr. Sci.,* 10, 81, 1982.
6. **Cartwright, P. S.,** Membranes separations technology for industrial effluent treatment — A review, *Desalination,* 56, 17, 1985.
7. **Kaup, E. C.,** Design factors in reverse osmosis, *Chem. Eng.,* 80, 46, 1973.
8. **Applegate, L. E.,** Membrane separation processes, *Chem. Eng.,* 91, 64, 1984.
9. **Kosarek, L. J.,** Removal of various toxic heavy metals and cyanide from water by membrane processes, in *Chemistry in Water Reuse,* Vol. 1, Cooper, W. J., Ed., Ann Arbor Science Publishers, Ann Arbor, Mich., 1981, chap. 12.
10. **Kiang, Y. H. and Metry, A. A.,** *Hazardous Waste Processing Technology,* Ann Arbor Science Publishers, Ann Arbor, Mich., 1982, 409.
11. **Reynolds, T. D.,** *Unit Operations and Processes in Environmental Engineering,* Wadsworth, Belmont, Calif., 1982, 235.
12. **Probstein, R. F., Calmon, C., and Hicks, R. E.,** Separation of organic substances in industrial wastewaters by membrane processes, in *Control of Organic Substances in Water and Wastewater,* EPA/600/8-83-011, Berger, B. B., Ed., Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C., 1983, 363.
13. **Gooding, C. H.,** Reverse osmosis and ultrafiltration solve separation problems, *Chem. Eng.,* 92, 56, 1985.
14. **Finkenbiner, K. T.,** Reverse osmosis for industrial wastewater treatment, presented at the 7th Annu. Am. Electroplaters and Surface Finishers Society/EPA Conf. Pollution Control for the Metal Finishing Industry, Kissimmee, Fla., January 27 to 29, 1986.
15. **George, D.,** Reverse osmosis in water reuse systems, in *Water Reuse,* Middlebrooks, E. J., Ed., Ann Arbor Science Publishers, Ann Arbor, Mich., 1982, chap. 10.
16. **Pepper, D.,** Pretreatment and operating experience on reverse osmosis plant in the Middle East, *Desalination,* 38, 403, 1981.
17. **Siler, J. L. and Bhattacharyya, D.,** Low pressure reverse osmosis membranes: concentration and treatment of hazardous wastes, *Hazardous Waste Hazardous Mater.,* 2, 45, 1985.
18. **Kinman, R. N., Nutini, D., and Stamm, J. W.,** Reverse osmosis membrane fouling: Electroless copper plating solutions, *Met. Finish.,* 83, 53, 1985.
19. **Shields, C. P.,** Five years experience with reverse osmosis systems using DuPont "Permasep" permeators, *Desalination,* 28, 157, 1979.
20. **Eisenberg, T. N. and Middlebrooks, E. J.,** *Reverse Osmosis Treatment of Drinking Water,* Butterworths, Stoneham, Mass., 1986, chap. 8.
21. U.S. Environmental Protection Agency, Technology Briefs: Data Requirements for Selecting Remedial Action Technology, EPA/600/2-87/001, U.S. Environmental Protection Agency, Cincinnati, 1987, 101.
22. **MacNeil, J. and McCoy, D.,** Membrane separation technologies, in *Standard Handbook for Hazardous Waste Treatment and Disposal,* Freeman, H. M., Ed., McGraw-Hill, New York, 1988.
23. **Finkenbiner, K. and Cartwright, P. S.,** Reverse Osmosis Technology for Toxic Heavy Metals Treatment, presented at HAZPRO '85, Baltimore, May 17, 1985.
24. **Eisenberg, T. N. and Middlebrooks, E. J.,** *Reverse Osmosis Treatment of Drinking Water,* Butterworths, Stoneham, Mass., 1986, chap. 1.
25. **Reid, C. E. and Breton, E. J.,** Water and ion flow across cellulosic membranes, *J. Appl. Polym. Sci.,* 1, 133, 1959.
26. **Loeb, S. and Sourirajan, S.,** Sea Water Research, Report No. 60-60, Department of Engineering, University of California, Los Angeles, 1961.
27. **Porter, M. C.,** What, when and why of membranes — MF, UF, and RO, *AIChE Symp. Ser.,* 73, 83, 1977.
28. Burns and Roe Industrial Services Corporation, *Reverse Osmosis Technical Manual,* PB 80-186950, U.S. Office of Water Research and Technology, Washington, D.C., 1979.
29. **Eisenberg, T. N. and Middlebrooks, E. J.,** *Reverse Osmosis Treatment of Drinking Water,* Butterworths, Stoneham, Mass., 1986, chap. 6.
30. **Belfort, G.,** Pressure driven membrane processes and wastewater renovation, in *Water Renovation and Reuse,* Schuvall, H. I., Ed., Academic Press, New York, 1977, chap. 6.
31. **Kosarek, L.,** Purifying water by reverse osmosis, *Plant Eng.,* 8, 103, 1979.
32. **Kamiyama, Y., Yoshioka, N., Matsui, K., and Nakagome, K.,** New thin-film composite reverse osmosis membranes and spiral wound modules, *Desalination,* 51, 79, 1984.
33. **Bhattacharyya, D. and Siler, J. L.,** Low pressure membranes: concentration and treatment of hazardous wastes, presented at the 2nd Int. Symp. Operating European Centralized Hazardous (Chemical) Waste Management Facilities, Odense, Denmark, September 1984.

34. **Belfort, G.,** Desalting experience by hyperfiltration (reverse osmosis) in the United States, in *Synthetic Membrane Processes: Fundamentals and Water Applications,* Belfort, G., Ed., Academic Press, Orlando, Fla., 1984, chap. 7.
35. **Cartwright, P. S.,** The Application of Membrane Separation Technologies for Contaminated Ground Water Treatment, presented at the 2nd Int. Conf. Environmental Contamination, Amsterdam, September 23 to 25, 1986.
36. **Eisenberg, T. N. and Middlebrooks, E. J.,** *Reverse Osmosis Treatment of Drinking Water,* Butterworths, Stoneham, Mass., 1986, chap. 7.
37. Bend Research, Inc., Techbrief: Reverse Osmosis Module, Bend, Oregon.
38. **Crossley, I. A.,** Desalination by reverse osmosis, in *Desalination Technology: Developments and Practice,* Porteous, A., Ed., Applied Science Publishers, New York, 1983, chap. 7.
39. Aerojet General Corporation, Development Progress Report 213, U.S. Office Saline Water Research, Washington, D.C., 1966.
40. **Nielsen, W. K., Madsen, R. F., and Olsen, O. J.,** Experience with plate and frame ultrafiltration and hyperfiltration systems for desalination of water and purification of waste water, *Desalination,* 32, 309, 1980.
41. Advertising brochures, DDS Division, Niro Atomizer, Hudson, Wis.
42. **Eisenberg, T. N. and Middlebrooks, E. J.,** *Reverse Osmosis Treatment of Drinking Water,* Butterworths, Stoneham, Mass., 1986, chap. 2.
43. **Sastri, V. S. and Ashbrook, A. W.,** Performance of some reverse osmosis membranes and their application in the separation of metals in acid minewater, *Sep. Sci.,* 11, 133, 1976.
44. **Eisenberg, T. N. and Middlebrooks, E. J.,** *Reverse Osmosis Treatment of Drinking Water,* Butterworths, Stoneham, Mass., 1986, chap. 4.
45. **Sourirajan, S. and Matsuura, T.,** Physicochemical criteria for reverse osmosis separations, in *Reverse Osmosis and Synthetic Membranes,* Sourirajan, S., Ed., National Research Council of Canada, Ottawa, 1977, chap. 2.
46. **Light, W. G.,** Removal of chemical carcinogens from water/wastewater by reverse osmosis, in *Chemistry in Water Reuse,* Vol. 1, Cooper, W. J., Ed., Ann Arbor Science Publishers, Ann Arbor, Mich., 1981, chap. 16.
47. **Matsuura, T. and Sourirajan, S.,** Reverse osmosis separation of hydrocarbons in aqueous solutions using porous cellulose acetate membranes, *J. Appl. Polym. Sci.,* 17, 3683, 1973.
48. **Wojcik, C. K., Lopez, J. G., and McCutchan, J. W.,** Renovation of municipal wastewater by reverse osmosis: a case study, in *Water Reuse Symposium,* American Water Works Association Research Foundation, Denver, 1979.
49. **Hrubec, J., Schippers, J. C., and Zoeteman, B. C. J.,** Studies on water reuse in the Netherlands, in *Water Reuse Symposium,* American Water Works Association Research Foundation, Denver, 1979, 785.
50. **Rozelle, L. T., Cadotte, J. E., Cobian, K. E., and Kopp, C. U., Jr.,** Nonpolysaccharide membranes for reverse osmosis: NS-100 membranes, in *Reverse Osmosis and Synthetic Membranes,* Sourirajan, S., Ed., National Research Council of Canada, Ottawa, 1977, chap. 12.
51. **Werschulz, P.,** New membrane technology in the metal finishing industry, in *Toxic and Hazardous Wastes: Proceedings of the Seventeenth Mid-Atlantic Industrial Waste Conference,* Kugelman, I. J., Ed., Technomic Publishing, Lancaster, Penn., 1985, 445.
52. **Donnelly, R. G., Goldsmith, R. L., McNulty, K. J., Grant, D. C., and Tan, M.,** *Treatment of Electroplating Wastes by Reverse Osmosis,* EPA/600/2-76/261, PB 265393, U.S. Environmental Protection Agency, Cincinnati, 1976.
53. **Cartwright, P.,** An update on reverse osmosis for metal finishing, *Plating Surf. Finish.,* 71, 62, 1984.
54. **Thorsen, T.,** Recovery of phosphoric acid with RO, *Desalination,* 53, 217, 1985.
55. **Cartwright, P.,** Today's RO, *Prod. Finish.,* May 1984.
56. **Rickabaugh, J., Martin, J., and Kinman, R. N.,** Reverse Osmosis Removals of Chlorinated Hydrocarbons, presented at the 41st Purdue Industrial Waste Conf., West Lafayette, Ind., May 13 to 15, 1986.
57. **Slater, C. S., Ahlert, R. C., and Uchrin, C. G.,** Treatment of landfill leachates by reverse osmosis, *Environ. Prog.,* 2, 251, 1983.
58. **Chian, E. S. K. and DeWalle, F. B.,** *Evaluation of Leachate Treatment, Vol. II,* EPA/600/2-77-186b, U.S. Environmental Protection Agency, Cincinnati, 1977.
59. **Whittaker, H.,** Applications Testing with the Environment Canada Mobile Reverse Osmosis Unit, presented at the 36th Can. Chem. Eng. Conf., Sarnia, Ontario, October 5 to 8, 1986.
60. **Whittaker, H.,** Development of a Mobile Reverse Osmosis Unit for Spill Cleanup, presented at the 1984 Hazardous Materials Spills Conf., Nashville, April 9 to 12, 1984.
61. **Feige, W. A., Clark, R. M., Lykins, B. W., Jr., and Fronk, C. A.,** *Treatment of Water from Contaminated Wells,* EPA/600/D-87/011 (PB87146239), U.S. Environmental Protection Agency, Cincinnati, 1987.
62. **Chian, E. S. K., Bruce, W. N., and Fang, H. H. P.,** Removal of pesticides by reverse osmosis, *Environ. Sci. Technol.,* 9, 52, 1975.

63. **Lykins, B. W., Jr. and Baier, J. H.,** *Agricultural Contaminants Removal from Ground Water by Carbon and Reverse Osmosis,* EPA/600/D-87/103 (PB87175626/AS), U.S. Environmental Protection Agency, Cincinnati, 1987.
64. **Regunathan, P., Beauman, W. H., and Kreusch, E. G.,** Efficiency of point-of-use devices, *J. Am. Water Works Assoc.,* 75, 42, 1983.
65. **Sorg, T. J., Forbes, R. W., and Chambers, D. S.,** Removal of Ra-226 from Sarasota County, Florida drinking water by reverse osmosis, *J. Am. Water Works Assoc.,* 72, 230, 1980.
66. **Sonksen, M. K., Sittig, F. M., and Maziarz, E. F.,** Treatment of oily wastes by ultrafiltration/reverse osmosis — A case history, in *Proceedings of the 33rd Industrial Waste Conference,* Ann Arbor Science Publishers, Ann Arbor, Mich., 1979, 696.
67. **Isooka, Y., Imamura, Y., and Sakamoto, Y.,** Recovery and reuse of organic solvent solutions, *Met. Finish.,* 82, 113, 1984.
68. **Klinkowski, P. R.,** Ultrafiltration: an emerging unit-operation, *Chem. Eng.,* 85, 165, 1978.
69. **Fane, A. G. and Fell, C. J. D.,** A review of fouling and fouling control in ultrafiltration, *Desalination,* 62, 117, 1987.
70. **Berkowitz, J. B., Funkhouser, J. T., and Stevens, J. I.,** *Unit Operations for Treatment of Hazardous Industrial Wastes,* Noyes Data Corporation, Park Ridge, N.J., 1978, 899.
71. **Strathmann, H.,** Water and wastewater treatment experience in Europe and Japan using ultrafiltration, in *Synthetic Membrane Processes — Fundamentals and Water Applications,* Belfort, G., Ed., Academic Press, Orlando, Fla., 1984, chap. 9.
72. **Cartwright, P. S.,** The Status of Ultrafiltration and Microfiltration Applications for the Metal Finishing Industry, presented at Am. Electroplater's Soc. Surface/Finishing 1985, Detroit, July 15 to 18, 1985.
73. **Paulson, D. J. and Comb, L. F.,** Two case histories of industrial water reuse via membrane technology, in *Future of Water Reuse — Proceedings of the Water Reuse Symposium III,* Vol. 2, American Water Works Association Research Foundation, Denver, 1985, 899.
74. **Roush, P. H.,** Ultrafiltration Treatment of a Combined Electroplating and Metal Finishing Wastewater, presented at the 1st Annu. Hazardous Materials Management Conf./Southwest, Houston, October 31 to November 2, 1984.
75. **Van Gils, G. and Pirbazari, M.,** Development of a combined ultrafiltration and carbon adsorption system for industrial wastewater reuse and priority pollutant removal, *Environ. Prog.,* 5, 167, 1986.
76. **Syzdek, A. C. and Ahlert, R. C.,** Separation of landfill leachate with polymeric ultrafiltration membranes, *J. Hazardous Mater.,* 9, 209, 1984.
77. **Meyer, K. H. and Strauss, W.,** Permeability of membranes: VI. Passage of current through selective membranes, *Helv. Chim. Acta,* 23, 795, 1940.
78. **Juda, W. and McRae, W. A.,** Coherent ion-exchange gels and membranes, *J. Am. Chem. Soc.,* 72, 1044, 1950.
79. **Leitz, F. B. and Eisenmann, J. L.,** Electrodialysis as a separation process, *AIChE Symp. Ser. 204,* 77, 205, 1981.
80. **McRae, W. A.,** Electrodialysis, in *Desalination Technology: Developments and Practice,* Porteous, A., Ed., Applied Science Publishers, London, 1983, chap. 8.
81. **Solt, G.,** Electrodialysis, in *Handbook of Water Purification,* Lorch, W., Ed., McGraw-Hill, London, 1981, chap. 9.
82. **Latour, S., Anderson, J., and Menningmann, J.,** *Data Collection and Analysis of Commercial Membrane Desalination Plants, Volume 1,* PB81-170573, U.S. Office of Water Research and Technology, Washington, D.C., 1980.
83. **Itoi, S.,** Electrodialysis of effluents from treatment of metallic surfaces, *Desalination,* 28, 193, 1979.
84. **Sweeney, M. J.,** Recovery of Metals from Electroplating Rinsewaters with Electrodialysis, presented at the Summer Natl. AIChE Meet, Seattle, August 26, 1985.
85. **Urano, K., Ase, T., and Naito, Y.,** Recovery of acid from wastewater by electrodialysis, *Desalination,* 51, 213, 1984.
86. **Rogers, A. N.,** Economics of the application of membrane processes, in *Synthetic Membrane Processes: Fundamentals and Water Applications,* Belfort, G., Ed., Academic Press, Orlando, Fla., 1984, chap. 13.
87. Franklin Associates, Ltd., Update of Waste Management Technologies/Economics for Wastes Generated by Electroplating and Electric Arc Furnace Processes, Prairie Village, Kan., 1986.
88. McCoy and Associates, Inc., Micellar-enhanced ultrafiltration, *The Hazardous Waste Consultant,* 5, 4, 1987.
89. Aquatech Systems, Advertising Brochure, Mt. Bethel, N.J., 1985.
90. **Basta, N.,** Use electrodialytic membranes for waste recovery, *Chem. Eng.,* 93, 42, 1986.
91. **Mani, K. N., Chlanda, F. P., and Byszewski, C. H.,** AQUATECH Membrane Technology for Recovery of Acid/Base Values from Salt Streams, Aquatech Systems, Mt. Bethel, N.J.
92. **Li, N. N.,** Separation of hydrocarbons by liquid membrane permeation, *Ind. Eng. Chem. Process Des.*

93. **Werschulz, P.**, Membrane technology in the metal finishing industry, *Chemtech*, 16, 743, 1986.
94. **Parkinson, G., Short, H., and McQueen, S.**, Liquid membranes — Are they ready?, *Chem. Eng.*, 90, 25, 1983.
95. **Frankenfeld, J. W. and Li, N. N.**, Liquid membrane systems, in *Ion Exchange for Pollution Control*, Vol. 2, Calmon, C. and Gold, H., Eds., CRC Press, Boca Raton, Fla., 1979, chap. 18.
96. **Schugerl, K., Mohrmann, A., Gutknecht, W., and Hauertmann, H. B.**, Application of liquid membrane emulsion for recovery of metals from mining waste waters and zinc liquors, *Desalination*, 53, 197, 1985.
97. **Cahn, R. P. and Li, N. N.**, Separation of phenol from wastewater by the liquid membrane technique, *Sep. Sci.*, 9, 505, 1974.
98. **Cahn, R. P. and Li, N. N.**, Separation of organic compounds by liquid membrane processes, *J. Membr. Sci.*, 1, 129, 1976.
99. **Babcock, W. C., Baker, R. W., Kelly, D. J., Kleiber, J. C., and Lonsdale, H. K.**, *Coupled Transport Systems for Control of Heavy Metal Pollutants*, EPA/600/2-79-181, U.S. Environmental Protection Agency, Cincinnati, 1979.
100. **Babcock, W. C., Baker, R. W., Kelley, D. J., and Lonsdale, H. K.**, Coupled Transport Membranes for Metal Separations, U.S. Bureau of Mines, Department of the Interior, Washington, D.C., 1978.
101. **Babcock, W. C., Baker, R. W., Kelley, D. J., Lonsdale, H. K., Ray, R. J., and Tuttle, M. E.**, Coupled Transport Membranes for Metal Separation, Final Report, Phases 1 and 2, U.S. Bureau of Mines Open File Report 114-79, U.S. Bureau of Mines, Washington, D.C., 1977.
102. **Smith, K. L., Babcock, W. C., Baker, R. W., and Conrod, M. G.**, Coupled transport membranes for removal of chromium from electroplating rinse solutions, in *Chemistry in Water Reuse*, Vol. 1, Cooper, W. J., Ed., Ann Arbor Science Publishers, Ann Arbor, Mich., 1981, chap. 14.
103. **Lee, K., Evans, D. F., and Cussler, E. L.**, Selective copper recovery with two types of liquid membranes, *AIChE J.*, 24, 860, 1978.
104. **Baker, R. W., Tuttle, M. E., Kelly, D. J., and Lonsdale, H. K.**, Coupled transport membranes. I. Copper separations, *J. Membr. Sci.*, 2, 213, 1977.
105. Bend Research, Inc., Techbrief: Coupled-Transport Membranes, Bend, Oregon.
106. Bend Research, Inc., Technology Summary: Sludge Reclamation Using Coupled Transport Membranes, Bend, Oregon.