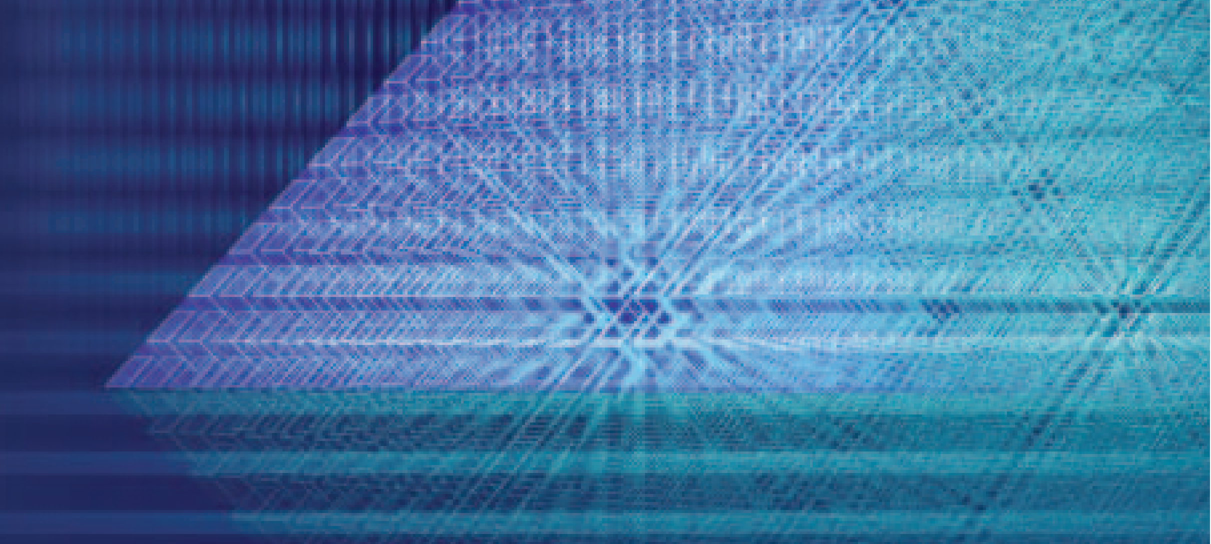

TECHNICAL REPORTS SERIES NO. 431

Application of Membrane Technologies for Liquid Radioactive Waste Processing

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APPLICATION OF MEMBRANE TECHNOLOGIES FOR LIQUID RADIOACTIVE WASTE PROCESSING

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FOREWORD

In recent decades various membrane separation processes have been developed and utilized in the field of potable water purification and, more recently, in the treatment of various process liquors and liquid waste. The widening application of membrane processes and technologies is a result of the increasing variety of commercial membranes and membrane apparatus available. Since the development of suitable membrane materials and their long term verification in conventional water purification fields, these membrane processes have been adopted by the nuclear industry as a viable alternative treatment method for liquid radioactive wastes. It has been demonstrated that pressure driven membrane separation processes can be successfully employed for the removal of radioactive substances and have some distinct advantages over the existing conventional processes. Membrane processes in combination with other conventional methods have proved to offer superior treatment capabilities, particularly in instances where conventional methods alone were not as efficient or effective.

Recognizing the growing importance of membrane technologies in processing different liquid radioactive waste streams it was decided to prepare this report which reviews and analyses the existing information on application of these technologies in the nuclear industry, in particular in the processing of liquid radioactive waste. The report reviews types of membranes, equipment design, range of applications, operating experience and performance characteristics of different membrane processes. The report intends to provide Member States with the basic information on applicability of membrane separation technologies for processing liquid radioactive waste.

The initial draft of this report was prepared by consultants from Canada and the Russian Federation and then discussed and further developed at a series of meetings between 2000 and 2003.

The IAEA is grateful to those who contributed to the preparation of this report and wishes to especially thank R. Kohout of Canada who compiled all the available information and prepared the final version. The IAEA officer responsible for the report was V. Efremenkov of the Division of Nuclear Fuel Cycle and Waste Technology.

CONTENTS

1. INTRODUCTION

1.1. BACKGROUND

The nuclear industry generates a broad spectrum of low and intermediate level liquid radioactive wastes (LRWs). These liquid wastes may be produced continuously or in batches and may vary considerably in volume, radioactivity and chemical composition. A wide range of treatment methods has been used throughout the industry to treat these wastes.

Treatment methods for LRWs have usually utilized the same conventional processes found in industrial and municipal water treatment. These processes typically include chemical treatment, adsorption, filtration, ion exchange and evaporation. They are limited by either their inability to remove all contaminants or, in the case of evaporation, the high operating costs involved and the large quantities of secondary solid waste produced, making satisfactory processing of LRWs difficult.

In recent decades various membrane separation processes have been developed and utilized in the field of potable water purification and more recently in the treatment of various process and waste liquors. Some of the membrane processes are capable of removing both dissolved and particulate contaminants. The best known and most utilized processes in the field of water and wastewater treatment are those utilizing pressure gradient as the process driving force. These processes include reverse osmosis, nanofiltration, ultrafiltration and microfiltration.

It has been demonstrated that pressure driven membrane separation processes can be successfully employed for the removal of radioactive substances, with some distinct advantages over the more conventional processes. After development of suitable membrane materials and their long term verification in conventional water purification fields, these membrane processes have been adopted by the nuclear industry as a viable alternative for the treatment of LRWs. In most cases the membrane processes are used as one or more of the treatment steps in complex waste treatment schemes combining conventional and membrane treatment technologies. These combined systems have proved to offer superior treatment capabilities, particularly in cases where conventional methods alone could not perform the task as efficiently or effectively.

Other membrane separation methods are in use or in various stages of development. These methods utilize electrical potential, concentration or temperature gradient as their driving force instead of pressure gradient. While some of these have been successfully tested and utilized in various industries, they have generally not proved to be technologies of choice for processing LRWs. However, some of these new membrane methods are being rapidly developed and could become technically significant in the future.

Pressure driven membrane separation processes may be considered either as alternatives to existing radioactive waste processing techniques or to complement existing radioactive treatment systems. In practice, most modern radioactive waste processing systems use a combination of membrane separation and conventional steps. In some systems the membrane separation process is the main treatment step, while in others it supports conventional technologies, increasing their effectiveness. Such combined systems are capable of producing high quality treated effluents, bearing an acceptable level of residual radioactivity, for discharge. In addition, the volumes of secondary radioactive waste residues are minimized and can be suitably conditioned to meet the waste form criteria for disposal.

1.2. OBJECTIVE AND SCOPE

The objective of this report is to provide Member States and their technical and regulatory bodies with meaningful information on membrane separation techniques and their applicability to the processing of liquid radioactive process streams and wastes. It is intended to provide an understanding of the unique features of membrane separation methods and their application for contaminant removal. The report also covers the operational sensitivities and limitations of membrane systems. Special emphasis is placed on factors that need to be carefully assessed when considering membrane technology for the processing of LRWs. These include equipment design, membrane configuration and arrangement, process application, operational experience, data for key performance monitoring, plant and organizational impacts.

This report covers the processing of aqueous low and intermediate level radioactive wastes by pressure driven membrane processes. The membrane processes covered in detail are reverse osmosis, nanofiltration, ultrafiltration and microfiltration. Other membrane separation methods, such as those using driving forces other than pressure, are not in the scope of this report but information on them is provided in Section 2 and Appendix II.

1.3. STRUCTURE

This report is structured to provide a general overview of pressure driven membrane separation processes and a summary of their application to the nuclear industry. An overview of membrane separation processes in general is presented in Section 2. Sections 3–5 provide theoretical and technical information on pressure driven processes. Design and performance requirements and operational considerations for these processes are provided in Sections 6 and 7. Examples of actual applications of membrane technology in the nuclear industry are given in Section 8. Section 9 provides concluding remarks on the requirements for implementation of membrane technology techniques in LRW processing. Appendix I contains case studies of membrane technologies successfully applied to the treatment of LRWs. Other membrane separation methods that have not been utilized for treatment of radioactive wastes are highlighted in Appendix II.

2. MEMBRANE TECHNOLOGY

A wide variety of membrane separation processes exist. These differ from one another in the type and configuration of the membrane, the mechanism of trans-membrane transport for various water solution components, the nature of the process driving force and other features. While some processes are well proven in full scale industrial applications, others are experimental, in development, or are in transition from the development stage to industrial use. The proven processes have been used for purification, desalination, ion separation, material recovery, or concentration process functions in industries such as water purification, wastewater treatment, pharmaceutical, medical, microelectronics, chemical processing, food processing, etc.

2.1. GENERAL OVERVIEW OF MEMBRANE SEPARATION TECHNOLOGY

Membrane separation processes may be classified and categorized by a number of criteria. An exhaustive variety of membrane classifications can be found in Refs [1, 2]. A basic distinction between the individual methods is the process driving force used to purify or concentrate a solution, which may be a pressure gradient, concentration gradient, electrical potential gradient or temperature gradient. In some instances, and specifically in some processes under development, more than one driving force may be used. Membrane processes can be classified as follows with respect to the process driving force:

Pressure gradient (P) as the process driving force:

— Reverse osmosis;
— Nanofiltration;
— Ultrafiltration;
— Microfiltration.

Electrical potential gradient (E) as the process driving force:

— Electrodialysis;
— Electrodialysis with application of liquid organic membranes;
— Membrane electrolysis;
— Electrosorption;
— Electrofiltration;
— Electrochemical ion exchange.

Concentration gradient (C) as the process driving force:

— Dialysis;
— Membrane extraction;
— Supported liquid membrane (SLM);
— Emulsion liquid membrane (ELM);
— Non-dispersive solvent extraction with hollow fibre contactors;
— Pervaporation.

Temperature gradient (T) as the process driving force:

— Membrane distillation;
— Thermo-osmosis.

Processes with combined driving forces:

— Electro-osmofiltration (P + E);
— Electro-osmotic concentration (E + C);
— Gas separation (P + C);
— Piezodialysis (P + C).

A simplified overview of the common membrane separation methods arranged by the main process driving force and the respective application range is shown in Fig. 1 [3]. Table 1 provides further information on these processes, such as membrane type, method of separation and range of applications [4].

2.2. RADIOACTIVE WASTE TREATMENT APPLICATIONS

2.2.1. Pressure driven membrane processes

The pressure driven separation processes such as reverse osmosis, nanofiltration, ultrafiltration and microfiltration have been preferred by the nuclear industry over other membrane processes for the following reasons:

(a) They are well proven in industrial water and wastewater treatment applications.
(b) They are mature technologies with over 30 years of design and operating experience.
(c) A large number of successful applications have already been used successfully in the nuclear industry.
(d) The process design is well understood and computer simulation codes are available.
(e) Flexibility in process configurations can optimize performance.
(f) They are suitable for system integration with conventional treatment steps.
(g) A broad spectrum of membrane materials and types is available for pressure driven processes and these membranes can match the characteristics of the contaminants to be removed.
(h) They are suitable to meet broad process objectives and needs. Pressure driven membrane systems cover the entire removal spectrum from large particles to ionic species (see Fig. 1).

It is envisaged that pressure driven membrane processes will remain the leading membrane processes for full scale utilization in the nuclear industry, especially where larger volumes of radioactive wastes with variable characteristics are involved. Consequently, pressure driven processes are covered in detail in this report.

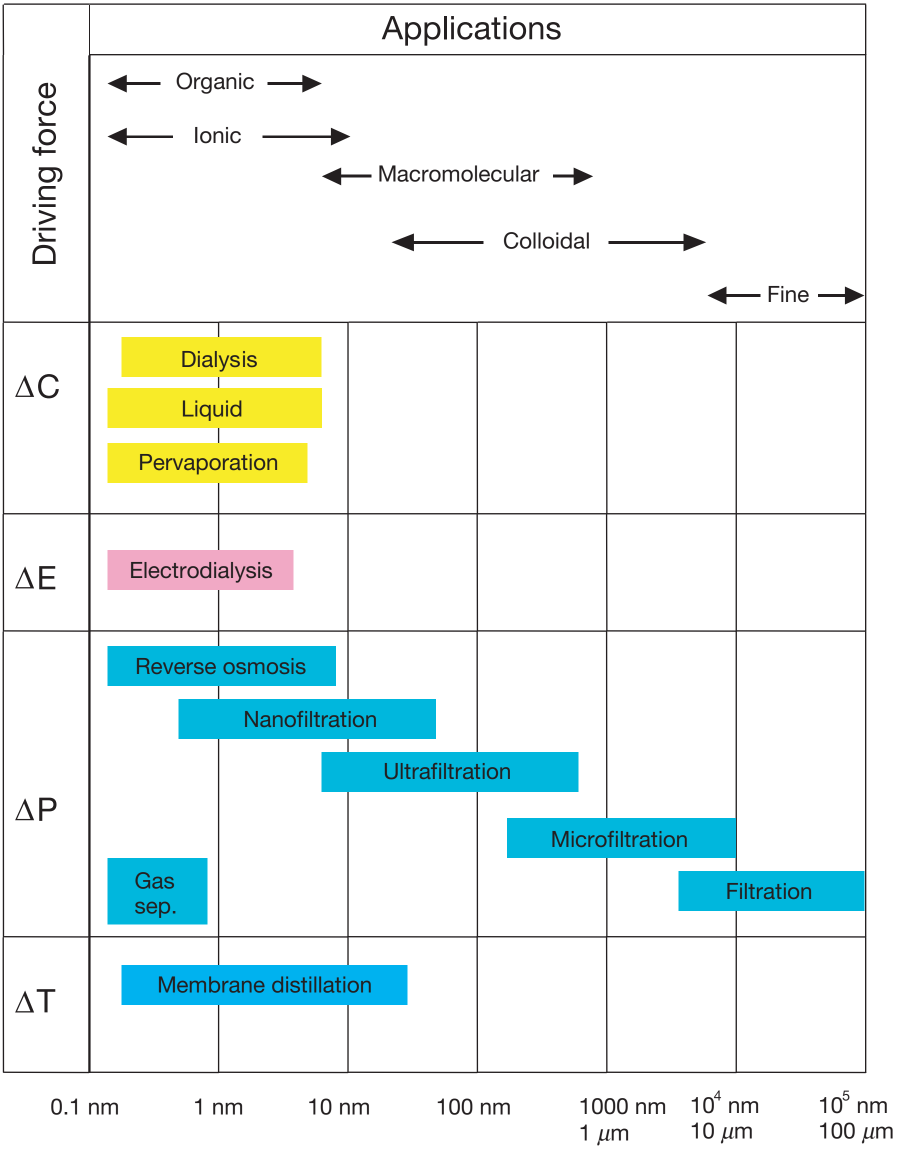


FIG. 1. Typical membrane separation methods.

TABLE 1. TYPICAL MEMBRANE SEPARATION PROCESSES: OPERATING PRINCIPLES AND APPLICATIONS

Separation process	Membrane type	Separation method	Range of application
Microfiltration	Symmetric microporous membrane	Sieving mechanism as a function of pore size and adsorption	Sterile filtration clarification
Ultrafiltration	Asymmetric microporous membrane	Sieving mechanism	Separation of macromolecular solutions
Nanofiltration	Asymmetric ‘skin type’ membrane	Solution diffusion mechanism	Separation of divalent ions from solutions
Reverse osmosis	Asymmetric ‘skin type’ membrane	Solution diffusion mechanism	Separation of salt and microsolutes from solutions
Dialysis	Symmetric microporous	Diffusion	Separation of salt and microsolutes from macromolecular solutions
Electrodialysis	Cation and anion exchange membranes	Selective transport of ions or molecules according to electric charge	Desalting of ionic solutions
Supported liquid membrane	Microporous membranes supporting adsorbed organic liquid	Solution diffusion via carrier	Separation and concentration of metal ions and biological species
Membrane distillation	Microporous membranes	Vapour transport into hydrophobic membrane	Ultrapure water concentration of solutions
Pervaporation	Asymmetric membrane	Solution diffusion mechanism	Separation of organics

2.2.2. Other membrane processes

Other membrane separation processes, such as those utilizing electrical potential, concentration and temperature gradient, or combinations of these, are numerous. Some of these processes have been tested in various countries for removal of radionuclides or treatment of nuclear power plant wastes, but to date have not seen widespread use in the nuclear industry, with some minor exceptions. For example, electrodialysis has been used in the Russian Federation for the treatment of LRWs but has not been used widely in other countries. A potential problem associated with electrodialysis is the formation of explosive and toxic gases which may deter the application of this technology for the treatment of radioactive waste. It is envisaged that some separation methods will undergo further development in the future and be considered for the treatment of LRWs. Information on membrane separation methods other than pressure driven ones is provided in Appendix II. This information includes references on their application for the treatment of LRWs, where applicable.

2.2.3. Objectives of application

The objectives and goals of the installation of membrane technology in a nuclear power plant or any other facility producing LRW are specific to each case. In most cases a number of objectives and goals together warrant incorporation of membrane separation technology. The following are examples of typical waste treatment objectives that may entail installation of membrane technology, depending on local conditions and the specific needs of the facility:

(a) Replacement or upgrade of an existing system which is not performing to satisfaction and/or is operating with ageing components;
(b) Volume reduction of bulk quantities of liquid waste to facilitate further processing by more conventional treatment techniques (such as evaporation);
(c) Reduction of the volume of radioactive wastes to be disposed of, typically to extend the life of on-site storage facilities or to lower waste disposal costs;
(d) Meeting ‘zero liquid’ discharge requirements on nuclear power plants (i.e. all water generated within the plant must be returned for recycling);
(e) Attainment of high product water purity levels to meet criteria for environmental discharges;
(f) Reduction of radiation exposures to operators and maintenance personnel;

(g) Attainment of the capability to process liquid waste that has varying concentrations of impurities while meeting product quality requirements;
(h) Removal or reduction in the concentration of selected substances (particulate or dissolved, organic or mineral, radioactive or non-radioactive);
(i) Reduction of operating costs;
(j) Reduction of labour requirements;
(k) Overall waste treatment economics.

2.2.4. Economics

One reason to consider separation technology in addition to, or as a replacement for, conventional processes is to reduce waste treatment costs. This depends to a great degree on local operating and licensing conditions for the particular facility. Some membrane processes, such as ultrafiltration and nanofiltration, can perform treatment functions that conventional techniques cannot, and therefore costs cannot be compared. However, the overall membrane treatment plan can be compared, for example, to an existing evaporation process in terms of decontamination efficiency, and the total treatment costs may then be compared.

The relative costs of all separation processes are an important criterion in the selection of a treatment process. For example, Fig. 2 shows the relative costs of some desalination technologies as a function of salt concentration in the feedwater [5]. This indicates that membrane technologies such as reverse osmosis or electrodialysis are generally not used at very low ionic strengths (where ion exchange is less expensive) or very high salt concentrations (where distillation (evaporation) is less expensive), but are usually cost effective for the range of feedwaters between these extremes.

2.2.5. System design

For treatment of LRWs, especially in nuclear power plants, membrane processes are most often installed to complement or enhance the performance of existing treatment systems. In these situations consideration needs to be given to the existing system and its capabilities, such as waste feed collection and storage, waste stream segregation provisions, availability of filtration and ion exchange equipment, and provisions for the treatment of secondary liquid waste streams. The size and/or choice of membrane system may be dictated by the available floor space and the control systems may need to be integrated with existing systems. The product water from the membrane system may require ion exchange polishing, utilizing existing equipment to meet the discharge or recycle quality requirements. The concentrate from the membrane process may be further reduced in volume by an existing evaporator, or conditioned directly utilizing existing immobilization systems.

Application of any specific membrane process must be considered in the context of the overall processing goals, which will include consideration of waste feed characteristics, desired product quality, process limitations, overall system flexibility, the final waste form desired, compatibility with existing treatment systems, and cost. Membrane systems are rarely acquired ‘off the shelf’ but must be designed and then built only after extensive on-site testing for each specific application. Aspects to be considered in the overall system design are addressed in Section 6, and examples of membrane technology applications for the treatment of a variety of LRWs are given in Section 8.

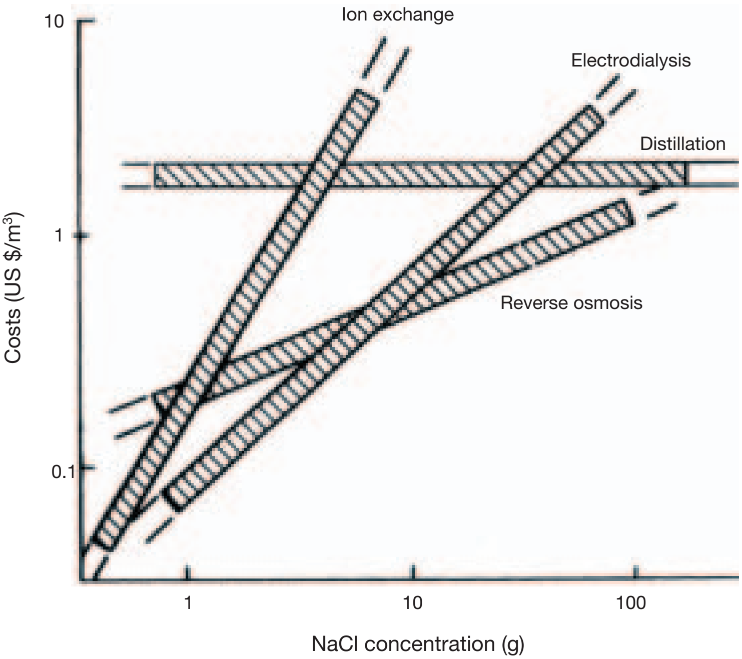


FIG. 2. Water desalination costs as a function of salt concentration.

3. PRESSURE DRIVEN MEMBRANE PROCESSES

3.1. GENERAL

Pressure driven membrane separation processes differ mainly in the pore size of their membranes, which makes a particular membrane effective for the removal of a specific range of impurities. Reverse osmosis is used to remove all ionic species and thus has the smallest membrane pore size. Nanofiltration is sometimes referred to as ‘loose reverse osmosis’ as it can remove divalent ions and low molecular weight contaminants while allowing monovalent ions to pass through. Ultrafiltration is used for removal of macromolecules such as proteins and small colloids, but not ionic species. Microfiltration is used to remove particulates, bacteria, and other larger colloids only. Semi-permeable membrane pore size ranges, with the categories of impurity for which the respective processes are effective, are shown in Fig. 3 [6].

The smaller the solutes or particulates to be separated, the smaller the pore size of the membrane and the greater the process pressures required. This has implications for both operating and capital costs. The process efficiency and

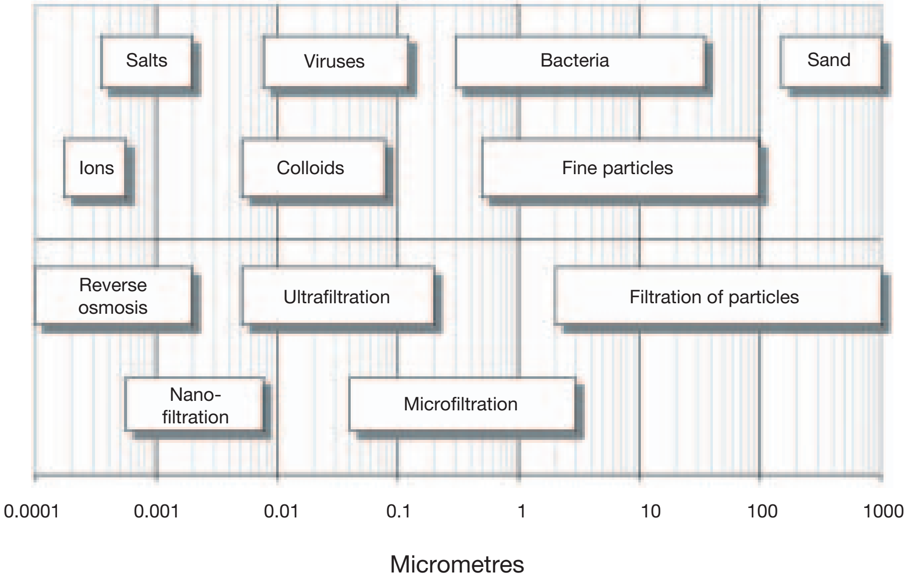


FIG. 3. Semi-permeable membrane pore size ranges, with categories of impurities for which they are effective.

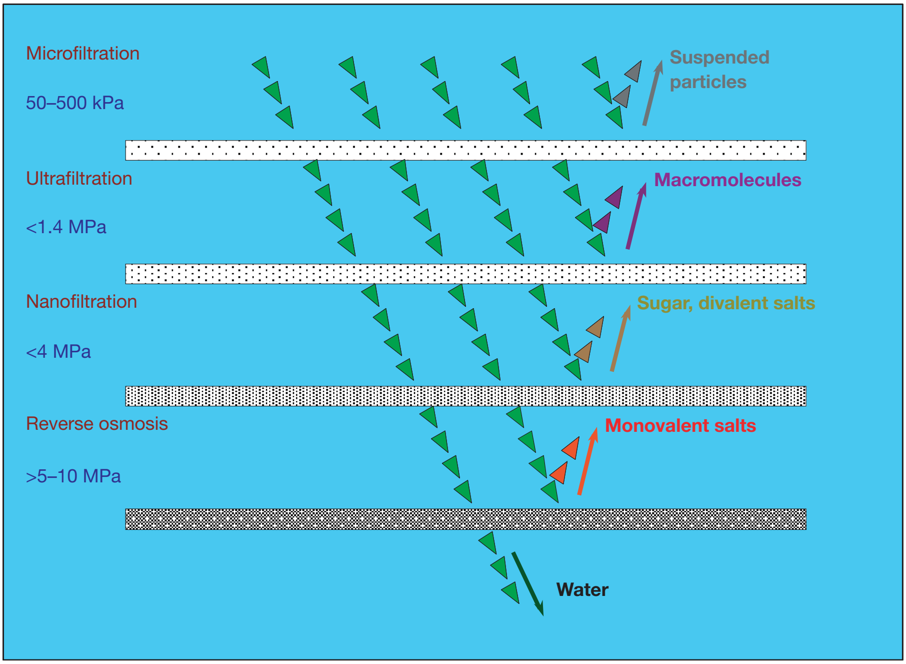


FIG. 4. Pressure driven membrane processes.

membrane performance, however, often depend on the operating conditions and their susceptibility to fouling, which may reduce the effective size of the pores. Nominal pore sizes provided by the manufacturer are only a rough guide and may lose their significance when membrane fouling occurs under operating conditions. Figure 4 illustrates the relationship between pore size and typical operating pressures for pressure driven membrane processes [3].

In pressure driven membrane systems the pressure of the feed solution permits passage of the major portion of the solution through a semi-permeable membrane. The portion of the feed solution that passes through the membrane is called permeate, product or filtrate. The portion of the feed solution that does not pass through the membrane is called concentrate, retentate or reject. A simple schematic representation of a membrane process is shown in Fig. 5.

3.2. CROSS-FLOW VERSUS DEAD END FILTRATION

Pressure driven membrane processes may be viewed as sophisticated filtration methods capable of separating fine particles, molecules and ions in

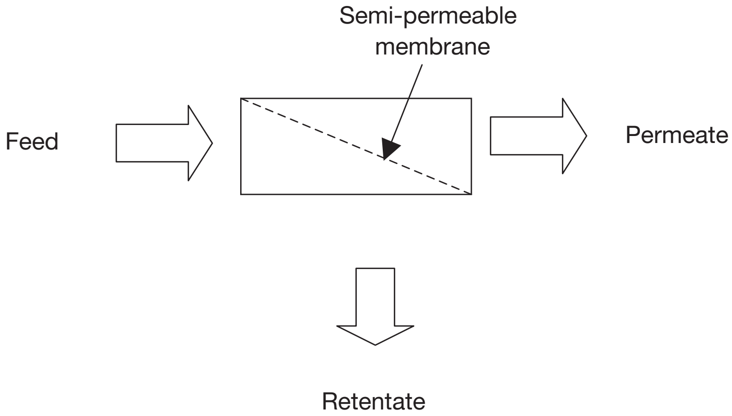


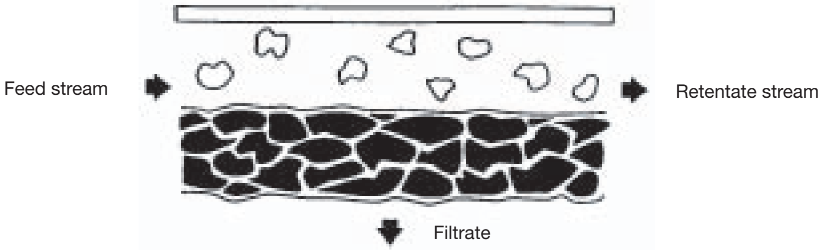
FIG. 5. Schematic representation of a membrane module.

solution. Pressure driven membrane processes can be operated in cross-flow mode or in dead end (conventional) mode. A schematic comparison of cross-flow and conventional filtration is shown in Fig. 6 [7].

In conventional filtration, feed flow is perpendicular to the membrane or filter surface. There is only one product stream, the filtrate. All of the feed solution passes through the filter and is recovered. In conventional flow configurations, the flow dead ends against the filter surface. Accumulating particles on the filter surface may cause significant pressure drop as the filter surface becomes plugged or fouled. This accumulation must be removed periodically, either by back-flushing gas or liquid through the filter (membrane) or by other means.

In most membrane separation process applications, pump pressure is utilized to drive the feed solution along the membrane surface in a cross-flow filtration mode rather than perpendicular to the membrane surface. Cross-flow filtration reduces material buildup on the membrane by sweeping the material away from the surface. However, there are limits to the type of membrane fouling that the cross-flow velocity can inhibit.

(a) Cross-flow filtration



(b) Conventional filtration

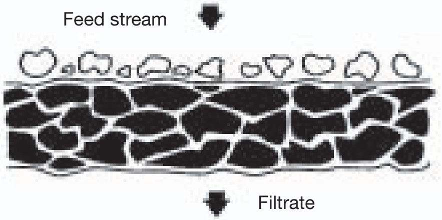


FIG. 6. (a) Cross-flow filtration versus (b) conventional (dead end) filtration.

3.3. REVERSE OSMOSIS

3.3.1. Reverse osmosis process

3.3.1.1. Direct osmosis

Osmosis is the spontaneous transport (diffusion) of solvent that takes place when two solutions of different concentrations are separated by a semi-permeable membrane that allows the solvent (but not dissolved species) to pass through it. The solvent, usually water, flows through the membrane from the less concentrated into the more concentrated solution (Fig. 7). The flow continues until the solutions on both sides of the membrane are at the same concentration or until the pressure exerted by the difference in height between the two solutions is sufficient to stop the flow. The pressure required to just

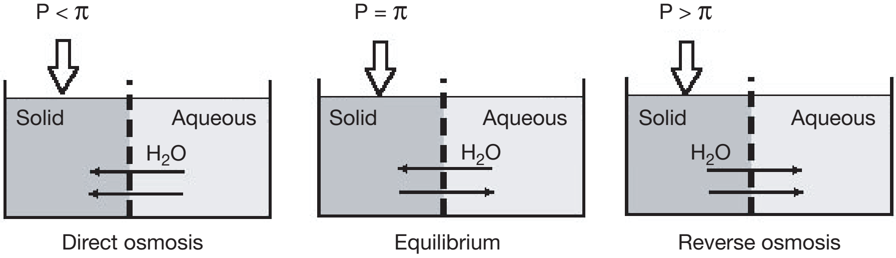


FIG. 7. Conditions of direct osmosis and reverse osmosis.

stop the flow is termed osmotic pressure, at which point the two solutions are in equilibrium. As the concentration difference between the solutions on the two sides of the membrane increases, the osmotic pressure increases.

3.3.1.2. Reverse osmosis

The osmosis process can be reversed. Pressure applied to the more concentrated solution will permit the solvent to flow through the semi-permeable membrane into the less concentrated solution (Fig. 7) [8]. The term reverse osmosis is reserved for separation of dissolved ions and small molecules that contaminate aqueous solutions. The pressure exerted to force the flow of water into the less concentrated solution must exceed the osmotic pressure of the feed solution.

The pressure imposed upon a feedwater in a reverse osmosis operation has two components — that required to overcome the osmotic pressure of the solution to liberate pure water and that required to overcome resistance to flow posed by the membrane. There is a straight line relationship between the driving pressure and the rate of water permeation through the semi-permeable membrane.

In reverse osmosis, pressure greater than the osmotic pressure (2–10 MPa) is applied to the concentrated solution to cause the solvent to flow from the concentrated side of a semipermeable membrane to the diluted side. In most applications of reverse osmosis, when the dissolved solid concentration reaches about 5–10 wt%, the osmotic pressure becomes too high to sustain the process. Reverse osmosis typically removes 95–99.5% of total dissolved inorganic solids and 95–97% of dissolved organic solids. Some basic patents covering reverse osmosis processes are described in Refs [9–13].

Reverse osmosis is used industrially for the production of drinking water from saline or brackish waters and is increasingly being used for the treatment of wastewaters. In general, reverse osmosis systems compete with other separation processes (such as evaporation) that are used for the total rejection of contaminants in feedwater.

3.3.2. Applicability of reverse osmosis to LRWs

Reverse osmosis is a well developed technology. Systems have been used in industrial settings for many years, being applied to separation, concentration of product streams and wastewater treatment. The technology has been used for removal of radionuclides from low level liquid wastes such as waste streams at nuclear power plants. Because reverse osmosis rejects nearly all contaminants from a solution (dissolved gases and tritium being two exceptions), the high purity product water may be recycled within the power plant. The purified water is usually of such low activity (sometimes after ion exchange polishing) that it is suitable for discharge to the environment (see Section 8 and Appendix I for examples of applications). In recent years reverse osmosis systems have been used to replace or augment existing evaporation and/or ion exchange technology. Reverse osmosis systems in the nuclear industry are usually a part of an overall liquid waste treatment system.

3.4. ULTRAFILTRATION

3.4.1. Ultrafiltration process

The ultrafiltration membrane is considerably more porous (i.e. its nominal pore size is larger) than the reverse osmosis membrane. As a result, most soluble species, including inorganic salts, pass through the membrane with the water. Colloids, suspended solids and high molecular weight organic molecules do not pass through the membrane with the water. They are rejected and remain in the concentrate (retentate) stream. The porous nature of the ultrafiltration membrane allows the process to be operated with high fluxes at relatively low pressures (e.g. 0.2–1.4 MPa). This is possible because the osmotic pressure of colloids and high molecular weight organics is extremely low. The degree and quantity of the separation are a result of the pore size of the membrane and the molecular structure, size, shape and flexibility of the colloids and organic molecules. Pore sizes ranging from 0.001–0.01 μm allow separation from solution of molecules with a molecular weight between 500 and 300 000.

Ultrafiltration units are usually operated on the cross-flow principle. Some basic patents covering ultrafiltration processes are provided in

Refs [14–16]. Ultrafiltration is used industrially for the removal of macromolecules and colloids from wastewater and has been used extensively in the food and dairy industries.

3.4.2. Applicability of ultrafiltration to LRWs

In some applications the primary function of ultrafiltration systems is to remove colloids and other particulate foulants from feed streams that are to be further treated by reverse osmosis systems. Ultrafiltration is often used for the removal of alpha activity from waste streams. Actinide wastes are often in colloidal or pseudo-colloidal form in a radioactive waste stream and can be effectively removed by ultrafiltration. Ultrafiltration can also be used to selectively remove dissolved metal ions from dilute aqueous solutions if these ions are pretreated to form solid particles, hydroxo complexes or other less soluble chemical species. An example of this is the addition of a high molecular weight chelating agent to the incoming waste solution to form macromolecular complexes. The solution is then processed through an ultrafiltration membrane system that rejects the macromolecular complexes (retentate) but allows uncomplexed ions such as sodium, potassium, calcium, chloride, sulphate and nitrate to pass through as filtered water (permeate).

Ultrafiltration is used in the treatment of fuel pond storage waters, solvent wash liquors and plutonium evaporator overheads from reprocessing lines, and of aqueous effluents from plutonium fuel fabrication plants. The use of complexing agents in combination with ultrafiltration has been seen as having the potential to yield high decontamination factors (DFs) for specific ions [17]. Inorganic ultrafilters based on zirconium/carbon and other matrices have shown potential in radioactive waste treatment [18]. Published information [19–21] indicates that DFs in the region of 1000 for α and 100 for β and γ species can be achieved, with an overall volume reduction of the order of 10^4.

3.5. MICROFILTRATION

3.5.1. Microfiltration process

Microfiltration is a membrane separation process with membrane pore sizes between 0.05 and 5 μm, operating at pressures up to 0.1 MPa. The membrane rejects particles and dissolved macromolecules larger than 0.1 μm. Microfiltration membranes have a relatively large average pore size and consequently can retain only relatively large impurities (i.e. suspended fine particles, but not colloidal matter), but operate at high flux rates. Some basic patents covering microfiltration processes are given in Refs [22–26]. Microfiltration is used industrially for the removal of particulate material and has been used extensively in drinking water treatment and for the treatment of domestic sewage.

3.5.2. Applicability of microfiltration to LRWs

Microfiltration is used for particle separation in wastewaters generated by LWR power plants and often provides a concentration factor (CF) of 100. The process can be used in conjunction with precipitation processes, provided the precipitated particles are suitably coarse. Organic as well as inorganic microfiltration membranes can be used, depending on the characteristics of the feedwater. Ceramic microfilters have been used in the nuclear industry for high activity wastewaters because of that material's radiation stability.

3.6. NANOFILTRATION

3.6.1. Nanofiltration process

Nanofiltration is a membrane separation process which uses thin porous membranes with pore sizes between 0.001 and 0.01 μm. Nanofiltration processes typically operate at pressures from 0.3 to 1.4 MPa. These membranes also reject organic compounds with a molecular weight of 200–500 or above [27, 28]. Nanofiltration thus represents a process that functions between ultrafiltration and reverse osmosis, and is often termed 'loose reverse osmosis'. The range of pore sizes makes this process unique since single-charged ions pass freely through the pores but multi-charged ions, which have larger dimensions, are retained. Nanofiltration membranes are also called demineralizing (or water softening) membranes [29].

Nanofiltration membranes are often negatively charged, so it is primarily the anion repulsion that determines salt rejection. These membranes can provide selective separations, including separation of salts with charge differences and separation of high molecular weight organics from high concentration monovalent salt solutions. In addition, these membranes can provide high fluxes at low pressures, as compared with conventional reverse osmosis membranes. These characteristics have been exploited for several wastewater treatment applications. Nanofiltration has been used industrially in water softening applications, removal of dissolved organic substances and fractionation of low and high molecular weight organic substances [30].

3.6.2. Applicability of nanofiltration to LRWs

In the nuclear industry, the major use of nanofiltration membranes has been in boric acid wastewater treatment. These have been used to reject radioactivity while allowing boric acid to pass through with the permeate, thus allowing the permeate to be recycled or discharged. Nanofiltration may also be used in fuel fabrication facilities to remove dissolved uranium ions from wash solutions, permitting their discharge with no further treatment.

4. MEMBRANE TYPES AND CONFIGURATIONS

Membrane separation processes are governed by both the chemical nature of the membrane materials and the physical structure of the membranes. The desired separation attainable with a particular membrane depends on the relative permeability of the membrane for the treated feed solution components. The most important characteristics of membranes are pore size distribution, porosity, surface chemistry, chemical and physical compatibility with process liquors, and cost.

For this report, the membranes of interest are those that have found widespread utilization in the nuclear industry. These are thin porous semi-permeable membranes constructed from polymeric materials, and membranes made of inorganic materials such as special ceramics, all suitable for use in pressure driven separation processes.

4.1. POLYMERIC MEMBRANES

4.1.1. Physical structure

Membranes can be categorized by their physical structure as homogeneous (symmetric), non-homogeneous (asymmetric) and composite. Homogeneous or symmetric membranes are made of one material with an identical structure throughout the thickness of the membrane. To ensure sufficient mechanical strength, the membrane has to be of suitable thickness to withstand hydraulic pressures. This characteristic is disadvantageous in operation as it creates a higher hydraulic resistance to flow. For this reason these membranes are usually only used for microfiltration.

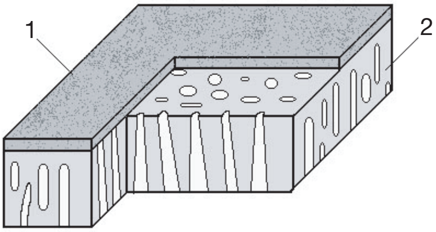


FIG. 8. Structure of an anisotropic membrane: (1) selective thin porous (active) layer with a thickness of 0.1–1 μm; (2) thick porous sub-layer with a thickness of 0.1–1 μm.

Historically, the conflicting requirements to have a membrane with low hydraulic resistance but containing pores small enough to effectively reject impurities were successfully reconciled at the end of the 1950s by Sourirajan and Loeb [31], who developed a two layer anisotropic thin porous semi-permeable membrane, shown in Fig. 8. These non-homogeneous or asymmetric single layer membranes are composed of a very thin active layer which is connected to a thicker porous supporting layer made of the same material.

The selectivity of the separation process, i.e. a measure of the passage of a given component through the membrane, is controlled by the properties of the active layer. The porous supporting layer only serves to improve the mechanical properties of the membrane. The finely porous active skin layer grades to a macroporous structure underneath. These membranes are used in the separation range from microfiltration to reverse osmosis.

Thin film composite (TFC) membranes consist of an active surface layer, a support layer and various intermediate layers. The intermediate layers usually consist of three layers, a support web, a microporous interlayer and an ultra-thin barrier layer on the top surface. Structural support is provided by the web, onto which the microporous interlayer is cast. The top barrier layer can withstand high pressures because of the support provided by the interlayer. All three layers are normally made of different materials. For example, a polyamide barrier layer may be supported by a polysulphone microporous support cast onto a polyester web [32], as shown in Fig. 9. These membranes are typically manufactured for nanofiltration and reverse osmosis applications.

Since the initial development of the first asymmetric cellulose acetate membrane, significant progress has been made in the field of non-cellulosic membrane materials that are more durable, less susceptible to biodegradation, and perform well within broad pH and temperature ranges. The materials most commonly used for the production of membranes are:

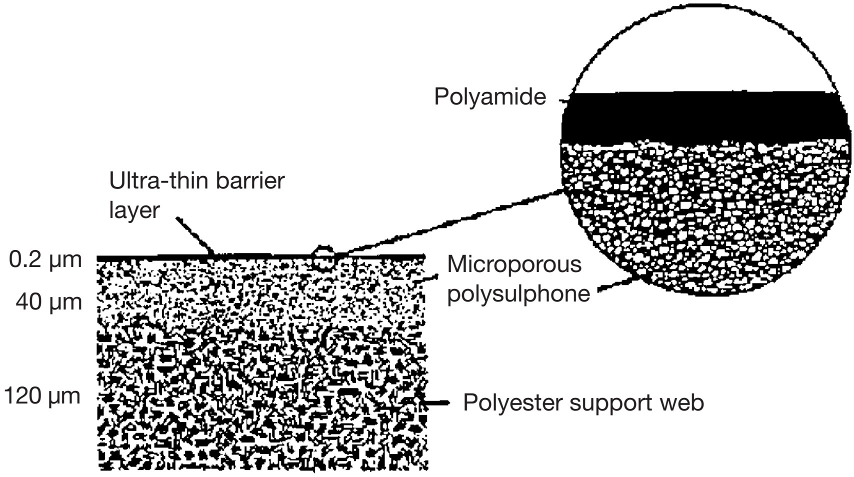


FIG. 9. Schematic cross-section of a TFC reverse osmosis membrane.

— Cellulose acetate;
— Polypropylene;
— Polysulphone;
— Polyvinyldenefluoride (pvdf);
— Polyamide/polysulphone TFCs.

While cellulose acetate was initially used to form asymmetric membranes, the development of TFC membranes represents the latest technological development. New membrane materials and production technologies are continually being investigated.

4.1.2. Geometric shape

Polymeric membranes are usually produced as flat films or hollow fibres. They can also be produced by coating the polymer onto supporting surfaces, such as those surfaces that have a tubular geometry. For commercial utilization, membranes are formed in elements that can be easily handled, installed and operated.

Flat membranes are most often arranged in a spirally wound configuration to fit within cylindrical piping, but they also may be produced as sheets to fit into specialized equipment shells (plate and frame). Hollow fibre membranes are typically arranged in cylindrical elements, formed into a ‘tube

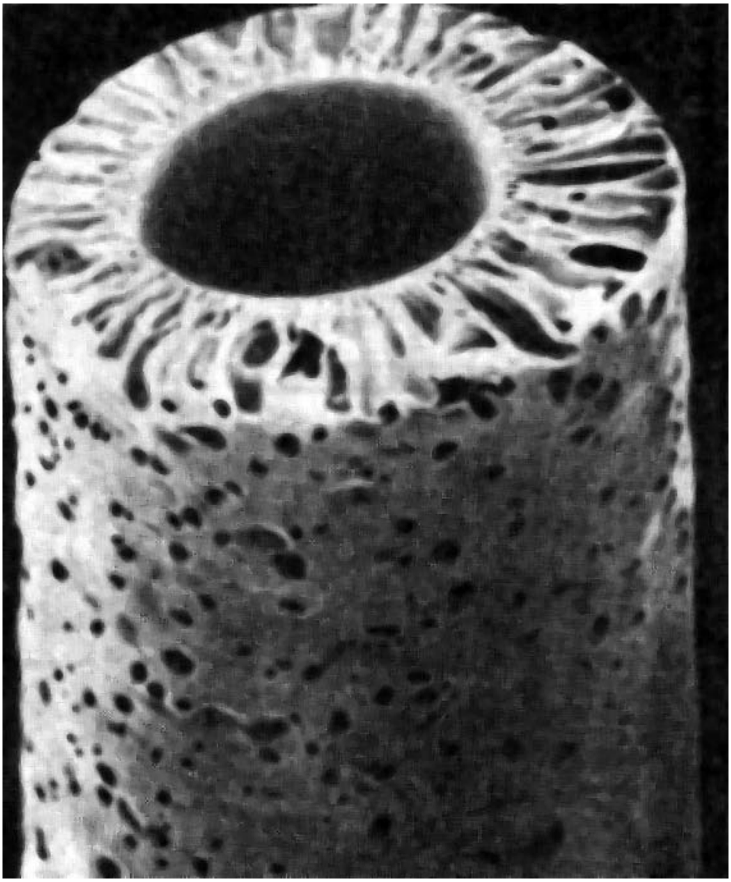


FIG. 10. AMICON hollow fibre ultrafiltration membrane with the active layer on the inside surface.

sheet' configuration. An active layer of hollow fibre membranes, having a nominal fibre diameter of tens of microns, can be on either the outside or the inside wall of the hollow fibre, as shown in Fig. 10 [2]. For tube diameters reaching several centimetres, the active layer of tubular membranes is usually placed on the inside of the tube. The membrane element shells are pressure vessels that form a pressure boundary for the treated feed solution under operating conditions.

4.1.3. Temperature limits

Cellulose acetate membranes operate satisfactorily in the 5–50°C temperature range. Above 50°C, cellulose acetate begins to hydrolyse, losing its ability to reject ionic species. Aromatic polyamide membranes have a similar operating temperature range of 5–46°C. Thin film composites can operate in a temperature range of 0–79°C with no degradation [33]. However, these are only typical temperature ranges which vary with the specific membrane material. Membrane suppliers must be consulted for operating temperature data.

4.1.4. Separation ability

The separation abilities of a membrane are characterized by its 'cut-off', which indicates the size of particles which are blocked by the membrane and kept on its feed flow side. In the case of microfiltration membranes, the cut-off is expressed as the mean pore size (usually expressed in micrometres), and in ultrafiltration membranes as the relative molecular mass of substances that do not pass through the membrane. Nominal pore sizes provided by the manufacturer are only a rough guide as most membranes have a wide pore size distribution. The separation ability of nanofiltration and reverse osmosis membranes is usually expressed by a rejection coefficient, usually determined for a 0.5% NaCl solution.

4.1.5. Radiation stability

The properties of most polymeric membranes remain stable up to radiation doses of 10^5 Gy [34].

4.1.6. Resistance to chemical attack

4.1.6.1. Oxidizing agents

The active layers of the majority of polymeric membranes can quickly decompose in the presence of oxidizing agents such as chlorine-organic substances, ozone and hydrogen peroxide. These oxidizing agents are often used to suppress the growth of bacteria and microorganisms on membranes. Since polymeric membranes can be destroyed by low levels of strong oxidants it is important to neutralize or remove the oxidizing agents before the feedwater is introduced to the membrane. This can be achieved by adding reducing chemical agents (e.g. sodium bisulphate, $NaHSO_3$) to the feed solution, or removing the oxidants with activated carbon or by other means.

While aromatic polyamide membranes cannot tolerate chlorine at all, thin film composite membranes tolerate chlorine levels of up to 100 ppm [33]. Many membrane manufacturers will provide data on the exposure limits to free chlorine. For example, the membrane may be rated at 1000 h of exposure to 1 ppm free chlorine before degradation begins to take place. The rate of chlorine attack will also depend on other factors such as the concentration of other ions which may act as catalysts to reduce the free chlorine. Allowable chlorine concentrations for various membrane materials are shown in Table 2 [35].

4.1.6.2. pH range

Cellulose acetate membranes operate in a limited pH range of 2.7–7. Aromatic polyamide membranes can tolerate a pH range of 4–11. Thin film composites can tolerate a broader pH range of <1–13 [33]. Allowable pH ranges for some polymeric membranes are given in Table 2.

TABLE 2. ALLOWABLE CONCENTRATIONS OF CHLORINE AND pH OPERATING RANGES FOR TYPICAL REVERSE OSMOSIS MEMBRANES

Reverse osmosis membrane type	Allowable chlorine concentration (ppm)	Allowable pH range
Cellulose acetate based	03–1.0	4–6
Polyamide[a]	<0.05	4–11
TFC not resistant[b]	0[c]	3–11
TFC with minimal resistance[d]	0.05	3–11
TFC chlorine resistant[e]	1.0	3–11

[a] Linear polyamide.

[b] Polyamide or polyurethane.

[c] Feed must be dechlorinated.

[d] Aromatic polyamide.

[e] Sulphonated polysulphone.

4.1.7. Biodegradability

The first generation of thin porous membranes manufactured from cellulose containing materials was degraded by biological activity. Biodegradation led to the membranes having increased porosity and surface damage that reduced the ability of the membranes to retain contaminants. The newer polymeric membranes available on the market today are less susceptible to biological attack. However, the membrane surfaces can still serve as breeding grounds for biological activity causing blockage (fouling) of the membrane pores, thus reducing the membrane's performance. Precautions that need to be taken to prevent biodegradation of the polymeric membranes are described in Section 7.

4.1.8. Useful life

Polymeric membranes used for conventional non-radioactive water purification may have lifetimes of over five years, depending on the application. Membrane lifetime in radioactive waste treatment applications may be similar, depending on the specific application, the radiation stability of the membranes and any synergistic effects of all the process variables. Manufacturers of polymeric membranes normally give the expected lifetime of their products as three years.

4.2. INORGANIC MEMBRANES

Inorganic membranes manufactured from materials such as ceramics, metal, graphite, and combinations of these have been produced or are under development in an attempt to alleviate some of the limiting features of polymeric membranes. They have gained popularity for applications in harsh operating environments where polymeric membranes would not perform well or would not survive at all. The available pore size range of inorganic membranes is still generally limited to microfiltration and ultrafiltration applications. They are usually manufactured in a tubular form.

Inorganic membranes exhibit greater mechanical durability in some operations than polymeric membranes. They do not suffer from the performance degradation that results from compaction of the membrane structure under pressure or ageing. The main disadvantage of inorganic membranes has been their considerable manufacturing cost compared to polymeric membranes. The most common materials used for inorganic membranes are:

— Zirconium oxide/carbon;
— Ceramic;
— Metallic oxides (alumina);
— Stainless steel.

Inorganic membranes can operate at elevated temperatures, with metal membranes remaining stable at temperatures as high as 500–800ºC. Many ceramic membranes are usable at temperatures exceeding 1000ºC. They are also much more resistant to chemical and radiation attack.

Ceramic membranes are being used increasingly in membrane separation applications. Their production technology has vastly improved with the introduction of ceramic 'nanostructural' materials. There are a number of methods of producing nanostructural materials and selective surface layers, all of them based on sol-gel processes. The most frequently used materials to produce nanostructural layers appear to be Al_2O_3, ZrO_2, CeO_2, TiO_2 [36]. Ceramic membranes usually have a coarse base (several millimetres thickness), a thin inter-layer (10–100 μm thickness) and a selective layer (1–5 μm thickness). The selective layer is the active layer with average pore sizes of up to 2.5 nm. This layer can be modified, for example, by impregnation of a polymeric material into its pores [37]. In this way it is possible to manufacture a highly durable reverse osmosis membrane on a firm base. For example, CARBOSEP ceramic membranes manufactured in France have a tubular macroporous carbon base coated by a thin selective ZrO_2 layer. These tubular membranes (Fig. 11) are available in two different geometries, single channel or 'trilobe', with a wide range of cut-off values (10–0.1 μm), particularly suitable for ultrafiltration

FIG. 11. CARBOSEP tubular inorganic membranes.

applications. CARBOSEP membranes are insensitive to solvents; highly resistant to radiation; have superior resistance to heat, chemical and mechanical constraints; and ageing. They can be sterilized with steam. Ceramic monolithic KERASEP tubular membranes (Fig. 12) are offered in several multi-channel geometries (7, 19 or 27 channels), with a range of cut-offs suitable for applications between nanofiltration and microfiltration. They also have excellent resistance to chemical constraints and ageing.

There are no data on the radiation resistance of inorganic membranes, but this is considerably higher than for polymeric membranes. This would permit processing of radioactive waste with higher levels of radioactivity, or greatly extending the useful lifetime of the membranes.

4.3. CONFIGURATION OF MEMBRANE ELEMENTS

To make practical use of polymeric membranes in treatment systems and satisfy throughput requirements, the membrane's surface area needs to be maximized in a configuration that is easily installed, maintained and occupies a minimum amount of space. These requirements have led membrane suppliers to develop membrane elements (modules) that meet these objectives in an optimal way for each type of membrane container: flat, tubular, spirally wound and hollow fibre. The advantages and disadvantages of the different membrane elements are listed in Table 3 [33].

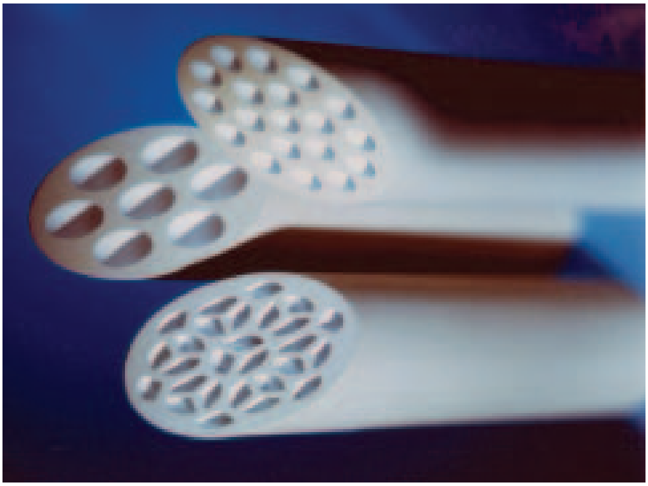


FIG. 12. KERASEP high flux ceramic monolithic membranes.

The various membrane configurations have the following ranges of membrane surface working area per unit of membrane element volume [2, 8, 38]:

- — Flat (60–300 m^2/m^3);
- — Tubular (60–200 m^2/m^3);
- — Spirally wound (300–800 m^2/m^3);
- — Hollow fibre (20 000–30 000 m^2/m^3).

TABLE 3. ADVANTAGES AND DISADVANTAGES OF VARIOUS MEMBRANE ELEMENTS

Element type	Advantages	Disadvantages
Flat (plate and frame)	Moderate membrane surface/ volume ratio Well-developed equipment	Susceptible to plugging at flow stagnation points Potentially difficult to clean Expensive.
Tubular	Easiest type to clean chemically or mechanically if membranes become fouled Can process high suspended solid feed with minimal pretreatment Good hydrodynamic control Individual tubes can be replaced High pressure (1500 psig*) equipment available	Relative high volume required per unit membrane area Relatively expensive
Spirally wound	Compact Good membrane surface/ volume ratio Less expensive than tubular and hollow fibre elements	Susceptible to plugging by particulates Badly fouled membranes are difficult to clean — basically limited to chemical cleaning
Hollow fibre	Compact Excellent membrane surface/ volume ratio Economical	Susceptible to plugging by particulates Badly fouled membrane elements are hard to clean — limited to chemical methods

* 1500 psig = 1.034×10^7 Pa.

TABLE 4. GENERAL CHARACTERISTICS OF VARIOUS MEMBRANE ELEMENTS

Element properties	Type of membrane element			
	Flat plate	Spirally wound	Tubular	Hollow fibre
Packing density (m^3)	Moderate (200–500)	High (500–1000)	Low–moderate (100–500)	High–very high (500–10 000)
Energy utilization	Low–moderate (laminar flow)	Moderate (depends on spacer design)	High (turbulent flow)	Low (laminar/dead end)
Cleaning	Moderate	Can be difficult (spacer blockage)	Good (physical cleaning of surface with spongy balls)	Good (back-flushing)
Replacement	Single sheet or cartridge	Entire element	Tubes or entire element	Entire element
Material	Polymeric, ceramic (small)	Polymeric	Ceramic/ polymeric/ sintered metal/ carbon	Polymeric, glass
Common applications	Microfiltration, ultrafiltration (small to medium scale)	Nanofiltration, reverse osmosis (large scale)	Microfiltration, ultrafiltration, reverse osmosis (small to medium scale)	Microfiltration (large scale)

This and other general characteristics of various membrane types are summarized in Table 4 [3].

4.3.1. Tubular membrane elements

The tubular membrane element configuration has a simple design. The membrane is usually inserted into, or coated onto the inside surface of a porous tube. The tube is designed to withstand the necessary operating pressures. Figures 13 and 14, respectively, give a schematic and general view of the tubular membrane design. The liquid feed is introduced into one end of the tube, and as it flows through the tube permeate passes through the membrane in cross-flow. The permeate is collected in an outer shell of the element that encases the

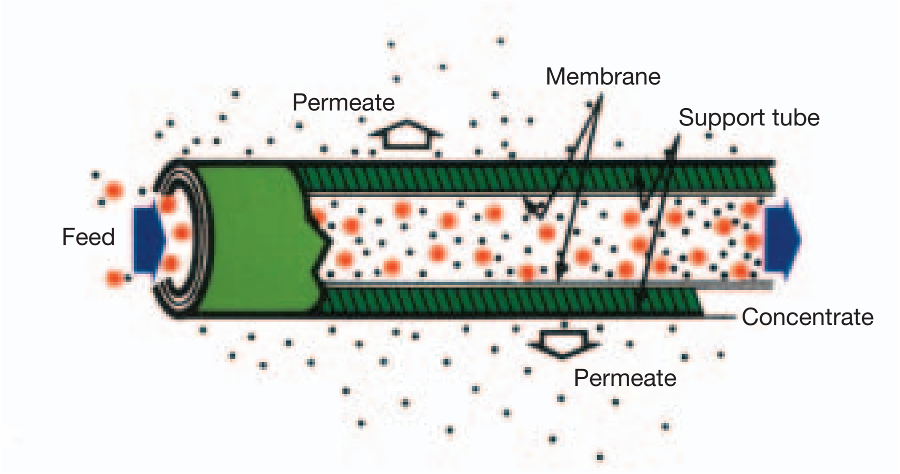


FIG. 13. Schematic view of a tubular membrane design.

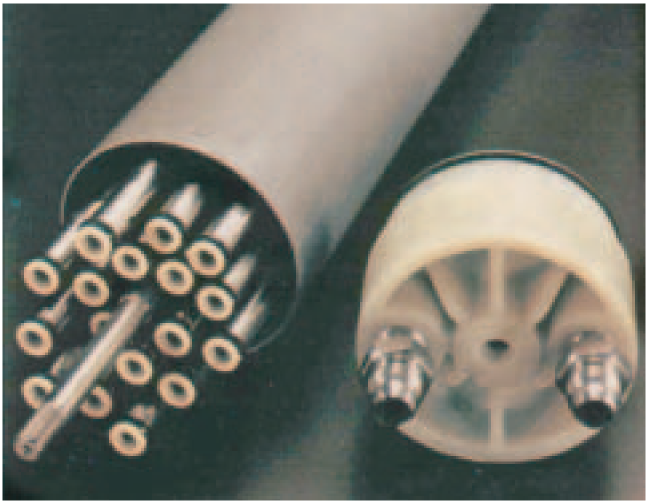


FIG. 14. General view of tubular membrane design.

An important advantage of the tubular arrangement is that the feed liquor can flow across the membrane surface at high velocities (up to 10 m/s), reducing the possibility of surface fouling. However, this in turn results in higher pumping costs. The membrane surface can easily be cleaned by periodically passing spongy balls whose diameter is slightly larger than the tube diameter through the tubes. The membranes are also easily cleaned by chemical cleaning solutions. Individual membrane tubes can be replaced easily in some designs, reducing the cost associated with replacement of the whole element. Tubular membranes have a high tolerance for suspended solids and are often chosen over other module designs for these applications. Ultrafiltration modules are often tubular in design.

The main disadvantage of tubular membrane systems is the low membrane packing density, which results in a large footprint for installations and a subsequent high cost in comparison with other membrane configurations. A disadvantage of processing radioactive solutions with tubular membranes is the high hold-up volume per unit of membrane area.

4.3.2. Spirally wound membrane elements

A spirally wound membrane element is simply a flat sheet assembly rolled into a central core. The elements contain two layers of spirally wound polymeric membrane with a porous woven fabric support sandwiched in between. The three sides of this assembly are sealed to form an envelope containing the porous support. The open fourth side is attached to a perforated central tube. A sheet of plastic mesh is placed on one side of the membrane envelope. The membrane envelope and the mesh are then wrapped around the perforated central tube in a spiral fashion. The mesh separates the membrane layers and also serves as a turbulence promoter.

The individual spirally wound membrane sections are inserted into a cylindrical pressure vessel to form a completed membrane element. A single element may contain several spirally wound sections connected in series. The feed solution is introduced into the first element at one end and flows along the inter-membrane gap created by the mesh. Product water permeates the membrane inside the membrane envelope in a cross-flow fashion and follows the flow channels in the fabric support that directs the permeate to the perforated central tube for collection. The remaining feed solution (now somewhat concentrated) enters the subsequent membrane section where the process is repeated. Schematic and general views of a spiral membrane element are given in Figs 15 and 16.

The main advantage of this design is the large surface area of the membrane that is packaged into a relatively small volume of the cylindrical membrane element. The volume of liquid hold-up is small, which is an advantage since radiation fields can be better controlled. A further advantage is that the membrane configuration allows easy chemical cleaning. However, the narrow flow channels are susceptible to fouling by turbid feed solutions.

The dead space between the spirally wound membrane section and its container makes this configuration susceptible to biological growth. Typically,

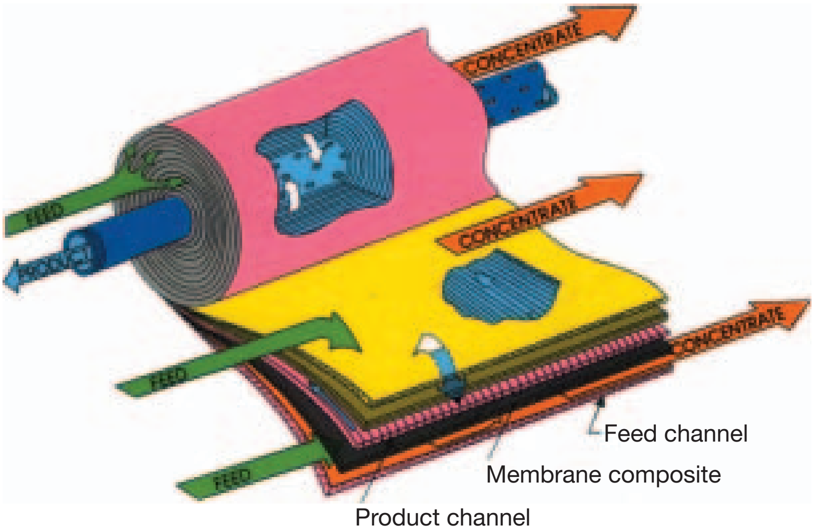


FIG. 15. Schematic view of a spirally wound membrane section.

fouling and biological growth are most likely at the leading edge of the last section of the element shell. The high hydraulic resistance of spirally wound membrane elements compared to other designs is also a disadvantage. Sometimes the element itself can break down if high pressure causes the element to come apart in a telescope-like fashion. Another disadvantage is that the entire element has to be replaced in the event of membrane damage or irreversible fouling. Spirally wound elements are of standard sizes, i.e. 5, 10, and 20 cm in diameter. As one of the least expensive and compact configurations they are commonly used in reverse osmosis applications and have been used extensively for desalination of seawater and brackish waters. They are rarely used without pretreatment of the feedwater to remove suspended solids.

4.3.3. Hollow fibre membrane elements

Hollow fibre elements contain membranes that have been produced from hollow hair-like fibres with outside diameters of 200 μm or less. The fibres have a thin dense skin that inhibits permeation of contaminants but allows product water to pass through. A thick porous layer under the active skin provides support for the skin while allowing free passage of water to and from the fibre pores. The fibres are wrapped around a support frame and bundled together into either a U shape or a straight-through configuration in an element with a

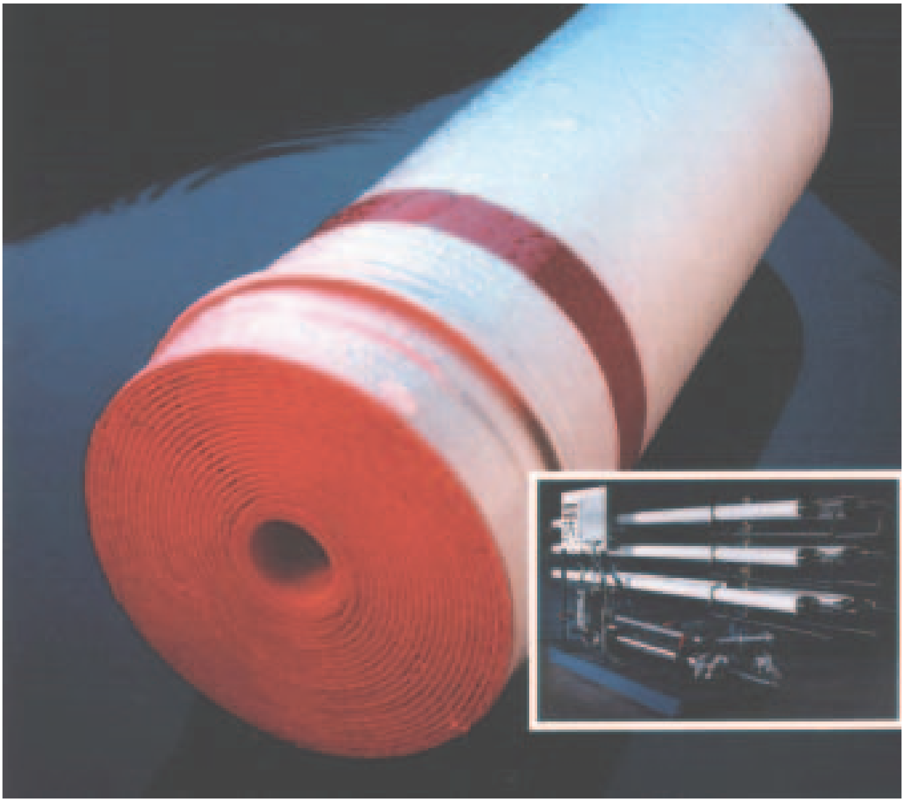


FIG. 16. General view of a spirally wound membrane element.

straight-through fibre configuration. The feed is directed into the inside of the fibres. The permeate passes through the membrane to the outside of the fibres where it collects inside the element shell. The concentrate exits from the opposite end of the element. Figure 17 gives a general view of an element containing hollow fibre membranes.

Hollow fibre elements are quite compact due to a very high packing density and require minimal floor space. Product recovery is high, typically 50–60% of the feed flow. The hollow fibres can withstand high operating pressures which are contained within the fibres, so the element shells are simple to design and relatively inexpensive to fabricate. Hollow fibre configurations can also be operated as dead end filters with cleaning by back-flushing of the fibre elements. They can also be operated under vacuum conditions because of the

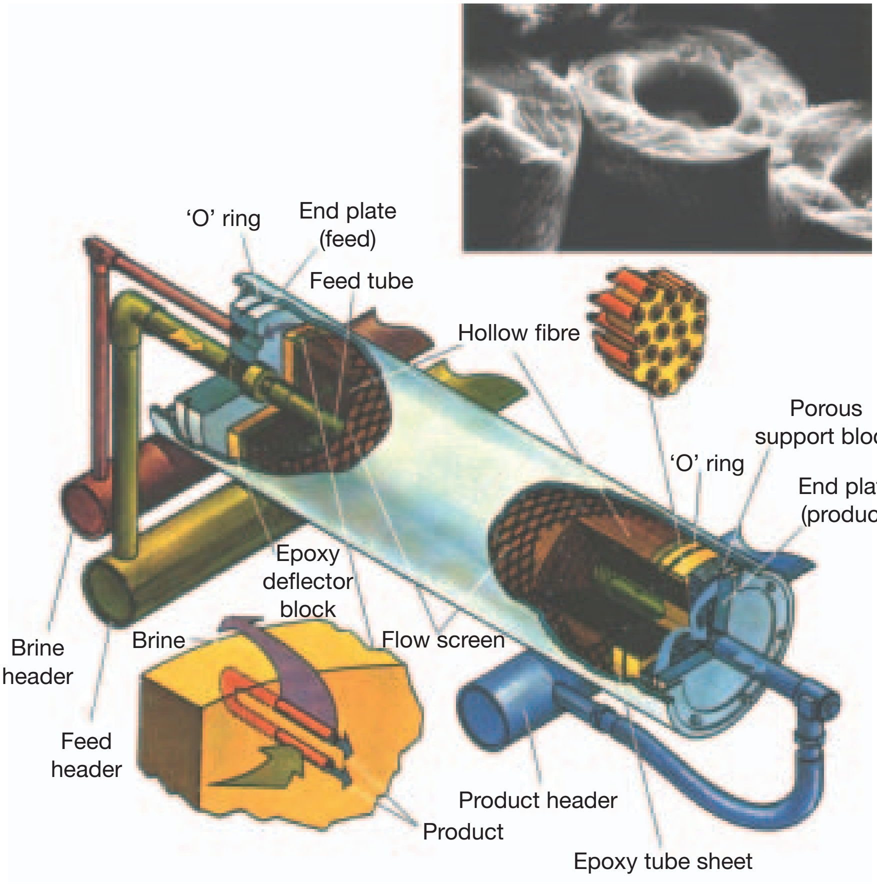


FIG. 17. General view of an element containing hollow fibre membranes.

strength of the individual fibres. Microfiltration hollow fibre systems have been used extensively in drinking water applications and in the polishing of treated sewage water because of the low cost per unit of membrane area.

4.3.4. Flat membrane devices

4.3.4.1. Flat polymeric membrane devices

The first semi-permeable membranes developed were geometrically flat and required a plate and frame press to operate. Figure 18 gives a general view of a typical design of flat (plate and frame) membrane equipment. The device consists of membrane support plates and spacers that are stacked alternately in

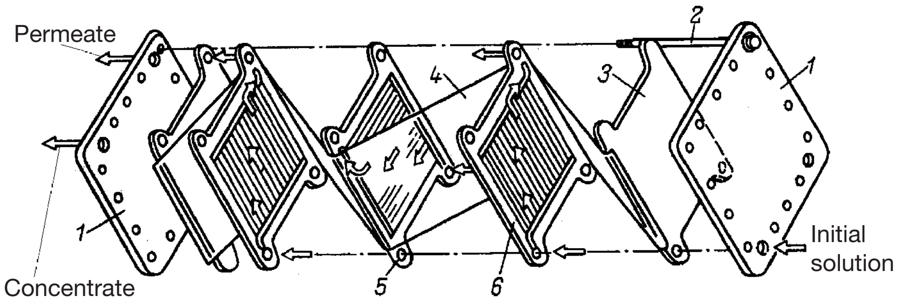


FIG. 18. *Filter press flat sheet membranes: (1) flanges, (2) tightening bolt, (3) strong plate, (4) membrane, (5) drainage plate, (6) separating plate.*

a sandwich-like array and held together by bolts. The membrane support plates provide a rigid backing for the membranes, but also provide flow channels that collect the permeate from the membrane and carry the permeate to an outlet tube. The spacer plates direct the feed solution uniformly over the membrane surfaces. The spacers and support plates may be made of metal or moulded plastics, with the rest of the assembly made of steel.

The plate and frame membrane assembly is simple to manufacture and easy to install and operate. The main disadvantage of this system is that it has a low membrane area/volume ratio, requiring much more floor space for the equipment. Another disadvantage is the method of membrane cleaning, which is labour intensive and requires disassembly of the stack. This is undesirable in radioactive liquid applications because of the potential radiation dose to operators and the possible spread of contamination.

4.3.4.2. Flat ceramic membrane devices

Flat ceramic membranes are mainly used in microfiltration and ultrafiltration equipment that operates by rotary tangential flows. There is little possibility of developing and manufacturing the same equipment with polymeric membranes because these would not be strong enough to withstand the gravitational forces created during rotation of the equipment.

4.4. MEMBRANE EQUIPMENT AND SYSTEMS

Membrane plants can be designed as skid mounted systems, stationary systems, or as mobile units that can be easily moved between applications. The membrane plant itself will consist of membrane elements, associated pumps and tanks, control equipment, dosing equipment, and cleaning systems.

4.4.1. Transportable skid mounted plants

Skid mounted systems normally contain membrane modules, pumps, controls, chemical dosing equipment, a clean-in-place (CIP) system, and connections for feed and product water, all within a self-supporting framed structure. Typical skid mounted systems are pilot plants and some smaller throughput permanent systems.

Figure 19 shows a skid mounted pilot plant for treating low level radioactive effluent. This particular pilot plant consists of a tubular ultrafiltration system that is used to pre-treat the feed, and a two stage and two pass reverse osmosis system that uses spirally wound elements. The plant was designed to process radioactive feedwater at a rate of 20 L/min.

4.4.2. Fixed stationary plants

Stationary systems typically are permanent systems having a larger throughput, with individual components fixed in place separately and connected by permanent piping and wiring to the process control centre located at some distance from the operating membrane equipment. Pumps, process control equipment and miscellaneous service equipment such as dosing facilities and cleaning tanks are installed separately from the skid mounted membrane elements.

Figures 20 and 21 show a permanent stationary system containing B-9 DuPont hollow fibre reverse osmosis elements used for the production of ultrapure water in the microelectronics industry in Canada [39]. The system shown has a throughput of 60 m^3/h.

Figure 22 shows a fixed membrane system containing reverse osmosis elements only. This is an industrial sized unit, with a throughput of 240 m^3/h, treating contaminated groundwater in a nickel refinery [40].

Figure 23 shows a fixed membrane system containing ultrafiltration and reverse osmosis membrane systems. This is a large installation with a throughput of 670 m^3/h, treating effluent from a municipal sewage treatment plant. The treated water is reused in a petroleum refinery [40].

FIG. 19. Two views of a skid mounted pilot plant containing tubular ultrafiltration and spirally wound reverse osmosis systems (courtesy of ANSTO).

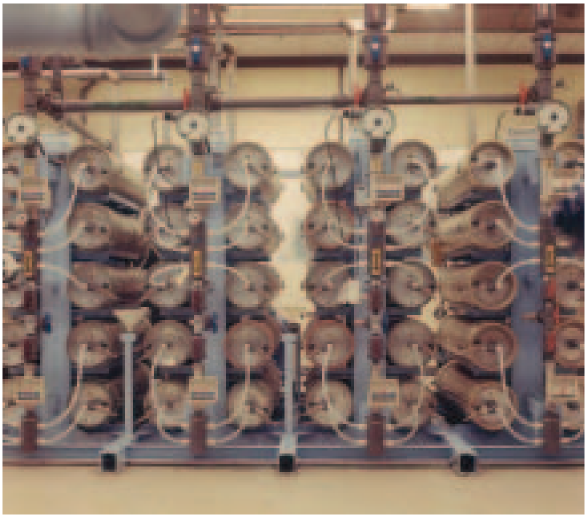


FIG. 20. A stationary hollow fibre reverse osmosis plant with a throughput of 60 m^3/h.

FIG. 21. High-pressure multi-stage pumping station of the 60 m^3/h hollow fibre reverse osmosis plant.

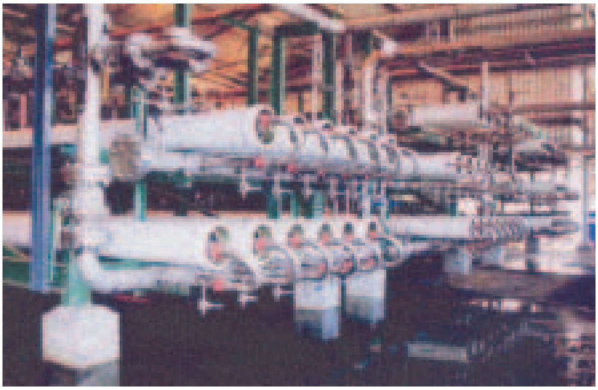


FIG. 22. Fixed membrane reverse osmosis system with a throughput of 240 m^3/h.

FIG. 23. Fixed membrane ultrafiltration/reverse osmosis system with a throughput of 670 m^3/h.

4.4.3. Mobile systems

Figure 24 shows a mobile system, 'ECO-2', used to treat small batches of liquid waste at various sites in the Russian Federation. Various mobile plants in the ECO series have a similar process configuration, consisting of filtration, spirally wound ultrafiltration, ion exchange softening, electrodialysis and adsorption. This particular mobile plant, ECO-2 (Fig. 24), was put into service in 1993. More than 450 m^3 of LRWs, originating as surface runoff from a solid

FIG. 24. The ECO-2 mobile system for LRW processing, containing ultrafiltration and electrodialysis equipment.

radioactive waste disposal site, were treated. In 1997, about 400 m^3 of low level liquid wastes were processed by this mobile plant at the RADON facility in Volgograd [41].

The main shortcoming of the ECO series of mobile systems has been their lack of flexibility to allow for a quick change of process technology to meet the particular treatment requirements of different sites. Furthermore, experience showed that it was necessary to adjust the process components even when treating radioactive wastes from different sources at the same site. This experience confirmed that each radioactive waste treatment application requires a custom-made treatment system, and that it is difficult to design a fully versatile system that has the capability of processing different substances.

5. OPERATING PARAMETERS

This section describes and defines the basic operating parameters used in the design and operation of pressure driven membrane separation processes such as reverse osmosis, ultrafiltration, microfiltration and nanofiltration.

5.1. FLUX

The rate at which the product (permeate) passes through the membrane per unit area of membrane surface is defined as flux. It is generally reported in terms of volume of processed product for a given area of membrane over a period of time. Flux is reported in units of $L{\cdot}m^{-2}{\cdot}d^{-1}$, $m^{-3}{\cdot}m^{-2}{\cdot}s^{-1}$, $m^{-3}{\cdot}m^{-2}{\cdot}d^{-1}$ or USgal/$ft^{-2}{\cdot}d^{-1}$. The ability to maintain a constant flux over an extended time period has an important bearing on the operating costs of a membrane system. The membrane is replaced when the output (permeate) falls to an unacceptable level and cleaning and regeneration procedures fail to restore the flux. Decreases in flux caused by surface fouling, internal pore fouling, concentration polarization and membrane compaction are discussed in Section 7.

Two of the key variables that affect the flux are temperature and pressure of the feed solution. Flux increases with higher temperature because fluid viscosity decreases. Consequently, water flux through microfiltration, ultrafiltration, nanofiltration and reverse osmosis membranes increases by about 3% per degree Celsius as water temperature increases. The thermal stability of the membrane limits the temperature to which the feed solution can be raised. For most organic based membranes this limit is approximately 45°C. Higher processing temperatures are possible with ceramic based microfiltration membranes.

In reverse osmosis and nanofiltration systems, as the pressure is increased, flux increases linearly and product quality increases. The osmotic pressure of the feed solution determines the flux/pressure relationship (Fig. 25) [3]. In ultrafiltration and microfiltration systems, the flux initially increases and then levels off and becomes independent of the pressure (Fig. 26) because of concentration polarization (discussed in Section 7) [3]. However, unlike reverse osmosis, the product quality of microfiltration and ultrafiltration systems decreases with increased pressure.

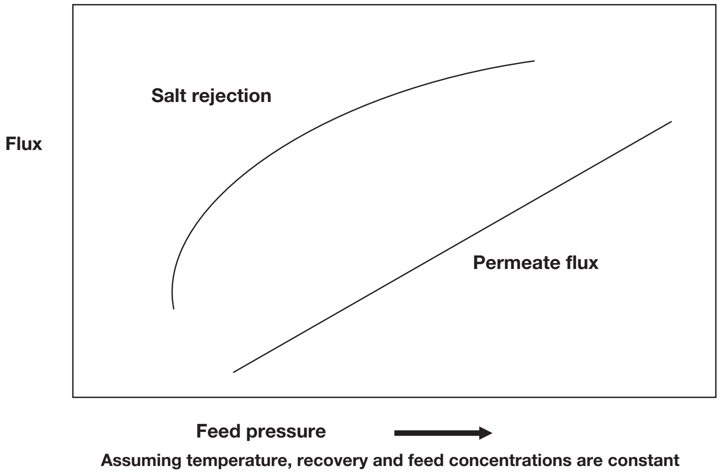


FIG. 25. The effect of pressure on reverse osmosis and nanofiltration.

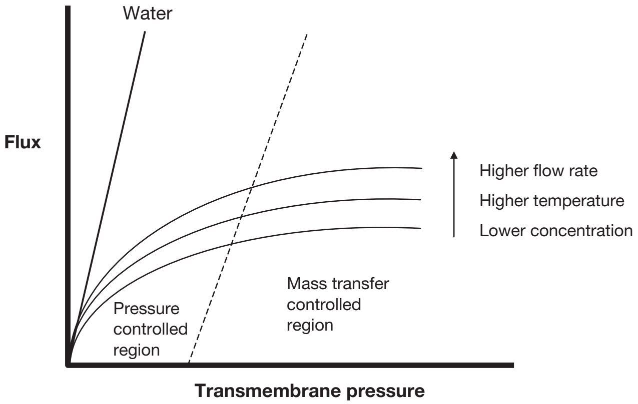


FIG. 26. The effect of pressure on microfiltration and ultrafiltration.

The pH of the feed solution will also affect the flux. Membrane processes are characterized by solute–solute interactions and membrane–solute interactions, and these can often be sensitive to pH. In ultrafiltration for example, the colloid or macro-solute charge varies with pH and the membrane used may also be sensitive to pH. The interaction of the two will determine rejection and the potential for fouling.

5.1.1. Normalized flux

To distinguish between normal phenomena such as permeate decrease with decreasing temperature and real performance changes, the measured permeate flow has to be normed. This means comparison with a given reference performance. For example, the permeate flux might be normed to an operating feed temperature of 25°C and a pressure of 2.76 MPa (400 psig). The observed permeate flux (*OBF*) in MPa is normed using a temperature correction factor (*TCF*) supplied by the manufacturer [42, 43]. The feed pressure (*FP*) in MPa is adjusted based on the permeate back pressure (*PBP*) in MPa and the osmotic pressure (*OP*) of the feed solution in MPa. The normalized permeate flux (*NPF*) is:

$$NPF = \frac{2.76}{[FP - PBP - OP]} \cdot \frac{1}{TCF} \cdot \mathrm{OBF} \tag{1}$$

5.1.2. Critical flux

The critical flux defines the permeate flux above which an irreversible deposit appears [44]. In cross-flow filtration the critical flux appears where the boundary layer is thickest, usually at the exit from the membrane channel [45]. Above the critical flux deposits will grow, eventually requiring mechanical or chemical cleaning. Thus, membrane processes may be distinguished by two distinct zones, one where no deposit appears and no cleaning is required and a zone where cleaning becomes necessary. Critical flux depends on the hydrodynamics and particle size charge on the membrane.

5.2. RECOVERY FACTOR

The recovery facture measures how much of the feed is recovered as permeate. It is reported as a percentage. Recovery is calculated using:

$$\text{Recovery} = \frac{Q_{\text{permeate}}}{Q_{\text{feed}}} \cdot 100 \tag{2}$$

where Q_{permeate} is the permeate (or product) flow rate and Q_{feed} is the feed flow rate.

For dead end filtration systems the recovery factor is 100% because all of the solution passes through the filter into the filtrate.

Extremely high recoveries are possible in microfiltration systems, but for reverse osmosis, nanofiltration and ultrafiltration systems typical recoveries are in the range of 75–95%. However, 80% is often the practical limit because of severe reductions in operating efficiency.

A key point to consider for reverse osmosis applications is that as the recovery is increased, the osmotic pressure increases and the amount of energy required to overcome the osmotic pressure increases. The purity of the permeate is also reduced as the feed concentration increases (Fig. 27) [3].

5.3. REJECTION FACTOR

Rejection, or retention, is a measure of the fraction of solute or solid that is retained or does not pass through the membrane. It is generally expressed as a percentage, calculated using the following equation:

$$R = \frac{\left(C_{\text{feed}} - C_{\text{permeate}}\right)}{C_{\text{feed}}} \cdot 100 \qquad (3)$$

where C_{feed} is the concentration of a specific component in the feed solution to the membrane process and C_{permeate} is the concentration of the same specific component in the cleaned discharge stream leaving the membrane system. The

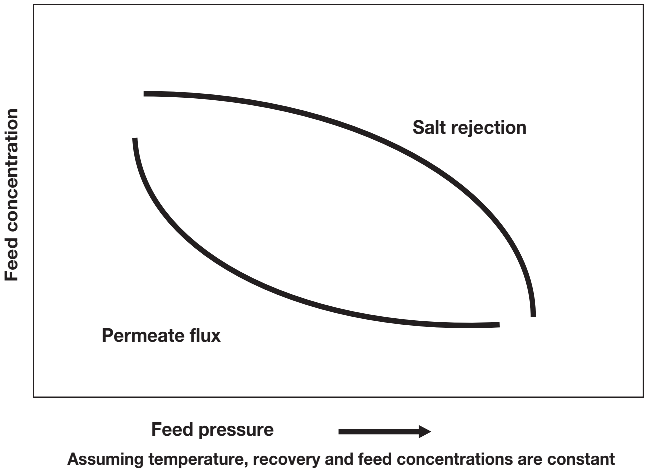


FIG. 27. The effect of feed concentration on reverse osmosis and nanofiltration.

apparent rejection factor is defined by the bulk concentrations sampled in the feed and permeate streams. The real or intrinsic rejection factor is taken to be the concentration of the specific component if it were measured directly at the boundary between the membrane and the solutions on either side of the membrane:

$$R = \frac{\left(C_{\text{wall}} - C_{\text{permate}}\right)}{C_{\text{wall}}} \cdot 100 \tag{4}$$

Rejection depends on the type and characteristics of the membrane and measures the effectiveness of separation. For nanofiltration and reverse osmosis membranes it measures the effectiveness of the membrane in preventing the passage of dissolved inorganics through the membranes.

Rejection may differ substantially between various feed solutions. In part these differences are explained by the different charges associated with the ions in solution. Higher charged ions are more easily rejected. This feature can be useful if, for example, extraction of radioactive strontium from a solution containing sodium is being attempted. Rather than using reverse osmosis to retain all of the solute, nanofiltration could effectively retain the strontium while permitting sodium to pass through the membrane.

The rejection efficiency of reverse osmosis membranes usually ranges from 85–99.5% and is quoted by the manufacturer for a standard set of feed conditions. A typical set of standard conditions is:

— Feed concentration: 2g/L NaCl;
— Temperature: 25°C;
— Pressure: 2.76 MPa (400 psig);
— Recovery factor: 10%;
— Operating time: 30 min.

For reverse osmosis systems, as increasing the operating pressure increases the flux through the membrane, the passage of solutes through the membrane will decrease and permeate quality will increase. For reverse osmosis, higher operating pressures are desirable because the degree of separation and the quality of the product are improved.

For microfiltration and ultrafiltration processes, where separation is based solely on size, increasing the flux through the membrane by increasing the operating pressure tends to increase the passage of solute or solid and decrease the permeate quality. For microfiltration and ultrafiltration systems, lower operating pressures are desirable because the degree of separation and product quality are improved.

5.4. TRANSMISSION OR SALT PASSAGE

Salt passage or transmission (T) is the percentage of solute or solid present in the feed that is not retained by the membrane. It is the percentage of species of interest that is transmitted through the membrane and is calculated using the following equation:

$$T = \frac{C_{\text{permeate}}}{C_{\text{feed}}} \cdot 100 \tag{5}$$

Rejection and transmission are related as follows:

$$R = 100 - T \tag{6}$$

5.5. DECONTAMINATION FACTOR

The performance of waste treatment processes can be valued in terms of the DFs achieved. Decontamination factors are particularly useful for performance evaluation in the treatment of radioactive wastewater. The DF in membrane processes used for radioactive waste treatment is defined as:

$$DF = \frac{\text{Specific activity of the feed}}{\text{Specific activity of the permeate}} \tag{7}$$

For the treatment of radioactive wastewater, DFs can be determined for specific radionuclides; for total alpha, beta or gamma emitters; and for total activity. For non-radioactive species, a DF may also be derived from the concentration of a solute (dissolved species) or solid in the feed and permeate solutions:

$$DF = \frac{C_{\text{feed}}}{C_{\text{permeate}}} \tag{8}$$

where C_{feed} is the concentration of the particular species in the incoming feed and C_{permeate} is the concentration of the same species in the purified stream (permeate) leaving the membrane system.

5.6. CONCENTRATION FACTOR

The concentration factor (*CF*) is the ratio of concentrations of the solute (dissolved species) or solid in the concentrate or reject stream to its concentration in the feed stream [46]:

$$CF = \frac{C_{\text{conc}}}{C_{\text{feed}}} \tag{9}$$

A high CF is desirable because it is equated with improved separation. High CFs are usually limited because they in turn result in a high osmotic pressure (reverse osmosis, nanofiltration) or cake buildup (microfiltration, ultrafiltration). This can lead to increased energy costs and the need for more frequent membrane cleaning or replacement.

6. DESIGN AND OPERATIONAL ASPECTS

6.1. GENERAL

The following is applicable to the design of pressure driven membrane processing systems, and primarily for designs incorporating reverse osmosis. A reverse osmosis system is the most complex to design and is the focus of this section. However, design and operational considerations for ultrafiltration, nanofiltration and microfiltration processes are similar and should be examined in the same detail.

An integrated system utilizing a membrane separation process usually consists of feedwater pretreatment, the membrane system, post-treatment (if required), reject stream treatment, and auxiliary equipment such as a CIP system. The performance of the membrane separation system is normally measured by two parameters, the permeate flow and the permeate quality. These should always be measured in relation to the given feed conditions and feed composition. The goal of a system design is usually to maximize contaminant rejection and recovery for a given permeate flow and to minimize feed pressure and membrane costs. Table 5 summarizes the fundamentals of system process conditions, design and operating conditions to achieve good membrane performance [47].

TABLE 5. CONSIDERATIONS IN SYSTEM DESIGN

Area to be considered	Condition	Response
Process conditions	Feedwater salinity	Known
	Permeate flow	Known
	Feedwater fouling tendency	Known
	Temperature	Select
System design	Element type	Select
	Flow configuration	Optimize
	Number of permeate passes	Optimize
	Elements per vessel	Optimize
	Vessels per stage	Optimize
	Number of stages	Optimize
Operating conditions	Recovery	Optimize
	Cleaning	Optimize
	Salt rejection	Maximize
	Pressure	Minimize

The relative importance of the above considerations determines the optimum design. One or more aspects will impact each design more than others. These are discussed below. Many membrane manufacturers offer design assistance, including computer programs, for using their products. The design of a system incorporating a membrane process can be considered as a series of steps as follows [40]:

- Step 1: Preliminary design requirements;
- Step 2: Selection of the membrane;
- Step 3: Process configuration;
- Step 4: Determination of pretreatment needs (fouling issues);
- Step 5: Pilot and/or on-site flow testing;
- Step 6: Final system design.

6.2. PRELIMINARY DESIGN

6.2.1. Initial design considerations

It is essential to determine the key drivers for the process (economic, environmental, performance, etc.) as the design phase gives the best opportunity to optimize costs and achieve a robust design. The following significant technical information must be gathered in the initial design stages [40]:

(a) Feedwater quality (range);
(b) Separation requirements;
(c) Required product flow quality specifications (of all output streams);
(d) Tests to confirm the existence of critical operational issues (scalants, foulants, chemical effects, biological activity).

Of these, understanding the nature of the feed stream is the most important. Very often not all the minor contaminants of the feed can be identified because of their low concentrations. A thorough understanding of the history and source of the wastewater can be valuable at this stage of the design. Once the key technical information has been gathered, the performance criteria can be established. These are:

- Acceptable limits for variability in performance;
- Recoveries (volume and mass rates).

A number of parameters can influence performance. However, a design so conservative as to include the most extreme variables can lead to excessive and often costly design.

6.2.2. Feedwater characterization

It is essential that the feedwater to the membrane system be well characterized. This allows operational changes in membrane performance to be better understood but also allows potential foulants to be recognized. Data on the chemical, physical, radiological and biological properties of the feed stream are required. The basic information required will include, but is not limited to, the range of:

(a) Suspended solids — determine the silt density index (SDI), see Section 6.4;
(b) Dissolved minerals;
(c) Radioactivity;
(d) Dissolved organic matter;
(e) Microorganisms;
(f) Temperature;
(g) Total salinity;

(h) pH level;
(i) Others, such as surfactant concentrations.

It should be recognized that in the treatment of LRWs the characteristics of a particular water stream or source may vary widely, and this needs to be considered in the system design. Sometimes very extensive sampling and analysis are needed to gain an understanding of this variance [48]. Variation in feed composition is best ameliorated in the design by including collection and storage facilities of suitable size. If several large storage tanks are used, the feed can be fully characterized before it is treated in the membrane plant and corrective action taken to minimize potential problems before the stream is treated. In this arrangement, the membrane plant treats 'batches' of feed yet still operates continuously. It allows the pretreatment of the feed to be adjusted in accordance with the change in feed characteristics before it is processed in the membrane plant.

6.2.3. Pre-design verification and testing

Membrane module performance can to some degree be predicted as a function of operating parameters and feedwater characteristics. Calculation methods [35, 49] exist for various membrane operating conditions, but computer modelling programs available from the membrane manufacturers have largely superseded these. These programs predict the performance of a membrane plant based on feedwater analysis and performance requirements.

Computer prediction alone is not rigorous enough to serve as the basis for the design of a full scale plant. While computer simulations are useful to examine the robustness of a proposed design, they should not be used solely as the design basis. Physical testing of the waste feedwater is required. Three basic types of testing can be used [40].

(1) Preliminary selection of the membrane

Different membranes can be chosen and tested in a small laboratory bench rig. This is done only to evaluate membrane types under a particular operating condition to ensure that the correct membranes have been selected. This approach can be considered as a screening test for membranes. No design data can be inferred from this test work.

(2) Testing of the process configuration

The selected process layout can be evaluated with a small pilot rig using actual feed. The performance of the proposed design is observed, and early indications of fouling and scaling can be detected. This testing can provide useful information on operating parameters such as permeate flow and quality as a function of feed pressure, but design data are not obtained because the rig (and therefore hydraulic parameters) is usually too small to scale up.

(3) Pilot demonstration

A pilot plant demonstration of the process involves construction of a ‘mini’ plant that typically processes 5–10% of the actual feed flow. This plant uses membrane modules of the same size as those in the full scale plant. The plant is usually operated for a minimum of six months so that membrane performance, fouling, pretreatment requirements and design data can be fully assessed. The testing should be carried out using the actual waste stream that will eventually be treated with a full scale membrane treatment system.

Although expenditure of 10–15% of the final capital (for a full scale plant) is required, this would be offset by savings in the costs of a full scale plant. One of the reasons for this is that the concentrations of potential foulants are often too small to be detectable in the feedwater or may not have been analysed in the initial screening of the waste solution. Only operation of a plant for a long period of time allows these foulants to build up in sufficient concentration to allow determination of their effect on plant performance. A pilot plant also allows assessment of cleaning procedures and evaluation of the secondary waste streams produced during cleaning and normal operation. Critical flux is also determined by pilot plant demonstration. This cannot be determined by computer modelling.

Pilot testing can also be carried out at sites with existing membrane equipment as a means of evaluating alternative process configurations. The value of on-site pilot scale testing is that it allows system performance to be verified with actual solutions to gain insight into membrane behaviour and fouling. Alternative membrane filtration systems have been evaluated at many sites with existing reverse osmosis treatment plants [50, 51]. These tests provide valuable information on the capabilities of alternative technologies for treatment of a particular waste stream. Pilot testing also allows innovative improvements, such as methods to improve DFs in the membrane process, to be tried out. In one pilot demonstration, for example, the DF was increased from 3 to 91 in the second pass of a reverse osmosis plant by testing an innovation [52].

Pilot plant demonstration is essential to test membrane technology for treatment of radioactive wastewaters. Operational issues such as membrane fouling are even more critical for radioactive wastewaters than for conventional wastewater applications and must be evaluated. This is because secondary waste generation and plant maintenance have significant impacts on the comparative benefits of one process technology over another for the treatment of radioactive wastes. In summary, the objective of a pilot plant is to confirm system design, fine tune the operating parameters, establish cleaning regimes, evaluate secondary waste formation and, above all, minimize risk.

6.3. MEMBRANE SYSTEM DESIGN

6.3.1. Selection of membrane type

Selection of the membrane material, its configuration and the operating parameters are critical to the membrane system design. A wide variety of membranes are commercially available with different operational characteristics (see Section 4).

The choice of a membrane must be based not just on the performance data (salt rejection, flux), but also take into account the interaction of the membrane with the feed solution and whether this will lead to stable operation and minimal fouling. Once these have been achieved the process configuration can be determined and optimized, usually by computer modelling.

6.3.2. Membrane process configuration

This section discusses the design of a membrane system in terms of the process configuration or how the membrane modules are arranged. The focus is on spirally wound elements, which constitute the majority of reverse osmosis and nanofiltration applications [40]. The most common configurations are:

(a) Straight through configurations with:
  - Series arrays,
  - Parallel arrays, or
  - Tapered arrays;

(b) Recycle configurations;
(c) Batch configurations.

6.3.2.1. *Straight through configurations*

These configurations are the simplest of the array structures and the most common (Fig. 28). An array is usually comprised of one or more pressure tubes, each containing 1–7 spirally wound elements [40].

In a series array, the entire flow is passed over all the modules. As permeate is drawn off the cross-flow is progressively reduced. This can lead to poor cross-flow at the tail of the array and increased fouling of the end elements in the array, limiting the length of a series array.

In the parallel array a greater feed flow is accommodated by splitting the flow. This array may still be limited by poor cross-flow at the tail. To maintain minimum cross-flow at the tail, the recovery is limited.

The tapered array overcomes the limitations of series and parallel arrays. The number of tubes in each section generally corresponds to the entrance volume feed rate. Systems with more than one array are used for higher system recoveries without exceeding the single element recovery limits. Concentrates from the first array become the feed to the second array. To compensate for the permeate that is removed and to maintain a uniform feed flow to each array, the number of pressure vessels per array decreases in the direction of the feed flow. Typically, two arrays will suffice for recoveries of up to 75% and three would be used for higher recovery rates.

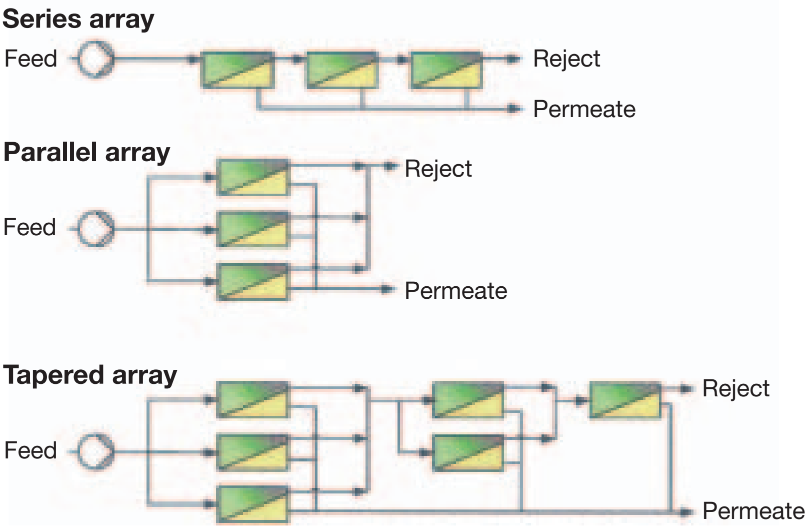


FIG. 28. Straight through configurations.

For each of the configurations shown in Fig. 28, the ‘depth of the array’ is the total number of elements in a series. The typical recovery rate of one element is 15%. For six elements in a pressure tube recovery rises to 50%. For two pressure tubes containing a total of twelve elements recovery is typically 75%. To accommodate changes in osmotic pressure, inter-stage pumping may be required as shown in Fig. 29 [40].

The applied pressure becomes a balance between the membrane driving pressures required (membrane type) and the osmotic pressure that has to be overcome, depending on the feed total dissolved solid (TDS) and recovery at each stage.

6.3.2.2. Recycle configurations

Recycle configurations are variations of the straight through configurations shown in Fig. 30 [40]. In these designs, reject is recycled to ensure sufficient cross-flow and an even hydraulic distribution in the membrane modules. This is crucial to avoid fouling and to minimize the concentration polarization layer.

These designs are suitable for small systems in which it is difficult to achieve a suitable hydraulic profile. They are also used where cross-flow is critical, such as in tubular ultrafiltration systems. Typical applications are in small plants requiring high recovery rates [40].

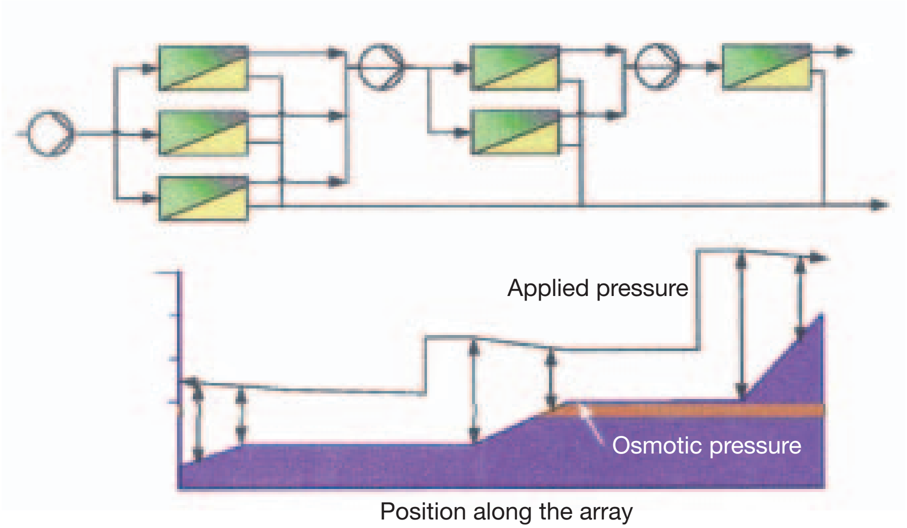


FIG. 29. Limitations in recovery.

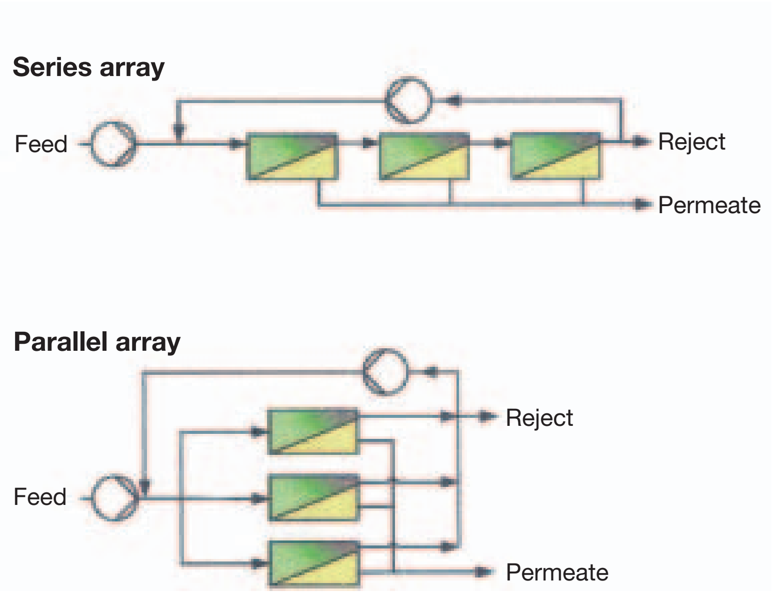


FIG. 30. Recycle configurations.

The number of membrane modules (array) used in a system depends primarily on the productivity design requirement. Small flow rate systems typically use a single module only, arranged as a batch or a continuous process. Larger flow rates will require several modules which can be creatively staged on the hydraulic side (feed, permeate, concentrate), either individually or in arrays. The term 'stage' refers to the number of modules treating feed and reject, and the term 'pass' refers to the number of modules treating feed and permeates. It is rare to find systems with more than two passes. However, a two pass permeate system may be considered in some designs when standard permeate quality would not be sufficient, for instance when polishing of the permeate by ion exchange is not available. Figure 31 [32] shows a multiple (two) pass system.

The desired recovery determines the configuration. Tapered arrays are normally used in ratios of 4:2:1. In general, the recovery data given in Table 6 apply to multiple stage reverse osmosis systems [40].

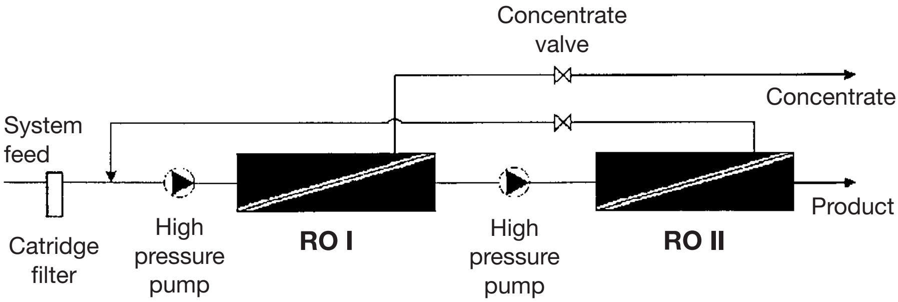


FIG. 31. Multiple pass reverse osmosis system.

6.3.2.3. Batch versus continuous processing

In full scale industrial applications a membrane system is usually designed for continuous operation. However, in certain applications, especially when relatively small volumes (batches) of waste liquor arise in a non-continuous manner, the batch operation mode may be preferred. The feedwater is collected in a tank. During treatment permeate is removed and the concentrate is recycled back to the tank. At the end of the batch process, a small volume of concentrate remains in the feed tank. After this has been drained, the membranes are typically cleaned before the tank is filled again with a new batch. Batch systems are usually designed with a constant feed pressure and a declining permeate flow as the feed becomes more concentrated.

A variation on the batch mode is the semi-batch mode. The feed tank is refilled with feedwater during operation. The batch is terminated when the feed tank is full of concentrate.

TABLE 6. RECOVERY WITH DIFFERENT MEMBRANE MODULES

Recovery (%)	Stages
<50	Single
50–75	Two
75–87	Three
>87	Return water for recycling

The batch process mode is simple, but its performance is not constant because the concentrate returns to the feed tank, changing the feed conditions. It is more difficult to predict the performance of a batch process and performance estimates are usually made at the start, middle and end of the batch. Control strategies must be in place to determine the end point of processing so that operational limits are not exceeded and extensive fouling is avoided.

6.4. FEEDWATER PRETREATMENT REQUIREMENTS

Each membrane system will require some sort of feedwater pretreatment, either to protect the membrane's integrity and/or to optimize its performance. The pretreatment requirements will be dictated by the membrane process selected, feedwater quality, the membrane selected and its configuration, together with the operational and performance requirements. Of these, the feedwater quality is usually the only variable and it is the removal of potential foulants in the pretreatment that often determines the overall performance of the membrane system. For this reason the pretreatment system is usually critical to the performance of the membrane. Feedwater pretreatment may include coarse filtration, chemical precipitation, pH adjustment, temperature adjustment, chlorination, coagulation, microfiltration or ultrafiltration, addition of anti-scaling agents and many others, depending on the feed stream analysis.

Reverse osmosis membranes usually require extensive pretreatment for wastewater applications. The pretreatment often includes other membrane technologies such as ultrafiltration or microfiltration. For example, to determine the need to pretreat feedwater to remove colloidal substances, an SDI is performed on the feed [53–55]. The colloidal and particulate substances, if not removed, would form a gel layer on a nanofiltration and reverse osmosis membrane surface, and would impair the membrane's function. The SDI is an arbitrary comparative measure of the degree of plugging in a given time period. It works by passing the test water through a 45 μm Millipore™ filter under constant pressure. Most membrane suppliers will provide the value of SDI above which removal of suspended solids is necessary. To remove these suspended solids and protect the reverse osmosis system, microfiltration or ultrafiltration are often selected as the pretreatment method. Another measure of water quality is the quantity of dissolved organic substances in the water. Two measures are often used, total organic carbon and dissolved organic carbon. Both are useful indicators of potential fouling by organics. It should be noted that some contaminants act as catalysts for other fouling mechanisms but on their own may not be considered problematic.

6.5. FINAL SYSTEM DESIGN

6.5.1. Equipment redundancy

The implications of plant maintenance, removal of membranes and equipment malfunction need to be considered in the design of a full scale plant. For this reason, some membrane plants have redundant equipment designed and built into them. This is especially important for plants treating radioactive wastewater. This redundancy can take the form of two or more parallel, identical plants, each capable of treating the design flow of radioactive wastewater [50], or built in redundancy of only specific equipment such as extra tanks for feed or product, or process pumps. The membrane plant designer must consider the relative importance of each unit and the impact of equipment not being available to process waste solutions in a timely fashion.

6.5.2. Process control

Membrane plants are usually designed with a high degree of process control. A programmable logic controller (PLC) is normally used to monitor and record the operating variables (pressure, temperature, flow, conductivity, pH, tank level). Some of these variables are used to directly control the membrane plant. The process control design will normally incorporate automatic startup and shutdown of feed pumps, dosing pumps and heating (if required). The plant design must include shutdown in the event of conditions that are detrimental to plant performance or unsafe. Automation of data collection permits the performance of the system to be monitored in real time with respect to initial flow conditions or design flows, and permeate quality. Records can be reviewed over longer time intervals to compare the impacts on performance of modifications to feed pretreatment, changes in operating strategies, etc.

In considering the process control design for a membrane plant treating radioactive wastewater, special consideration needs to be given to locating process control equipment away from potential hot spots and/or contamination, and the degree of automation required to minimize operator contact.

6.5.3. Radiological considerations in system layouts

Ensuring radiological safety is an important part of membrane system design. The following factors need to be considered in terms of radiological safety during the review of pilot plant trials:

(a) Containment of leaks, ease of decontamination;
(b) Sufficient space to permit membrane removal;
(c) Maintenance of pumps, instrumentation;
(d) Location of process control equipment, cleaning tanks, dosing equipment;
(e) Sampling requirements;
(f) Identification of potential hot spots;
(g) Location of shielding to avoid interference with operation and maintenance;
(h) Degree of automation/duration of operator contact.

6.5.4. Secondary liquid wastes

Membrane processes generate secondary waste streams as they are, in principle, separation processes. The generation of secondary waste streams needs to be considered in terms of downstream processing. Ideally these streams are considered well before implementation of the new membrane plant, but even then the streams may become problematic and new strategies may need to be devised [56].

The concentrate from a reverse osmosis process will normally undergo further volume reduction, either by another membrane process or by evaporation. For microfiltration and ultrafiltration, the reject stream containing particulate matter needs to be treated or directed to another part of the site processing facility. In each case the characteristics of the concentrated waste stream must be considered in terms of their impact on other (downstream) processes.

The other source of secondary waste is spent cleaning solutions. These can be voluminous if repeated cleaning is required due to unexpected fouling conditions. The impact of greater than expected volumes of spent cleaning solutions must be considered during the design phase.

Recycling of secondary waste streams to the feed of a membrane treatment plant must be evaluated with extreme caution as a buildup of unwanted contaminants may have a severe impact on plant operation through reduction in permeate quality, more frequent cleaning cycles or progressive, irreversible fouling.

6.5.5. Secondary solid wastes

The membranes themselves, as well as the related hardware, will eventually become secondary solid waste and the design of a new plant incorporating membrane technology must take the expected generation of this waste into account.

6.6. OPERATIONAL ASPECTS

6.6.1. Scale control

In reverse osmosis systems in which high recoveries are required, the solubility limits of many salts and other materials that may precipitate on the membrane surface are quite important. Compounds that are frequently encountered as scale deposits in reverse osmosis systems are calcium carbonate, sulphate salts of calcium, barium and strontium, calcium fluoride and silica [32].

Several methods are used to minimize or eliminate the formation of these scale deposits. These methods may be used in pretreatment rather than in the membrane plant itself. One method of controlling carbonates is acidification by acid injection. Acid injection converts bicarbonate alkalinity to CO_2, eliminating the formation of $CaCO_3$ scale. Another method sometimes used in pretreatment is water softening using lime or lime soda. In this process, hydrated lime or soda ash is added to soften the water. Calcium and magnesium hydroxides are then removed as a precipitate [32]. Coagulants are often added to the treated water to aid in the removal of the precipitate.

A third method used is the addition of anti-scaling agents. This is the most common method when the concentration of the scale forming species is low. These compounds reduce the rate at which scale forms, allowing the system to operate with concentrations above the solubility limit. For example, a common anti-scaling agent used to control calcium sulphate (gypsum) formation is sodium hexametaphosphate (SHMP). In reverse osmosis systems these anti-scalants are injected into the particular feed stream of the module that is likely to suffer from scaling, for example the second stage of a reverse osmosis process. The design of a membrane plant should allow for anti-scalant injection.

6.6.2. Chlorine content control

The presence of chlorine in the feedwater can result in chemical damage of reverse osmosis membranes. Chlorine is often added to feedwaters to control microbial growth. Unfortunately, many reverse osmosis membranes, especially polyamide membranes, are damaged by even low chlorine concentrations. If chlorine is present the feedwater must be dechlorinated before it enters the reverse osmosis system. Table 2 gives an example of allowable chlorine concentrations for some reverse osmosis membranes.

Membrane manufacturers will provide chlorine tolerance levels for their products. Chlorine is usually removed from reverse osmosis feedwater by injection of sodium metabisulphite. This is a reducing agent that neutralizes the oxidizing potential of chlorine. The design of a membrane plant should allow for sodium metabisulphite injection prior to the first stage reverse osmosis module.

6.6.3. Control of acidity/alkalinity

Excessive acidity or alkalinity of the waste feed is detrimental to most membrane materials. This is particularly important for membranes based on cellulose acetate. These membranes undergo rapid hydrolysis below pH4 and above pH7. Feed pH is normally adjusted as part of the pretreatment. However, during the reverse osmosis process, pH correction may also be required between stages. Compared to the feed, it is typical for the permeate stream to have a reduced pH and for the reject stream to have an elevated pH. As the permeate is low in ionic species it approaches the quality of pure water, which is acidic. If solution conductivity is used as a measure of permeate quality, the measurement may be meaningless (at high purity levels of around 1 μS/cm) due to the presence of protonated water molecules.

For similar reasons injection of dilute acid to a second stage feed stream may be required to reduce the pH of the feed to this module. Injection of both acid and alkali streams between membrane stages or passes needs to be considered in the design.

6.6.4. Prevention of fouling

Based on the pilot scale testing programme recommended during the preliminary design phase, the final design should integrate measures to control various types of fouling, such as colloidal, organic and/or biological, that may have taken place during the extensive pilot scale trials. Prevention of these forms of fouling is discussed in Section 7.6.

6.6.5. Cleaning of membranes

All membrane systems require cleaning to remove potential foulants. Cleaning is usually begun when the normalized flux drops by 10–15% or more (see Section 7.5). The design and type of the cleaning system (physical, chemical or both) is usually determined after pilot testing. The impact of the cleaning waste liquors must also be considered as the design progresses, as well as how these wastes will affect the secondary waste streams (Section 6.5.4).

The cleaning system is usually designed in consultation with the membrane and/or equipment module supplier to establish the choice and concentration of cleaning agents, flow rates, time of cleaning and flushing regimes.

7. MEMBRANE PERFORMANCE AND MAINTENANCE

The overall performance of a membrane based separation process depends on the characteristics of the membrane, the feed solution being treated and the general operating practices that are employed. During the operation of membrane systems, membrane performance typically will decrease over time. This is generally caused by:

- Membrane compaction;
- Concentration polarization;
- Membrane fouling.

7.1. MEMBRANE COMPACTION

The compressive force applied to the membrane under the system hydraulic pressure causes membrane compaction. It is a plastic creep process in which the thin membrane skin grows in thickness as it is compressed into the underlying porous substratum that supports the membrane [46]. As the membrane thickens, its permeability decreases.

When pure or clean water feed is processed at a constant pressure, the flux through asymmetric reverse osmosis membranes will gradually decrease

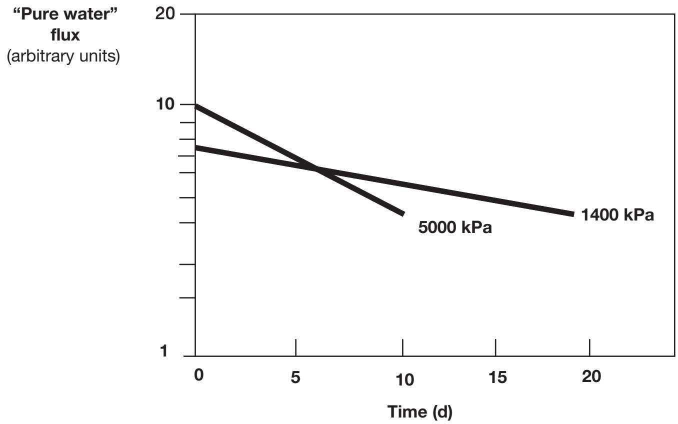


FIG. 32. The effect of time and pressure on pure water flux through reverse osmosis membranes susceptible to compaction.

(Fig. 32) [46]. The effect of compaction on the maximum attainable flux for the applied pressure can be predicted. The flux losses are irreversible. Figure 33 gives an example of flux decline for a spirally wound reverse osmosis element at Chalk River Laboratories [57].

Compaction of the membrane structure usually takes place during the initial period when feed is introduced to the membrane system. After pressure is continuously applied to the membranes, the loss in membrane flux should not exceed 10%.

7.2. CONCENTRATION POLARIZATION

Concentration polarization takes place when species that are retained or rejected by the membrane accumulate at the membrane surface. The concentration increases as they approach the membrane surface (see Fig. 34) [3]. The impact of this accumulation depends on the solute. The consequence of concentration polarization is that the membrane surface is subjected to a feed concentration that is higher than the concentration of the bulk feed stream. In reverse osmosis and nanofiltration, high osmotic pressures develop due to electrolyte

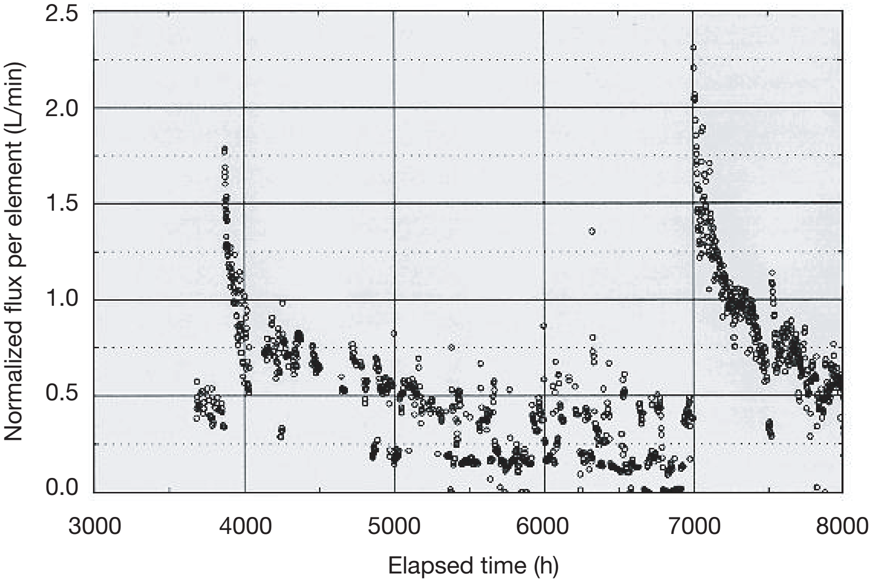


FIG. 33. Normalized permeation flux in an individual spirally wound reverse osmosis element.

accumulation near the membrane wall. In ultrafiltration, osmotic pressure and possible gel formation may result from the presence of macromolecules. In microfiltration, stagnant and irreversibly bound cake may form.

Concentration polarization is generally detrimental because it decreases flux and retention and increases the potential for fouling through bacterial growth or chemical reactions such as precipitation. Although concentration polarization is reversible, the fouling it causes may not be. If the flux is dropped either by reducing feed pressure or closing off the permeate outlet, the accumulated solutes should dissipate. Concentration polarization affects the observed rejection of solute by the membrane. The real rejection of the species may be high (90%) but the wall concentration may be 10 times the bulk concentration, yielding a real rejection of only 9% compared to the bulk concentration [3].

Using low flux rates, membrane modules that have narrow feed channels or high feed rates can reduce concentration polarization. These latter two approaches promote turbulence and reduce the boundary layer of concentrated solutes. These approaches have economic consequences.

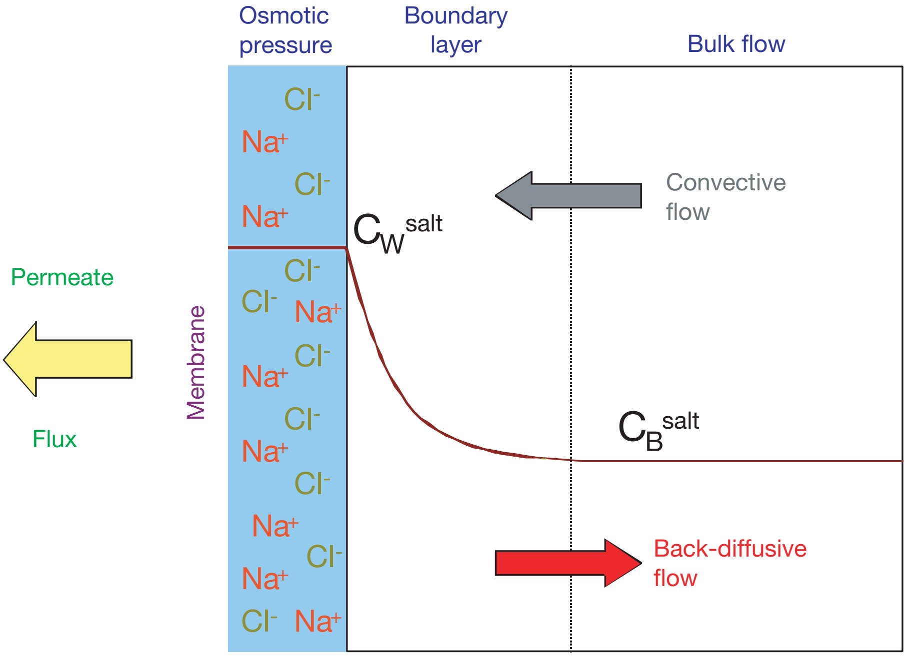


FIG. 34. Example of concentration polarization in reverse osmosis.

If the flux is kept low, a larger membrane area is necessary to maintain the desired throughput. In reverse osmosis and nanofiltration systems, the quality of the permeate will decrease, while with ultrafiltration the opposite is true.

If the feed flow rate is kept high, more energy is required to pump the feed solution through the membrane modules. At the higher pressure needed to maintain the increased flow rate, the membrane's life may be shortened due to membrane compaction.

7.3. MEMBRANE FOULING

The problem of membrane fouling is much more severe than either membrane compaction or concentration polarization, although the latter does contribute to the onset of fouling. Chalk River Laboratories has gained much experience with membrane systems used for the treatment of LRW [57, 58]. The flux decline with time observed in Fig. 34 was determined to be the result of concentration polarization coupled with surface fouling. Surface fouling takes place when there is a deposition of sub-micrometre particles on the surface, as well as crystallization and precipitation of smaller solutes. It occurs when rejected solids are not transported from the surface of the membrane back to the bulk stream. Fouling can also occur in the pores of the membrane and is more difficult to rectify than surface fouling.

In general, there are four major types of fouling — dissolved solids, suspended solids, non-biological organics and biological organisms [59]. The different types of fouling frequently occur simultaneously and each can influence the rate of fouling from the other mechanisms.

Dissolved solids are inorganic scale and gel forming materials such as calcium, barium and silica, which may be present in the feedwater in low concentrations. They are either cations (positively charged ions) or anions (negatively charged ions) which may complex and precipitate in the brine stream as their concentrations increase during membrane processing, particularly in reverse osmosis. Examples of such precipitated cation/anion compounds include calcium carbonate, calcium sulphate, barium sulphate and strontium sulphate. Dissolved solids form and attach to the membrane in layers according to their chemical type. Calcium carbonate forms in the brine spacers above the membrane surface and impedes flow. Sulphates form in small pools on the surface of the membrane. Silicate gels ‘wet out’ the membrane surface, spreading over it in a thin layer and slowly blinding the membrane.

Suspended solids maintain their suspension through a process of repulsion by a double layer of charge. Examples of suspended solids include colloidal forms of metal oxides such as iron, aluminium or silica. The charge repulsion characteristics of suspended solids also stabilize particulates such as carbon fines that may inadvertently leak from mixed media or carbon filters. Suspended solids tend to agglomerate and settle onto the membrane surface when concentrated past the point of their charge related stability. Suspended solids (colloids and particulates) agglomerate at the membrane surface, usually in the leading membranes of an array.

Biological foulants are aerobic and anaerobic living materials such as bacteria, fungus, algae and the metabolic waste they generate. Such foulants tend to be present in low concentrations and grow into massive quantities that effectively block flow through the membrane surface. Biological growth occurs in areas where ‘food’ is available. Iron reducing bacteria, for example, grow in areas containing iron fouling. Fungus tends to grow in areas such as those with a supply of silica-phosphate gel, which provides both protection from flow and food for additional growth.

Non-biological organic foulants are substances that contain carbon based chemical structures but which are not living organisms. Examples of non-biological organic foulants are oil, plant materials, cationic surfactants and hydrocarbons. Organic foulants are carbon based molecules which have a natural affinity for the membrane surface. Because of this affinity, organic foulants such as oils wet out the membrane, spreading directly onto the membrane surface.

7.4. SYMPTOMS OF MEMBRANE FOULING

Fouling is inevitable, but can be controlled by prediction and compensation to decrease its severity [60]. The potential for an onslaught of fouling can be anticipated during design or during the operational phase by using the Langelier saturation index (LSI) and the SDI. If the LSI calculations show that the membrane system is susceptible to scaling, preventive steps should be undertaken to minimize fouling. If tests to establish the SDI of the incoming feed indicate that plugging from suspended particles can take place, appropriate feed pretreatment must be incorporated to minimize further fouling.

A key to understanding fouling of the membrane system is the gathering of sufficient operating data to develop a reasonable baseline for future comparisons with system performance. It is to be expected that over time the membrane's performance will deteriorate (Fig. 35).

The deterioration in performance will depend upon the membrane type, system design and feedwater quality. It is important to continuously collect data to permit useful comparisons with past operating experience. Table 7 lists the more common fouling symptoms, their likely cause, methods to confirm the fouling mechanism, methods to clean the membrane, and longer term preventive steps to reduce future disruptions to the operating system [60]. These latter steps will be discussed in Section 7.5.

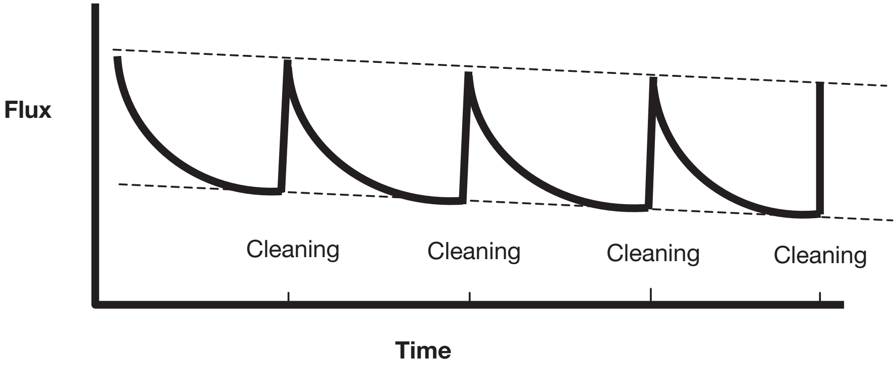


FIG. 35. Membrane flux deterioration over time.

TABLE 7. MEMBRANE FOULING SYMPTOMS AND TREATMENTS

Symptom	Likely cause of fouling	Diagnostic steps	Cleaning/control method
Significant increase in passage Moderate increase in pressure gradient Slight to moderate flow loss All effects usually most noticeable in last stage or element	Scaling Calcium, magnesium or salts (most common) Barium or strontium (less common) Metal hydroxides (e.g. iron)	Check water analysis Recalculate LSI	Acid clean Reduce recovery Adjust pH Use antiscalant Increase softener regeneration frequency
Significant increase in ΔP Moderate flow loss Moderate increase in passage All effects usually most noticeable in first stage or in last element	Dissolved organics/ suspended colloids Clay or silt particles, often organic and inorganic constituents Humic and fulvic acids (tannins, ‘colour’) Some synthetics such as common herbicides or pesticides	Run SDI or particle sizing to determine if pretreatment is effective Check for visible foulant in membrane elements and housings Compare total organic compound levels in the feed with baseline measurements	High pH clean (Chelants, detergents) Improve prefiltration Increase cross-flow Reduce recovery
Rapid and significant flow loss No or slight to moderate increase in passage Generally no or slight increase in ΔP	Suspended organics Fats and oils Hydrocarbon compounds Synthetic coagulation/flocking agents	Check fluid–membrane compatibility Check for contamination of the system	Often hard to clean Change membrane type, remove organics with granular activated carbon upstream High pH soaks may be effective depending on organic type
Significant, steadily increasing flow loss Slight to moderate increase in passage Moderate but rapidly increasing ΔP	Biofouling Biofilm Free floating’ microorganisms (not likely without concurrent biofilm)	Check micro-counts (cfu/mL*) in concentrate/permeate Check for visible evidence in system (slime layers) Check sampling valves for contamination	Sanitize Eliminate ‘deadlegs’ Do not allow system shutdowns, unless biostat is used Sanitize all system components, including pretreatment

* cfu/mL: colony forming units per millilitre.

Fouling generally results in decreased permeate flow, increased feed pressure to maintain the same flow, and usually an increase in the pressure differential, across the array. Pressure and permeate flow rates must be monitored closely and these critical parameters kept within the manufacturer's recommended specifications.

Understanding the makeup of the foulants is critical to improving the overall performance of the system and developing appropriate strategies to minimize fouling. At Chalk River Laboratories it was found that the chemical scale on the fouled reverse osmosis membranes was comprised primarily of aluminium, silica, calcium, phosphorus and, to a lesser extent, iron and sulphur [57, 58]. Calcium hydroxylapatite and octacalcium phosphate scales were identified as major fouling species on the spirally wound reverse osmosis membranes. Clay and aluminium silicate based scale was also thought to account for the initial large flux decline associated with concentration polarization, and is the most difficult scale to remove with standard chemical cleaning procedures. Precipitates were observed on the surface of the membrane. These precipitates were difficult to dissolve in concentrated acids. Alkaline cleaning chemicals at pH12 became the most effective means of restoring permeate flux. At this pH, silica solubilizes to silicic acid and can be removed.

During operation, reverse osmosis membranes take on an anion charge on the surface [43]. This causes cationic foulants such as aluminium and ferric hydroxides to be attracted to the surface along with cationic coagulant polymers. With composite membranes, fouling occurs faster and is more noticeable than with other membranes because these are operated at higher flux rates.

7.5. CLEANING AND RESTORATION OF MEMBRANES

Membranes should be cleaned when there is a 10–15% decrease in system performance, manifested by either a 10–15% reduction in permeate flow or a 10–15% increase in the pressure needed to maintain the same flow. Failure to clean according to the 10–15% rule may result in serious and irreparable damage to the membranes. For example, silica may crystallize in a surface pore of a membrane. As the crystal grows, it expands and tears the membrane pore, decreasing the membrane's rejection of solutes and compromising the permeate quality. Inorganic scale formation may also physically damage membranes, causing permanent rejection loss and resulting in scale formation that is difficult or impossible to remove.

Cleaning techniques have been developed to meet specific requirements. The main methods of membrane surface cleaning include mechanical, air assisted, and the use of chemical reagents.

Tubular arrays can be cleaned mechanically by injecting sponge balls to remove the foulant from the membrane surfaces. In some applications, passing spongy balls with diameters that exceed the tubular diameter of the membrane is effective [61]. However, this technique is restricted to specific membrane designs. It is not effective for the removal of chemical or organic foulants or for cleaning membrane pores.

Another mechanically assisted method is to back flush membranes with compressed gas and/or water. If this method is to be used, the organic membranes have to be strong enough mechanically to withstand the back flush, or they must be rigidly constructed so that the membranes do not collapse when the force of the air stream or water stream is applied in the reverse direction to displace the foulant layer. Compressed gas may cause spirally wound membranes to telescope and the excess pressure may dislodge mechanical seals.

Another mechanically assisted technique is to apply a shock wave to the flow system to dislodge the fouled material from the membrane surface. This is done by suddenly depressurizing the flow [36]. Again, this technique can only be applied to systems that utilize rigid membranes because soft, pliable membranes may be ripped from their support tubes as the shock wave migrates through the array.

A novel approach has been developed for cleaning the membrane surface without interrupting the filtration process [62]. Direct membrane cleaning was done with conductive stainless steel membranes in which an electric current was applied in pulses. Currents up to 2000 A/m^2 were pulsed for five seconds every 15 minutes to demonstrate that the flux could be continuously maintained.

After feed pretreatment, the most effective method to control fouling on a membrane surface is to clean the membrane chemically. The composition of the cleaning solution will vary according to the waste being processed. The cleaning solutions are many and diverse and include various acids, alkalis, chelated compounds and surfactants. Most membrane systems are now designed with CIP systems integrated into their process piping and control systems.

While these techniques can be effectively utilized to recover permeate flux, it is crucial to understand (if possible) the cause of the loss of the permeate flux or permeate quality before adopting a cleaning strategy. Membrane cleaning and restoration may include several sequential steps. If several cleaning agents are used, it is important to consider the order in which they are introduced. In general, biological growth and colloidal silts should be removed first. A second cleaning to remove metals and scales should then be attempted. Finally, attempts should be made to remove layers that contain silica and barium sulphate formed closest to the membrane.

Other factors that must be considered with chemical cleaning include the selection of cleaning agents, redirection of permeate and concentrate waste streams during cleaning, and minimization of cleaning waste volumes (secondary waste generation). Generic cleaning agents such as sulphuric acid, sodium hydroxide, sodium tripolyphosphate, sodium ethylendiaminetetraacetate and citric acid are inexpensive and can be effective in reducing feed pressures and increasing permeate flux. However, it may be beneficial to use specially formulated cleaning agents. While higher in price, they may remove the foulants completely because residual foulants often serve as nucleation sites, causing more rapid fouling when the system is returned to service [59]. Some of these proprietary cleaners will keep the foulants in suspension and prevent their redeposition onto other areas of the membranes, especially during recirculation of the chemical solution when foulants can be redeposited on the front end of the array.

During the cleaning solution recirculation and rinsing procedures, pressures should be reduced to reduce or prevent permeate flow. Reduced pressures cause the membrane foulants to be attracted into the cleaning solution and away from the membrane surfaces.

The secondary waste volume generated from cleaning of the membranes should be minimized. Good cleaning agents will reduce the quantity of waste generated because their improved effectiveness for removal of foulants reduces the volume of solution that has to be applied. The most effective cleaning solution for Chalk River Laboratories' reverse osmosis membranes was 'Memclean', an alkaline based detergent containing EDTA [57, 58]. Secondary wastes from cleaning accounted for about 5% of the annual waste feed volume to the plant. Generic acid based cleaning solutions were generally not effective for removal of the scale forming compounds. Silica scale was not effectively removed from the membranes with any of the cleaning chemicals that were investigated. It was concluded that the silica scale formed a tightly adherent layer immediately on top of the membrane surface. This caused a continuous drop in permeate flux and the need for premature replacement of the membranes.

7.6. PREVENTIVE MEASURES

7.6.1. General

Understanding the basic principles of fouling will allow effective intervention to prevent premature membrane fouling. As stated earlier, it can be expected that fouling will take place in almost all membrane systems, but proper maintenance procedures and membrane cleaning methods will improve system operation over the long term.

Pretreatment processes should be integrated into the initial design of the operating system. Information on what pretreatment steps should be incorporated is dependent on knowledge of the waste feedwater. Aside from a wide ranging chemical analysis of the feed, design should be based on actual pilot tests conducted on the waste streams that will be processed by the membrane system.

As a general rule, particles suspended in pretreatment, iron compounds and other colloid particles that can form a dense gel layer on the membrane must be removed prior to membrane separation. It may be necessary to eliminate some volatile organic compounds and oxidizing agents such as dissolved active chlorine, ozone and peroxides if these chemicals are used to reduce the microbial activity in the feedwater. Organics can be decomposed by breaking up their structures with oxidants, adding coagulants such as alum or ferric chloride, or adding powdered activated carbon to prevent their deposition on the membrane surface [63]. Adjustment of the solution's pH by addition of acid is often required to prevent low solubility cations such as calcium, magnesium and barium from exceeding their solubility and precipitating onto the membrane surfaces. Inhibitors (antiscalants) can be added to shift fouling from the membrane surface into the bulk phase of the solution. Surfactants can also be added to form a hydrophobic layer of polar organic molecules that can reduce the adhesion of sludge particles on the membrane surface.

Scaling inhibitors can be polyphosphates such as SHMP, polyacrylates or polycarbooxilites [54]. Normally, if information on the chemical composition of treated water is sparse or absent, the inhibitor should be applied at a rate of not less than 10 g/m^3 of water treated. The chemical composition of the majority of inhibitors is proprietary. Many compositions of inhibiting products are known, e.g. Permatreat, Flocon, AF-150, AF-200, Aqua Feed, TRC-233, EL-5600 and Dequest. For example, at Chalk River Laboratories it was determined that the most effective antiscalant chemical for the spirally wound reverse osmosis system was Pretreat Plus, which is manufactured by King Lee Technologies (San Diego, California) [57, 58].

7.6.2. Prevention of colloidal fouling

Colloids are usually charged particles smaller than 1 μm in diameter. They are common in surface waters and if not removed from feedwaters can drastically reduce the productivity of a membrane. Several techniques can be used to remove colloids. A common pretreatment method is coagulation/flocculation followed by conventional filtration. Typical coagulants used are alum $(Al_2(SO_4)_3$, ferric chloride $(FeCl_3)$, and polymer or polyelectrolyte materials [35]. However, the use of these methods in pretreatment may cause problems in the later stages of the lifetime of a reverse osmosis plant. Unprecipitated iron or aluminium may concentrate in a downstream reverse osmosis stage and initiate coagulation on the surface of the reverse osmosis membrane, causing fouling. Alternatively, ultrafiltration may be used to remove colloidal particles and is often a very good pretreatment for reverse osmosis. While ultrafiltration can be used to produce a high quality feed for reverse osmosis, the ultrafiltration membranes themselves can foul (but not necessarily by colloids). Therefore, pretreatment systems employing ultrafiltration membranes to remove colloids must be designed to maintain the performance of the ultrafiltration membranes.

One particular cause of colloidal fouling that can often result in problems in reverse osmosis is silica. If silica is already present in the feedwater supply to the site it will need to be controlled to avoid fouling in the reverse osmosis plant. Some sites have studied silica in their feedwater extensively in an effort to reduce silica fouling in the wastewater treatment membrane plant [64].

7.6.3. Prevention of organic fouling

The adsorption of organic matter onto the membrane surface causes flux loss, especially in the first array. Most membrane manufacturers recommend pretreatment to remove organics if the total organic carbon in the feedwater is more than 3 mg/L. The two most common removal methods are chemical oxidation (chlorine, hydrogen peroxide, ozone) or adsorption onto activated carbon. Organics can foul ultrafiltration and reverse osmosis membranes, depending on the size and charge of the organic molecules. The precise method of removing the organics can be determined in pilot plant tests. Even if there are normally very few organics in the feedwater, the plant design should incorporate some contingency for their removal. An accidental oil spill into the feedwater is a good example of how this may be overlooked, but the consequences of such a spill can be severe for the membrane plant.

7.6.4. Prevention of biological fouling

The formation of biological foulants or slimes on the membrane surface is undesirable because it reduces the flux through the membrane and reduces the effective salt rejection of the membrane. To prevent biological activity, the feedwater is often disinfected before it enters the reverse osmosis system. Chlorination to 0.5 ppm by injection of chlorine gas or addition of hypochlorite is the most common method used. However, as discussed in Section 6.6.2, reverse osmosis membranes are damaged by chlorine. Therefore, after the feed has been chlorinated for biological control it must be dechlorinated, usually with sodium metabisulphite, before it enters the reverse osmosis system. Other disinfectants that may be used for biological control include ozone, ultraviolet light, formaldehyde, concentrated sodium bisulphite and copper sulphate [35]. The amount of biological activity in the feedwater must also be reduced before it reaches the wastewater treatment plant as microorganisms, whether alive or dead, can foul membrane surfaces. For this reason it is useful to carry out audits of the main sources of biological activity in the site wastewater and implement control strategies [50, 65].

Biological fouling may also occur in the membrane plant if it is shut down for long periods. This is because microorganisms will feed off any source of carbon that is available. One common type of anti-scalant is a form of carboxylic acid, which becomes a food supply for bacteria when equipment is idle. The bacteria will then form a slime on the membrane surface. For this reason continuous operation is favoured over operating regimes with shutdown periods of 24 hours or more, and this should be considered in the design.

7.7. MONITORING OF MEMBRANE PERFORMANCE

To maintain high throughputs and high quality permeate the process must be continuously monitored and compared with expected performance. Data are routinely collected and analysed using computers that are an integral part of the process control systems of membrane separation systems. It is crucial that when fouling develops it is expected, so that corrective action can be taken to avoid irreversible losses in productivity and quality. The penalty for not preventing irreversible fouling is premature and costly membrane replacement.

In practice, membrane treatment shows that despite protective measures fouling will take place on a membrane surface. Fouling on a membrane surface always results in a decrease in its flux. In the treatment of radioactive wastes fouling will result in a gradual increase in radiation field buildup around the equipment. These radiation fields will increase the radiation dose to staff and may cause radiation damage to the membranes.

7.7.1. Chemical/physical monitoring parameters

Chemical monitoring allows the system to operate within the membrane manufacturer's recommended guidelines. Feedwater that is chlorinated to arrest the growth of microorganisms must be analysed on-line to avoid deterioration of the membranes [66]. Chlorine content is reduced by adding sodium bisulphate. Typically, this process is automated. The feed must also be monitored to ensure that the incoming pH solution is within tolerated levels. On-line conductivity measurements are collected and used to establish rejection and monitor permeate quality. If organics are a component of the feed stream, an on-line total organic carbon analyser is recommended. Routine sampling is required to conduct off-line chemical analyses to monitor for the presence of the identified foulants, to ensure the chemicals are being introduced at the right dosage, and to perform quality assurance checks of the on-line process monitors.

The important physical monitoring parameters include measurements of the incoming feed rate and pressure, discharge feed rate and pressure, permeate flow and pressure, process temperatures, and on-line determination of SDI that should be kept below certain levels to avoid early fouling by suspended particles and colloids (see Section 7.7.2). These measurements allow calculation of trans-membrane pressures (TMPs), mass balances, recovery and rejection factors, decontamination and volume reduction factors, and concentration factors. All of this information can be recorded by a PLC and continually provided to operations staff, plotted as a function of time. These plots permit operations staff to be aware of operating changes and to take corrective action to avoid losses in throughput.

7.7.2. Performance monitoring methods

Traditionally, system performance is evaluated by analysing trends in terms of permeate flux and salt rejection. Performance is evaluated analytically by normalizing the membrane system operating data using American Society for Testing and Materials (ASTM) standard method D4512 [67]. In the case of low to moderate fouling the method may not account for variations that might lead to severe or irreversible fouling. An enhanced method (the MASAR method), based on overall system dependent changes, as well as the physical and mechanical design limitations, has been developed [68, 69]. The prediction of membrane fouling trends is based on a sensitive performance trend parameter. The fouling monitor represents the relative difference in normalized product flows using both the ASTM and the MASAR normalization methods. An example of the sensitivity of this monitoring technique is provided in Fig. 36.

Permeate flux may also be monitored by observing the normalized trend over time [70]. The declining trend obeys a power law function so that:

$$A_n = t^{-m} \qquad (1)$$

where A_n is the NPF at time t. The coefficient m resides within a set of values from 0.008 to 0.08.

The LSI is determined for the feedwater to confirm the potential for scaling from calcium deposition. It provides an indication of the driving force for scale formation and growth in terms of pH, but gives no indication of how calcium carbonate or scale will actually precipitate. The LSI can be calculated

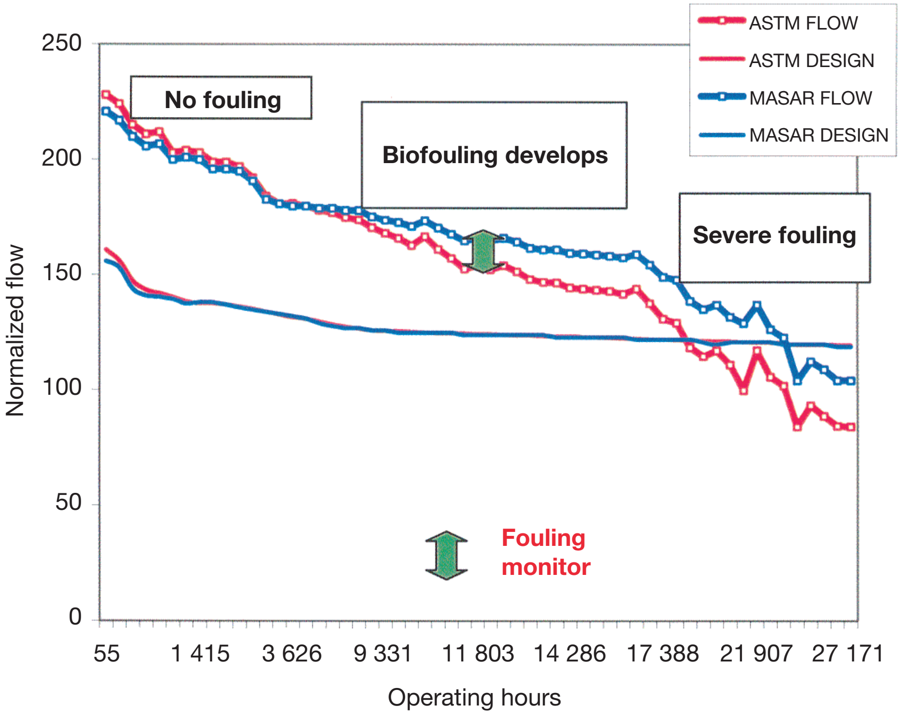


FIG. 36. *Monitoring of flux decline.*

using ASTM standard method D 3739 [71]. If the LSI is negative there is no potential for scaling and the water will dissolve calcium carbonate. If the LSI is positive, scale can form and precipitation is likely to take place.

The SDI is a measure of the quantity of sub-micrometre particles present and is determined by monitoring the flux decline over 15 minutes when the feedwater is filtered continuously through a Millipore 0.45 mm membrane at a transmembrane pressure of 207 kPa (15 psig). The SDI can be calculated using ASTM standard method D4189 [72]. The SDI must be kept at a value less than 3 for reverse osmosis membranes to avoid plugging.

8. TREATMENT OF RADIOACTIVE LIQUIDS

8.1. GENERAL

The use of membrane technology varies with the characteristics of the radioactive liquid to be treated, the desired separation objectives and the volume of liquid to be treated. These factors are influenced by the facility type (nuclear research facility, nuclear power plant, radiopharmaceutical production or fuel reprocessing facility), nuclear power plant type (boiling water, pressurized light or heavy water reactors), type of primary coolant or moderator (light water or heavy water), local conditions (floor space availability, distance from waste storage tanks, height restrictions), limits on environmental discharges, and other factors.

8.2. WASTE SOURCES, TYPES AND CHARACTERISTICS

8.2.1. Nuclear power reactors

8.2.1.1. Pressurized water reactors

Four types of LRWs are commonly produced in a PWR plant — miscellaneous waste, secondary system waste, chemical waste and detergent waste. Miscellaneous wastes come from a variety of sources and therefore vary greatly in content. Secondary waste is usually low in conductivity and is produced primarily by steam generator blowdown and turbine building drains. Chemical wastes are usually high conductivity liquids containing large quantities of total solids. Detergent waste usually contains a very small amount of radioactivity but contains a large amount of organic chemicals, chelating agents and suspended solids.

8.2.1.2. Boiling water reactors

Liquid radioactive wastes in a BWR plant include high purity waste, low purity waste, chemical waste and detergent waste. Each type differs in quantity and source. High purity waste is usually the result of equipment drains from the drywell and the reactor, turbine and radioactive waste buildings; ultrasonic resin cleaner wash; and resin backwash and transfer water. Low purity waste is usually of moderate to high conductivity. The contents of the chemical waste stream and detergent waste streams are similar to those found in a PWR plant.

8.2.1.3. Heavy water reactors

Since these power reactors use heavy water as a primary coolant and/or moderator, the system design is such that heavy water leaks from equipment and drains are collected, upgraded for isotopic purity and returned to the system. As a result there is usually no liquid heavy water waste to be treated. Light water wastes are typically generated as floor drains during maintenance and refurbishment activities and usually have low specific activity that can generally be handled by delayed storage and dispersal after decay. Heavy water reactors generate detergent and liquid chemical wastes similarly to light water reactors. It should be noted that tritium, present in the heavy water reactor coolant and moderator, cannot be removed by pressure driven membrane processes.

8.2.2. Institutional activities

Nuclear research and radiopharmaceutical production facilities produce LRWs. The volumes and characteristics of these sources may vary widely. For a description of these waste sources and their characteristics, see Ref. [73].

8.2.3. Other sources

Sources of LRWs requiring processing can be found in other segments of the nuclear fuel cycle (i.e. fuel fabrication, fuel reprocessing, uranium enrichment, environmental remediation, miscellaneous decontamination activities). The volumes and characteristics of these potential sources vary widely. It is not practical to identify or to categorize these streams. Reference [73] describes these waste sources and their characteristics.

8.3. MEMBRANE TECHNOLOGY IN THE NUCLEAR INDUSTRY

During the past 5–10 years membrane technology has been gradually introduced into nuclear power plants for treatment of LRWs. The main reason for this has been the desire to achieve one or more of the following:

- Reduction of radioactivity discharge to the environment,
- Reduction of solid waste from existing effluent treatment facilities,
- Recycling of boric acid.

Many power plants in the United States of America, for example, have traditionally treated low level liquid effluent by direct evaporation of the liquid waste, by conventional filtration and ion exchange, or by combinations of these. The common limitation of these processes is that they generate significant quantities of radioactive solid waste to be disposed of. Furthermore, the treated liquid effluent is not pure enough for environmental discharge or recycling.

The major limitation of evaporation is the considerable operating cost with high energy consumption. The limitation of conventional filtration and ion exchange is that colloidal particles, some radioactive, pass straight through to the product (treated) water. Colloidal particles containing $^{58/60}$Co, ^{54}Mg, ^{55}Fe, and ^{125}Sb are typical examples of these. Ultrafiltration is capable of removing these particles completely and has been adopted at a number of sites to complement the existing conventional filtration/ion exchange systems. At other sites, ultrafiltration has been implemented in combination with reverse osmosis, and ion exchange has been discontinued or is utilized as a polishing step.

In most of these cases, the reverse osmosis units actually utilize nanofiltration membranes to allow passage of boric acid to the permeate side while rejecting any residual dissolved radioactivity. This allows the permeate to either be discharged to the environment or recycled. This represents the most widespread use of reverse osmosis (or nanofiltration) in nuclear power plants.

As each application of membrane technology in a nuclear plant or elsewhere is unique due to specific local conditions, different processing objectives and various other factors, the membrane systems used vary from application to application. Examples of this are given in Table 8). Additional information on selected applications and detailed operational experience and results are presented in Appendix I. Table 8 shows where information on the selected systems can be found in this report.

8.3.1. Reverse osmosis

8.3.1.1. Reactor coolant cleanup with boric acid recovery (Atomic Energy of Canada Ltd (AECL), Canada)

A number of membrane systems have been designed, tested and operated in the nuclear industry for boric acid reclamation [74]. Reverse osmosis with cellulose acetate membranes has been tested in Canada by AECL's Chalk River Laboratories to recover boric acid from radioactive waste streams [75]. The concept of using cellulose acetate reverse osmosis membranes evolved from a basic study from the year 1971 [76]. Figure 37 gives an outline of this process [74]. As shown in the figure, radioactive feed is introduced to RO-1. The undissociated boric acid permeates through the membranes, rejecting radionuclides other than tritium. About 90% of the boric acid is recovered with RO-1. The dilute boric acid from RO-1 can be concentrated to about 7% by RO-3. The pH can be elevated to about 9.5 to ensure that boric acid is rejected with an efficiency of about 99.9% with the TFC polyamide membranes after purification by electrode ionization technology. The concentrated boric acid could be recycled to the plant. Permeate can be discharged to drains. Waste concentrate from RO-1 containing about 99% of the radioactivity and about 10% of the original boric acid present in the feed is sent to RO-2 for further volume reduction.

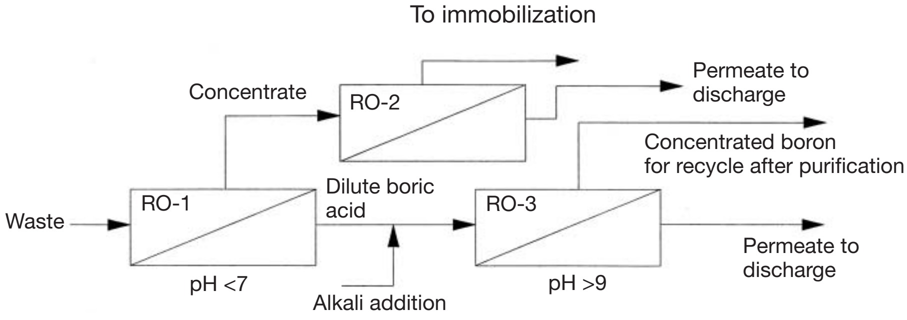


FIG. 37. Boric acid recovery with reverse osmosis.

TABLE 8. EXAMPLES OF MEMBRANE TECHNOLOGY USE

Membrane process	Facility	Wastes processed	Reference(s)	Section giving further information
Reverse osmosis (nanofiltration membranes)	AECL Chalk River Laboratory (Canada)	Reactor coolant cleanup with boric acid recovery	[78, 80]	8.3.1.1
Reverse osmosis with conventional pretreatment	Nine Mile Point nuclear power plant (NMP) (USA)	BWR floor drains and various other wastes	[81, 97, 98]	8.3.2.1, Appendix I, Example 1
	Pilgrim nuclear power plant (USA)	BWR floor drains and various other wastes	[81]	8.3.2.2
Reverse osmosis with ultrafiltration pretreatment	Wolf Creek nuclear power plant (USA)	PWR floor drains, reactor outage waste, spent resin sluice water, etc.	[82, 83]	8.3.3.1
	Comanche Peak nuclear power plant (USA)	Floor drains, resin sluice water, boron recycle water	[100, 101]	Appendix I, Example 2
	Dresden nuclear power plant (USA)	Inventory of TRU contaminated batch of liquid waste	[101]	Appendix I, Example 3
Reverse osmosis with ultrafiltration pretreatment	Bruce nuclear power plant (Canada)	Aqueous wastes from steam generator chemical cleaning	[84]	8.3.3.2
Reverse osmosis with microfiltration pretreatment	Savannah River site (SRS) (USA)	Reprocessing/defence wastes	[52, 70]	8.3.4.1
	AECL Chalk River Laboratory (Canada)	Nuclear research wastes	[60, 61, 85, 87]	8.3.4.2, Appendix I, Example 10
Ultrafiltration	Diablo Canyon nuclear power plant (USA)	Spent media transfer liquid	[85]	8.3.5.1, Appendix I, Example 8

TABLE 8. (cont.) EXAMPLES OF MEMBRANE TECHNOLOGY USE

Membrane process	Facility	Wastes processed	Reference(s)	Section giving further information
	River Bend nuclear power plant (USA)	BWR floor drains	[101]	Appendix I, Example 4
	Salem nuclear power plant (USA)	PWR floor drains, equipment drains and other sources	[102]	Appendix I, Example 5
	Seabrook nuclear power plant (USA)	PWR floor drains and spent resin tank drain-down	[101]	Appendix I, Example 6
	Callaway nuclear power plant (USA)	Floor drains, equipment drains, reactor coolant	[103]	Appendix I, Example 7
	Mound Laboratory (USA)	Wastes from fuel reprocessing activities	[34, 104]	Appendix I, Example 9
	Projected facility for treatment of laundry (detergent) wastes	Laundry (detergent) wastes	[89–92]	8.3.5.2
Microfiltration	AECL Chalk River Laboratory (Canada)	Contaminated groundwater	[60, 61, 71, 72, 93–96]	8.3.6.1, Appendix I, Example 11
	Rocky Flats (USA)	Contaminated groundwater	[95]	8.3.6.2

8.3.2. Reverse osmosis with conventional pretreatment

8.3.2.1. Nuclear power plant floor drains and various other wastes (NMP units 1 and 2, USA).

Units 1 and 2 of the NMP BWR operate under a ‘zero-liquid’ discharge philosophy that requires all radioactive wastewaters generated within the plant to be recycled. In the original LRW system design, liquid waste was segregated into two major streams, clean waste (i.e. high purity waste from equipment drains) and floor drain waste (i.e. low purity water from floor drains). After a comprehensive development programme, including an off-site pilot testing programme, similar full scale reverse osmosis systems (Thermex^{TM} systems) were installed for both units, primarily to treat the floor drain wastewater. The objective of employing reverse osmosis technology at NMP was to reduce solid waste generated from water processing, reduce disposal costs associated with water processing, maximize long term on-site storage capacity, reduce plant equipment maintenance costs and improve water chemistry. Figure 38 shows the LRW system schematic at unit 2 of NMP, retrofitted with the Thermex reverse osmosis system [77].

The Thermex reverse osmosis system with its pretreatment and polishing components is depicted in Fig. 39 [77]. The system consists of a control module, two deep bed filters (SS separators) configured for parallel operation, followed by a bag filter (SS polisher), a 'reverse osmosis pre-filter' (a single bag non-membrane filter), a reverse osmosis dissolved solids separator (DSS unit), a photo-oxidation unit, and deep bed ion exchange polishing demineralizers (DSS polishers). The control module is a small skid (107 cm × 152 cm × 122 cm)

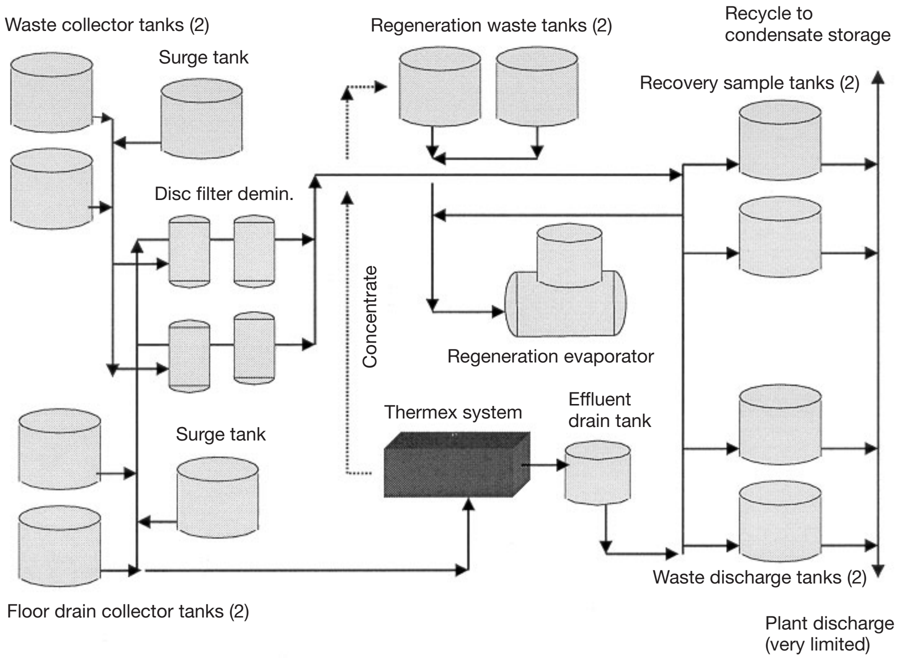


FIG. 38. The NMP unit 2 LRW system schematic, including the Thermex reverse osmosis system.

that is utilized to monitor and sample influent/effluent flow and provide service air and water to various system components. The suspended solids separators (107 cm × 249 cm) remove suspended solids and a portion of the total organic carbon from the feed stream through the use of granular media. The DSS removes fine particulate, colloids, organics and dissolved solids through the use of reverse osmosis. The reverse osmosis system represents a multi-stage design in which the concentrate from the first reverse osmosis stage becomes the feed for the second reverse osmosis stage. The permeate from both reverse osmosis stages is sent to deep bed demineralizers for polishing prior to entering the treated collector tanks, while the rejected concentrate is returned to the process feed tank for recirculation through the membranes. Upon reaching a predetermined upper concentration limit, the tank content is drained for processing. The DSS permeate is low in conductivity (<10 mS/cm) and contains no colloidal or particulate material. The photo-oxidation unit (46 cm × 122 cm × 150 cm) ionizes total organic carbon through the use of ultraviolet light. The ion exchange media in the polishers remove ionic impurities that have migrated through upstream processing components.

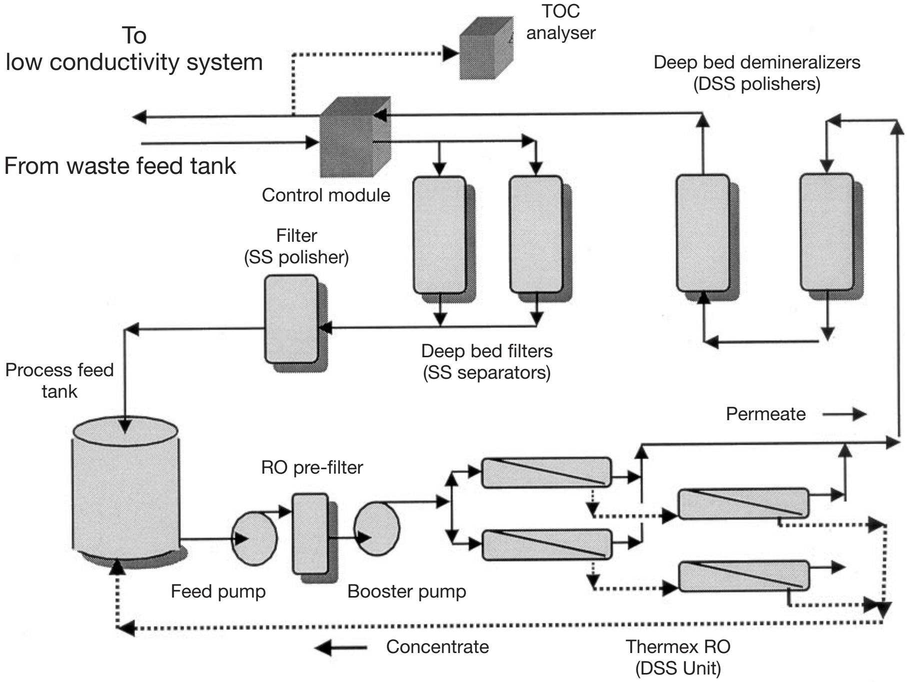


FIG. 39. Schematic of the NMP unit 2 Thermex system utilizing reverse osmosis.

The general arrangement of the Thermex system at unit 2 of NMP [77] is depicted in Fig. 40, which shows typical radiation fields that have been taken from radiation surveys. Appendix I gives a case history of this application, including operational results.

8.3.2.2. BWR floor drains and other wastes (Pilgrim nuclear power plant, USA)

The original radioactive waste system at the Pilgrim nuclear power plant was designed to segregate the liquid waste into three distinct streams:

(1) Clean waste (high purity from equipment drains);
(2) Chemical waste (low purity water from floor drains);
(3) Miscellaneous wastes (consisting of a range of low quality water from such activities as laundry and decontamination activities).

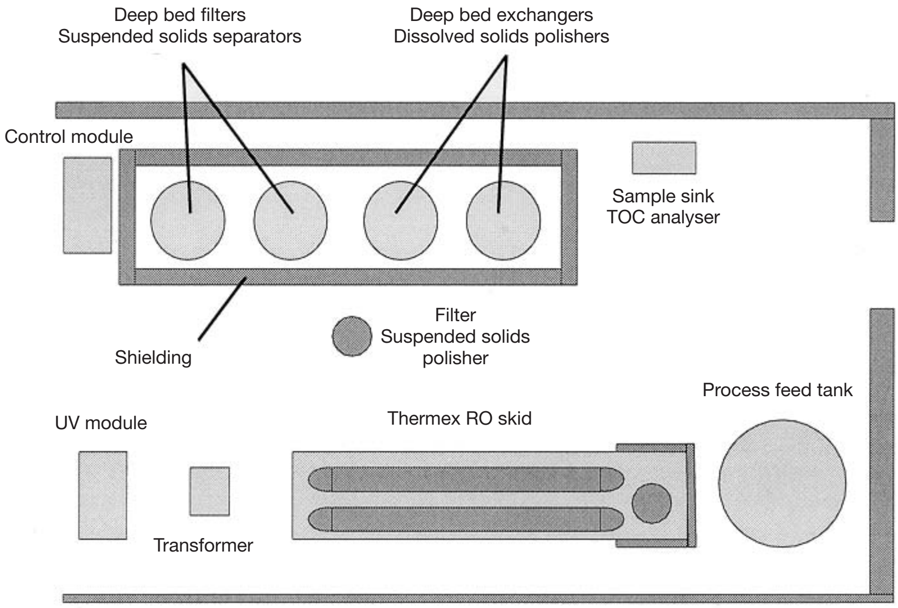


FIG. 40. General arrangement of the NMP unit 2 Thermex system utilizing reverse osmosis with feed pretreatment and product polishing.

A Thermex reverse osmosis system was later installed to improve the overall performance of the system. The goals were to:

(i) Reduce waste processing and disposal costs;
(ii) Reduce personnel exposure related to radioactive waste operations;
(iii) Reduce waste disposal volumes;
(iv) Reduce plant equipment maintenance costs;
(v) Improve total organic carbon removal from floor drain wastes;
(vi) Improve the quality of recycled water with respect to conductivity, total organic carbon, chloride and sulphate [77].

The modified system, incorporating Thermex reverse osmosis, was designed primarily for processing low purity floor drain wastes. However, the Thermex system was integrated into the overall existing system with the goal of acquiring the capability of processing both the 'clean' and the floor drain waste. This arrangement allows either the original or the new membrane based system to back one another up should the need arise. A system schematic of the Thermex system is given in Fig. 41 [77].

In the Thermex system, oils and particulate materials are removed by means of graded charcoal (suspended solids separators), followed by a 1 μm

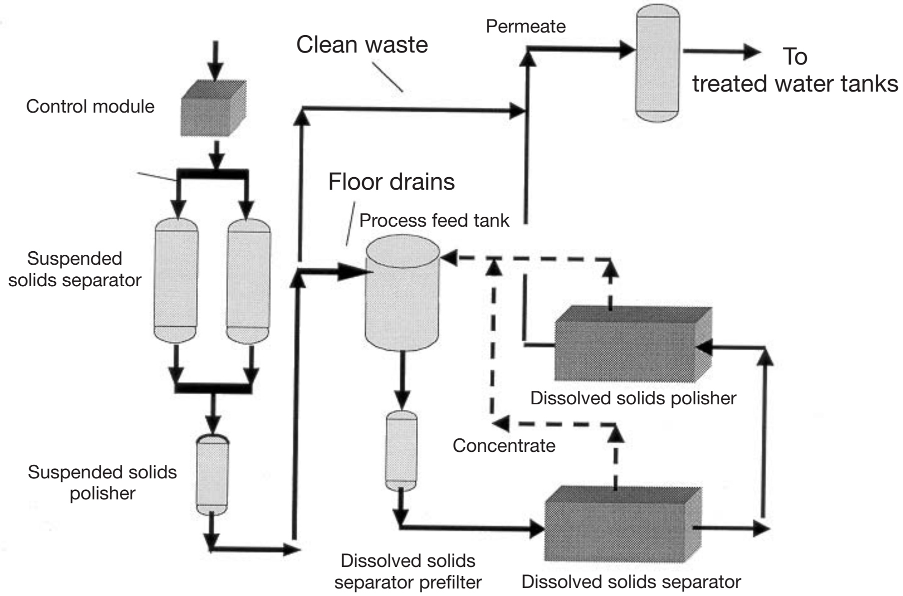


FIG. 41. The Pilgrim nuclear power plant Thermex system schematic, showing the standard processing pathways.

bag filter (suspended solids polisher) for removal of any fines prior to their delivery to the reverse osmosis system. The reverse osmosis unit is assembled in two sections to accommodate equipment installation (see Fig. 42 for a description of the general arrangement). In this arrangement, permeate from the first reverse osmosis section (dissolved solids separator) flows to the next reverse osmosis stage (dissolved solids polisher). The final concentrate is recirculated back to the process feed tank for reprocessing through the reverse osmosis system. The purified liquid permeate from each stage is collected and delivered to the post-treatment section of the Thermex system (a deep bed ion exchange demineralizer).

The Pilgrim nuclear power plant has taken a unique approach to the treatment of the reverse osmosis system concentrates. The concentrate is routed to the plant's spent resin storage tank, where it is brought into contact with spent resin from the condensate demineralizer system. At the time of removal this resin still possesses a major fraction of its ion exchange capacity, which is available for removal of contaminants from the reverse osmosis concentrate.

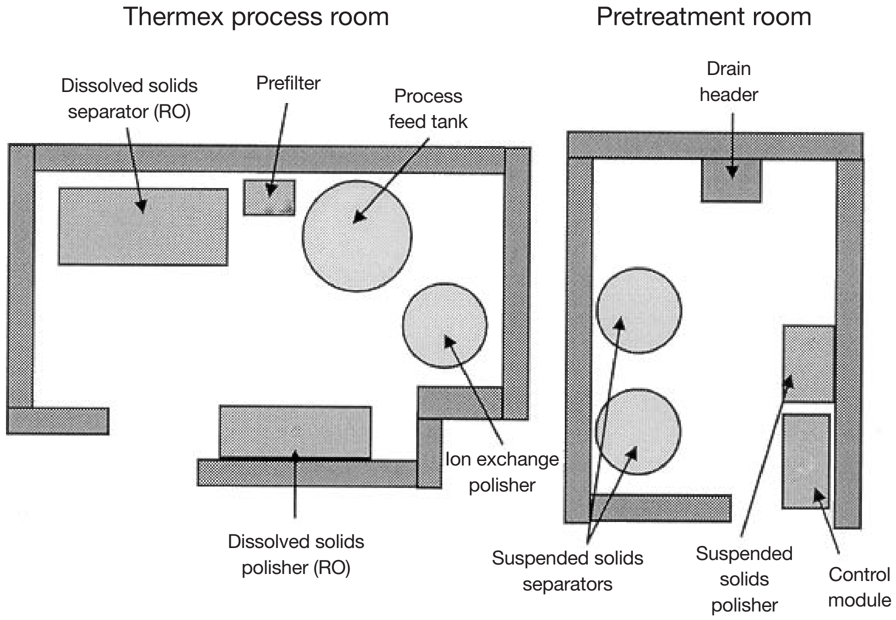


FIG. 42. General arrangement and radiation fields of the Pilgrim nuclear power plant Thermex system. The distance between the two rooms is approximately 3 metres (data taken from radiation surveys of February 2001).

In the year 2000 the plant personnel concluded that all of the goals established by the plant for radioactive waste processing had been met. In particular, the waste volumes had been dramatically lower than those experienced before system modification, and the personnel exposure associated with the radioactive waste operation had been significantly reduced.

8.3.3. Reverse osmosis with ultrafiltration pretreatment (ultrafiltration + reverse osmosis)

8.3.3.1. PWR floor drains, reactor outage waste, spent resin sluice water and other miscellaneous streams (Wolf Creek nuclear power plant, USA)

The Wolf Creek nuclear power plant is a 1250 MW PWR that began commercial operation in September 1985. In early 1998, the Wolf Creek Nuclear Operating Corporation set a corporate goal of reaching the ‘top quartile position’ as recorded by the US Institute of Nuclear Power Operations for effluent activity releases. Their strategy was to evaluate various process methods available and install the most efficient, cost effective, reliable system available. A complete ZERO^{TM} system consisting of a tubular ultrafiltration

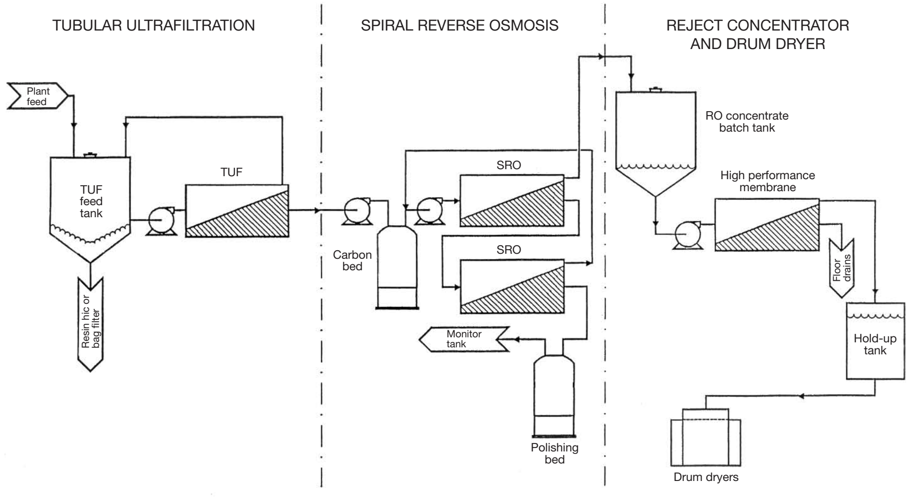


FIG. 43. The Wolf Creek nuclear power plant ZERO system utilizing TUF and SRO.

(TUF) unit, spiral reverse osmosis (SRO) unit, concentrates drum dryer^{TM} (DD) unit and demineralizer system was installed in October 1998 to meet this goal [78]. The system was designed to primarily treat the plant wastes, including floor drains, reactor outage wastes, spent resin sluice water and other miscellaneous streams [78, 79].

Figure 43 gives a schematic overview of the system. The wastewater feed from floor drain tanks, waste hold-up tanks, recycle hold-up tanks and the secondary liquid waste monitor tanks are supplied to their influent tank by plant pumps. This feedwater is routed to the TUF unit for removal of suspended solids and the permeate serves as feed for removal of soluble species in the SRO unit. The ultrafiltration concentrate is recirculated to the ultrafiltration feed tank. The reverse osmosis unit is built as a multi-stage design in which the permeate from the first reverse osmosis stage becomes the feed for the second reverse osmosis stage. The concentrate from the second reverse osmosis stage is recycled back to the feed of the first reverse osmosis stage since its quality is still better than the system's feedwater. The concentrate from the first reverse osmosis stage represents the reverse osmosis system concentrate. The SRO permeate is routed through a downstream demineralizer system for final polishing. The effluent of the demineralization system is sent to the monitoring tanks for sampling and release [79].

The reverse osmosis system concentrates were originally treated directly in a DD unit. However, since the concentrate volumes were greater than the DD's capacity an additional reverse osmosis unit was added for further processing of these concentrates. Utilization of proper high performance (seawater type) reverse osmosis membranes in this additional step made it possible to reduce the concentrate volumes by a factor of 10–20, which increased the processing rate of the DD from 192 to 4620 L/d (from 50 to 1200 Gal (US)/d). The reverse osmosis membrane allowed passage of a high fraction of boric acid and silica while it promoted generation of good quality permeate that could be returned for processing through the standard membrane system. A case history of this application, including operational results, is presented in Appendix I.

8.3.3.2. Treatment of aqueous wastes from chemical cleaning of steam generators (Bruce nuclear power plant, Canada)

Ultrafiltration and reverse osmosis were employed for the treatment of contaminated aqueous wastes arising from chemical cleaning of steam generators and heat exchangers at the Bruce nuclear power plant (Canada) [80]. The EDTA based solvents used for the cleaning were similar to those developed by the Electric Power Research Institute's Steam Generator Owners

Group. The Bruce nuclear power plant used wet air oxidation (WAO) technology, coupled with ultrafiltration and reverse osmosis, for waste treatment. The principal goal of WAO is to oxidize most of the organics to CO_2 and water. Removal of excess ammonia from wet air oxidized copper and iron wastes is accomplished through a high temperature air stripping process. Finally, ultrafiltration and a two stage reverse osmosis step were utilized to treat the oxidized, ammonia stripped liquors. The process is shown schematically in Fig. 44 [80].

The ultrafiltration system employs four parallel banks of ten Zenon ZPF-12 tubular membranes in series. The first reverse osmosis stage contains two parallel banks in series, operating at a pressure of 6.5 MPa. The second reverse osmosis stage operates at a pressure of 4.1 MPa and consists of eight vessels arranged with three parallel pairs of vessels in series, followed by two individual vessels in series. Each reverse osmosis vessel contains six spirally wound elements (Filmtec SW30HR). Permeate from the final stage is disposed of via sewage treatment plant, meeting the criteria for sewer usage. The reverse osmosis concentrate is returned for further processing, either through the WAO process or for solidification and on-site landfill disposal, subject to de minimis regulations.

8.3.4. Reverse osmosis with microfiltration pretreatment (microfiltration + reverse osmosis)

8.3.4.1. Defence wastes (Savannah River, USA)

The SRS is a key US Department of Energy industrial complex dedicated to processing nuclear materials from the national defence programme. The separation area of the effluent treatment facility (ETF) was designed to treat liquid wastes from the separations area to reduce contaminants, permitting safe discharge to the environment [50].

Routine effluent to the ETF contains many soluble and sparingly soluble salts with the predominant component sodium nitrate. The goal of the ETF is to reduce the volume of waste that must be disposed of by concentrating the hazardous components. The majority of the concentrated waste is disposed of in a waste form that is a composite of concrete and salt containing waste. The flowsheet of the ETF is shown in Fig. 45. The major individual treatment steps in the overall process are:

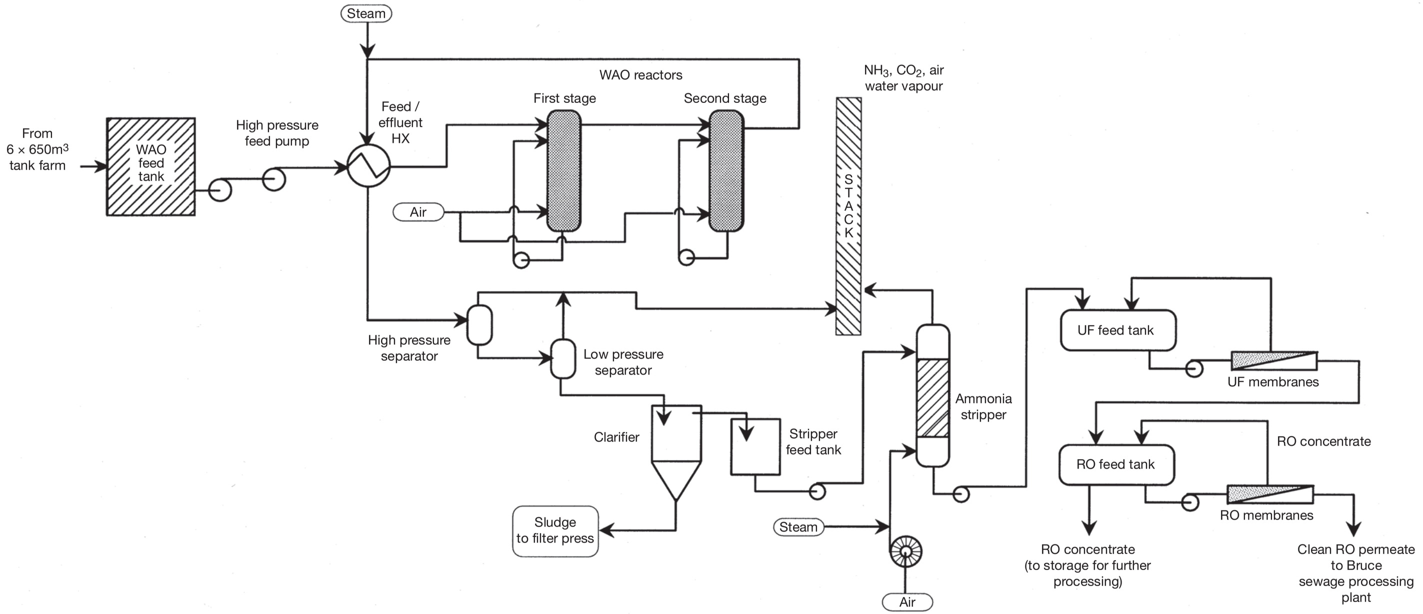


FIG. 44. Schematic of the Bruce nuclear power plant spent solvent treatment facility.

— pH adjustment;
— Microfiltration;
— Mercury specific ion exchange;
— Activated carbon for organic removal (O/R);
— Reverse osmosis;
— Polishing ion exchange;
— Evaporation [50, 65].

The ETF facility has three trains of 3 stage systems in parallel. The microfiltration step utilizes cross-flow ceramic filters with a nominal pore size of 0.2 μm. The reverse osmosis system consists of high salt rejection spirally wound elements. The first stage consists of two pressure vessels, each containing six membrane elements. The second and third stages consist of one pressure vessel each. Each treatment train can process 385 L/m. The system design allows for redundancy of equipment and variable production flows. Since startup in October 1988 the plant has operated successfully, meeting the discharge criteria. The major operational problem concerning this plant has been biofouling of the microfilters by bacteria [65].

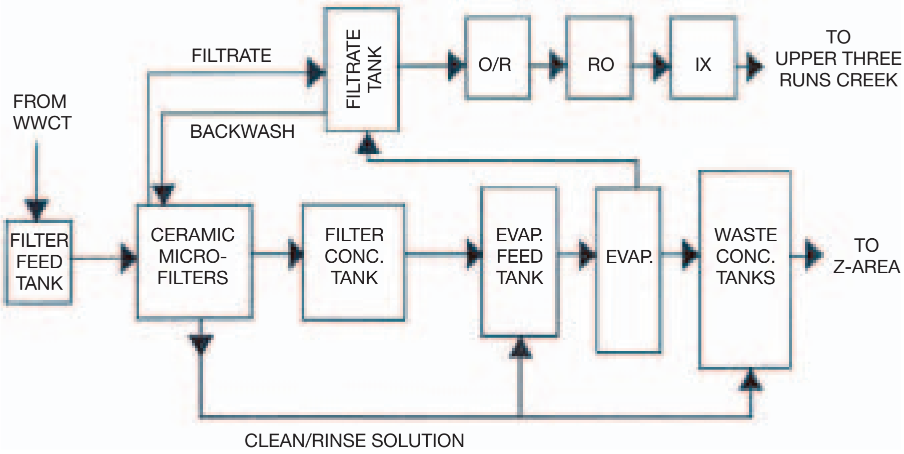


FIG. 45. The SRS ETF process flowsheet containing ceramic microfiltration and reverse osmosis.

8.3.4.2. Nuclear research wastes (AECL Chalk River Laboratory, Canada)

Nuclear research activities may produce low level radioactive wastes that contain a wide spectrum of dilute concentrations of chemicals and radionuclides. Application of membrane technologies to treat these wastes in research institutes has generated a wealth of data and useful experience which can be used in the design of systems for treatment of nuclear wastes.

Considerable pioneering efforts in this respect were made at AECL's Chalk River Research Laboratory, beginning in the 1970s [81]. The objective was the development and acquisition of a two stage reverse osmosis system with a productivity of 28 000 m^3/a. The concentrated reject from the reverse osmosis system was to be bitumenized [57, 58, 81–83]. Research and exploratory work was conducted in the 1980s, which enabled design of a full scale system consisting of cross-flow microfiltration, spirally wound reverse osmosis (first stage), and tubular reverse osmosis (second stage), as shown in Fig. 46. The system processed approximately 2200 m^3 of LRW annually. Appendix I gives a detailed case history of this application including the operational results and a flow diagram.

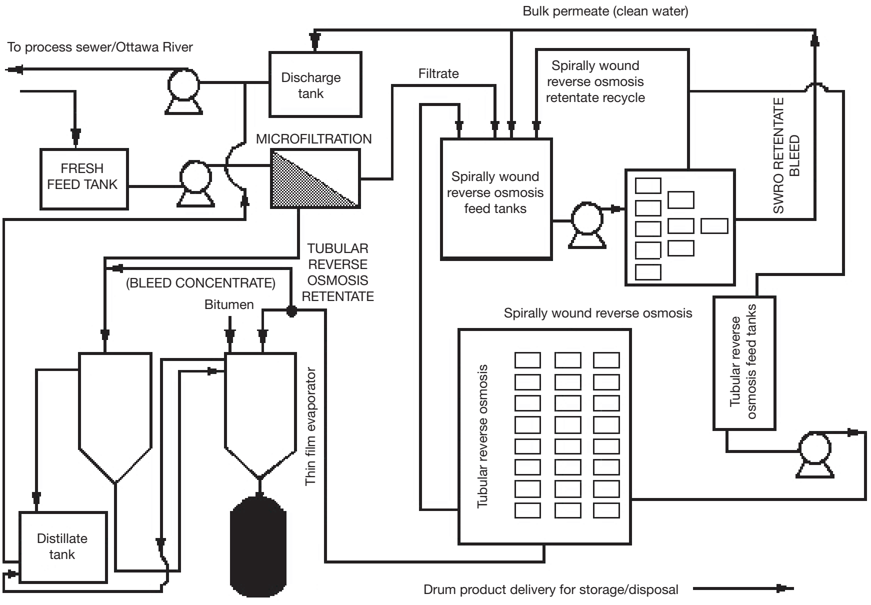


FIG. 46. Integrated plant for processing mixed LRWs.

8.3.5. Ultrafiltration

8.3.5.1. Nuclear power plant spent media transfer liquid (Diablo Canyon nuclear power plant, USA)

The Diablo Canyon nuclear power plant has tested two ultrafiltration systems to process separate batches of spent media transfer liquid (sluice water). The liquid was high in sub-micrometre particulate activity and has proved to be the most difficult liquid for the in-plant system to process [84]. Appendix I gives a detailed case history of this application, including the operational results.

8.3.5.2. Radioactive laundry (detergent) wastes

Laundry wastes are generated during laundering of contaminated protective clothes and footwear. The main laundry liquid wastes are characterized by high salinity, high surfactant contents, sodium hydrocarbonate and phosphate, and high alkalinity. The other stream, the laundry rinsing water, usually has salinity close to that of the water source used and contains much smaller amounts of surfactants and radionuclides.

Processing of the main laundry wastes by evaporation usually results in considerable foaming in the evaporator, with a carry-over of the treated solution into the distillate that would normally be discharged. The high salinity of the washing solutions limits the CF. On the other hand, the detergents in the laundry waste retain their functional properties, and if the suspended particles, fibres, biological matter and radionuclides are removed, the solution can be reused.

Suggestions to recycle washing solutions after ultrafiltration treatment appeared simultaneously in different countries during the mid-1980s [85–87]. For example, processing by ultrafiltration membranes with pore sizes of 0.03–0.05 μm suggested that 90% of the treated solution could be recycled [86]. Experience with the processing of laundry washing solutions by an ultrafiltration system utilizing membranes with a nominal pore size of 0.05 μm is described in Ref. [87].

Despite the positive results obtained with the operation of membrane systems as described in Refs [85–87], it was later shown that ultrafiltration systems for laundry wastes create problems such as the accumulation of microorganisms within the treatment system and difficulties in maintaining the desired chemical composition of the recycled solution [88].

Based on experimental work, a concept for a combined installation for processing the laundry wastes was proposed. Its main feature is that the low salinity rinse wastes are treated by reverse osmosis, while the high salinity effluents are treated by an ultrafiltration system whose objective is to recover the laundry solution in the permeate while removing the suspended particles, fibres and biological matter in the retentate [88].

8.3.6. Microfiltration

8.3.6.1. Contaminated groundwater (AECL Chalk River Laboratory, Canada)

Microfiltration can be utilized for the removal of radionuclides from soils and groundwaters contaminated by radionuclides. For the cleanup of soils the contaminants are leached by various methods, for example by counter-current reagent leaching [57, 58, 82, 83, 89–92]. The soil particles and the leaching process residues are then removed from the leachate by microfiltration. Alternatively, enhanced removal of the radionuclides can be achieved by microfiltration after coagulation of the radionuclides in the feed stream with flocculants.

A hollow fibre microfiltration system with a nominal pore size of 0.2 μm for groundwater remediation was installed at the AECL Chalk River Laboratory in 1988. Figure 47 is a flow diagram of the system. Feed flows tangentially across, over and around the hollow fibre membranes at a sufficient cross-flow velocity to keep the solids in suspension, thus minimizing deposition

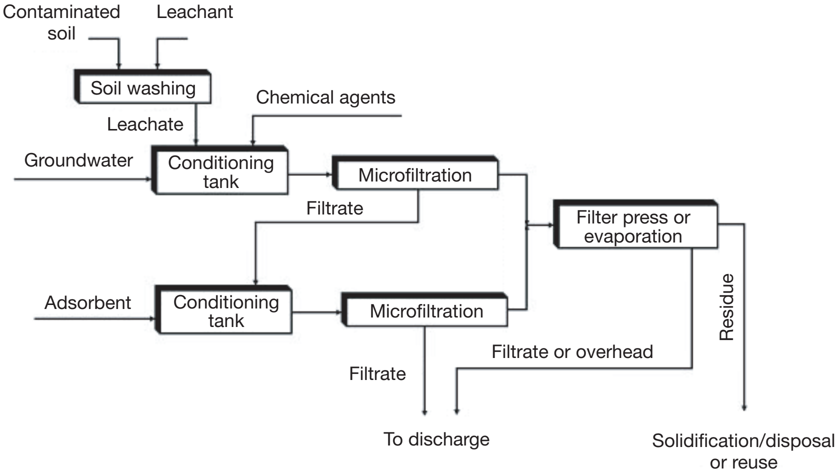


FIG. 47. Flow diagram of a two stage chemical treatment/microfiltration process for cleaning contaminated groundwaters and soils.

and fouling. A small fraction of the total feed flow exits as a filtrate. It was demonstrated that microfiltration successfully competed with ultrafiltration as long as reagents were carefully selected to allow sedimentation of the inorganic impurities (including radionuclides) from the radioactive groundwaters and the soil leachate [92]. Appendix I gives a detailed case history of this application, including the operational results.

8.3.6.2. Contaminated groundwater (Rocky Flats, USA)

Another microfiltration system for processing groundwater and wastewater contaminated with isotopes of uranium, heavy metals and organic toxic materials was installed at Rocky Flats (USA) in 1996. This system, called the sitewide water treatment facility, consists of a tubular microfiltration apparatus with a membrane pore size of 0.1 µm. This system was installed for pretreatment of the contaminated feedwater, after the feedwater was first coagulated. The reported removal of uranium isotopes was in excess of 99.9% [91].

9. CONCLUSIONS

The nuclear industry generates a broad spectrum of low and intermediate level LRWs. Treatment methods for processing LRWs have usually utilized the same conventional processes found in industrial water and wastewater treatment, such as chemical treatment, adsorption, filtration, ion exchange and evaporation. These processes are limited by their inability to remove all contaminants, the large operating costs involved (e.g. evaporation), or the potential to generate significant quantities of secondary solid waste. Furthermore, some LRWs have proven difficult to process satisfactorily by these conventional methods.

Membrane based processing of nuclear radioactive wastes and radioactive liquids in general has rapidly gained acceptance within the nuclear industry. After development of suitable membrane materials and their long term verification in conventional wastewater treatment, these membrane processes have been adopted by the nuclear industry as a viable alternative for treatment of LRWs. In the nuclear industry, the most utilized membrane processes are those with pressure gradient as the process driving force. These processes include reverse osmosis, nanofiltration, ultrafiltration and microfiltration and are distinguished from one another primarily by the pore size of the membrane. This allows pressure driven membrane processes to be used for selective separation over the full range of contaminant size, from micrometre sized particles to dissolved ions.

In most cases the membrane processes are used as one or more of the treatment steps in complex waste treatment schemes which combine conventional and membrane treatment technologies. These combined systems have proved to offer superior treatment capabilities, particularly in instances where conventional methods alone could not perform a similar task as efficiently or effectively. They are capable of producing high quality treated effluents with an acceptably low level of residual radioactivity for discharge, or for recycle and reuse. The concentrate waste stream containing the removed radioactivity invariably needs further processing by evaporation or other means to facilitate final conditioning to a solid waste form suitable for intermediate storage and disposal.

As membrane processes are often part of a total waste treatment scheme, the application of any specific membrane process must be considered in the context of the overall processing goals. This will include consideration of the waste feed characteristics, desired product quality, process limitations, overall system flexibility, the final waste form desired, compatibility with other existing treatment systems, and cost.

Membrane systems are rarely acquired off the shelf but must be designed and then built only after extensive on-site testing for each specific application. Selection of proper membrane materials and the membrane module configuration is a prerequisite for the successful application of a membrane system. A broad range of polymeric membranes is available from different suppliers who have accumulated a wealth of operating experience. The use of advanced inorganic (ceramic) membranes should also be considered as these are now available on the market at costs comparable to polymeric membranes. Although a membrane system can be designed using computer modelling programs and the feedwater characteristics, computer prediction alone is not rigorous enough to serve as the basis for the design of a full scale plant. Physical testing of the wastewater and pilot scale equipment is necessary.

The operating parameters of a membrane system must be well understood so that the system's performance can be maintained. This is normally achieved by monitoring the normalized flux of the membrane unit(s). Knowledge of the characteristics of the feedwater is paramount to understanding any changes that may occur in the plant's performance. It is the non-radioactive components of the feedwater that will determine the overall throughput of the plant, with considerations of radioactivity provided for in the design and layout of the plant. Prevention of membrane fouling by colloidal, organic, biological or scaling materials is the most important operational consideration for membrane systems. The generation of further secondary wastes from excessive cleaning or membrane changes can have a severe detrimental effect on overall performance and costs. Strategies must be in place to prevent and/or minimize fouling and deal with unexpected incidents (such as an oil spill) that may occur in operation. These strategies must be determined during pilot testing of the proposed membrane system prior to full scale design.

Pressure driven membrane processes are now well established in the nuclear industry. In general, the introduction of these membrane processes has reduced waste treatment costs, improved the quality of water discharged to the environment, and increased the possibility of recycling treated water (or boric acid in some power plant applications). Other membrane separation methods are in use or in various stages of development. These methods utilize electrical potential, concentration or temperature gradient as their driving force instead of pressure gradient. While some of these have been proven and utilized in various industries they have generally not proved to be technologies of choice for processing LRWs. However, some of these membrane methods are being rapidly developed. The results of these efforts could become technically significant in the future.

Membrane systems, while somewhat more complicated to operate than traditional treatment systems, represent a major step forward in providing an effective capability for treating LRWs. Successful design and operation of a membrane system requires a collective commitment and dedicated teamwork by the system designers, operators, and the membrane suppliers.

Appendix I

EXAMPLES OF MEMBRANE TECHNOLOGY INSTALLATIONS WITH OPERATING RESULTS AND LESSONS LEARNED

General principles and key examples of the application of schemes for treatment of LRWs incorporating membrane technology are discussed in Section 8. This appendix provides information on the actual reasons for and objectives of the selection of a membrane technology for radioactive waste treatment at various nuclear facilities. The information includes detailed operational results and data and, where available, the lessons learned.

Example 1

Facility name: Nine Mile Point nuclear power plant, units 1 and 2 (USA)
Membrane system: Thermex reverse osmosis
Objectives:
- Reduce solid radioactive waste generation rates
- Process wastewater feeds with widely varying concentrations
- Reduce on-site processing costs

Unit 1 of NMP is a 610 MW(e) BWR that operates under a ‘zero-liquid’ discharge philosophy. Therefore, all water generated within the plant has to be returned for recycling. In 1994, a Thermex reverse osmosis system was installed and tested. This advanced system reduced the secondary waste generation rates by over 500% when compared to the demineralizer system already in use at the plant. The new system has also maintained high water purity levels despite encounters with high conductivity and high total organic content feedwater conditions [77, 93, 94].

The first goal of the new system was to reduce generation rates of solid (secondary) radioactive wastes. The second goal was to process feeds with widely varying concentrations of impurities while maintaining ultrapure quality standards. An ancillary goal was to reduce the concentration of organic anions that were recycled to the reactor. Reducing the level of organic anions returning to the reactor increases fuel integrity and minimizes corrosion, thereby reducing overall utility/plant life cycle costs. The final goal of the system was to reduce operating costs.

A pilot test was performed using the Thermex reverse osmosis unit to ensure that equipment installed on-site at unit 1 of NMP was appropriately sized and specified to treat the plant specific waste stream. The unit processed two 4.5 m^3 (1200 Gal (US)) samples of floor drain water. Table 9 shows the chemical characteristics of this process.

The pilot system was chemically cleaned and preserved between samples to maintain membranes within their baseline performance specifications. The volume reduction factor was extremely high due to the low conductivity and small amount of solids present in the waste sample. Table 10 shows the results of the pilot test.

TABLE 9. CHARACTERISTICS

Characteristic	NMP unit 1	NMP unit 2
pH	6.35	6.96
Conductivity (mS/cm)	18.6	34.3
TDS (ppm)	14.9	25
Total suspended solids (ppm)	3	250
Turbidity (NTU)*	4	16
Oil and grease (ppm)	0	0
Silica (ppm)	2.6	2.52
Calcium (ppm)	0.81	3.4
Magnesium (ppm)	0.5	0.6
Chloride (ppm)	4.7	8.5
Sulphate (ppm)	1.4	2.5
Iron (Fe^{2+}) (ppm)	0.02	0.03

* Nephelometric turbidity unit.

TABLE 10. PILOT SCALE TEST RESULTS

Product water quality			Final waste characteristics		
Conductivity (mS/cm)	Silica (ppb)	Total organics (ppb)	Waste volume (cm^3)	Volume reduction factor	Waste class/type
0.083	<5	189	73	62 200	A/A

The system at unit 1 of NMP was evaluated again in 1997. Following its initial pilot testing phase, the Thermex system processed a total of 50 300 m^3 (13.3 million Gal (US)) from 1995 to June 1997. This process water included reactor shroud swarf, sanitary waste, lake water and oily waste. The system met the plant's first goal of solid radioactive waste volume reduction. Solid radioactive waste generation by the liquid treatment system was reduced by 89%. In addition, the system met the plant's goal of reducing the concentration of organo-anions in the recycle water. The post-UV chromatography showed minimum concentrations of organic anions. Product water from the evaporator, which had initially processed floor drains from startup until 1992, had average total organic carbon concentrations of approximately 400 ppb. However, it was shown that ultraviolet light did not significantly impact the product water quality when total organic carbon concentrations were already low (<200 ppb). The impurities rejected from the membrane system and contained in the concentrate have consistently produced class A/type A waste after dehydration.

Processing of LRW using Thermex reverse osmosis technology began at unit 2 of NMP in 1996 [95]. Unit 2 is a 1225 MW(e) BWR unit. The original radioactive waste treatment system design consisted of a flat bed filtration unit, an evaporator and a deep bed demineralizer. Its annual floor drain and equipment drain volume is 81 100 m^3 (21 424 150 Gal (US)). Annual unprocessed waste generation is 260 m^3 (9154 ft^3) per year. Modifications to this original design were made between 1992 and 1995 that led to a decrease in annual waste and volume generation. However, the plant management was interested in further improving its processing system. The Thermex reverse osmosis system processed approximately 36 300 m^3 (9.6 million Gal (US)) of floor drain water per year. Its average solid waste generation is 11 m^3 (380 ft^3) per year (including treatment media, membranes and filters). The total organic carbon in the effluent stream was <50 ppb. An average conductivity of 0.058 mS/cm in the effluent stream was achievable. In summary, all of the plant's goals were met.

Example 2

Facility name:	Comanche Peak nuclear power plant (USA)
Membrane system:	Ultrafiltration and reverse osmosis
Objectives:	— Demonstrate removal of activity, in particular colloidal ^{58}Co — Remove caesium and iodine to non-detectable levels — Evaluate reverse osmosis as a viable processing option for reduction of secondary waste volume (e.g. spent ion exchange resin)

The Comanche Peak nuclear power plant is a two unit PWR plant with each unit rated at 1150 MW(e). Prior to evaluating advanced ultrafiltration/reverse osmosis technology, the plant used a filter and demineralizer system to process all liquid waste prior to discharge. A 38 L/min (10 gal/min) pilot ultrafiltration/reverse osmosis/demin unit supplied by RWE NUKEM was installed in parallel with the original process so that a side-by-side comparison could be made while each waste stream was being processed [96, 97].

The objectives of the pilot unit tests at Comanche Peak were to:

(a) Demonstrate the removal of activity, colloidal ^{58}Co in particular, to below discharge limits of 1×10^{-05} mCi/mL;[1]
(b) Remove caesium and iodine to non-detectable levels;
(c) Evaluate reverse osmosis as a viable processing option for reduction of secondary waste volume, i.e. spent ion exchange resin;
(d) Determine the volume reduction achievable by reverse osmosis.

Floor drain water, resin sluice water and boron recycle system water were processed during the testing. Total suspended solids were first removed from the feed by an ultrafiltration unit, and dissolved contaminants were then removed from the ultrafiltration permeate by reverse osmosis. The reverse osmosis unit was single-pass and had an internal recycle of the reject stream. Specific reverse osmosis (nanofiltration) membranes were used for passage of boron. Cation and anion resins were used to polish the reverse osmosis permeate before discharge to a plant product water collection tank. Both the ultrafiltration and reverse osmosis rejects were returned to the floor drain.

The results of the pilot testing at Comanche Peak are summarized below. Table 11 shows a comparison of DF of the plant filter/demin system and the alternative ultrafiltration/reverse osmosis/demin unit that was tested.

Other results were as follows:

(1) The ultrafiltration/reverse osmosis technology, when used with demineralizers, performed better than the demineralizer technology currently used at Comanche Peak.
(2) Product water was immediately and consistently below activity discharge limits.
(3) The ultrafiltration/reverse osmosis technology produced 151 m^3 (40 000 Gal (US)) of clean water and generated approximately 151 L (40 Gal (US)) of reject, with a CF of 1000.

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[1] 1 Ci = 3.70×10^{10}Bq.

TABLE 11. DECONTAMINATION FACTORS FOR THE FILTER/DEMIN SYSTEM AND ULTRAFILTRATION/REVERSE OSMOSIS/DEMIN UNIT

Equipment decontaminated and date	Filter/demineralizer DF	Ultrafiltration/reverse osmosis/demin DF
Floor drain tank (FDT) 2000-02-01	6.81	57 200
Recycle Holdup Tanks 2002-02-07	1.12	1310
FDT 2002-02-14	7.97	478.5

(4) No coagulants or chemicals for pH adjustment were added.

(5) The ultrafiltration/reverse osmosis technology may reduce treatment media usage by 40–50%. The handling of reject waste produced by the ultrafiltration and reverse osmosis may offset any potential savings in treatment media usage.

Example 3

Facility name:	Dresden nuclear power plant unit 1 (USA)
Membrane system:	Ultrafiltration and reverse osmosis
Objectives:	— Process batch of transuranic (TRU) contaminated power plant LRW

Unit 1 of the Dresden nuclear power plant (PWR) installed a system utilizing a combination of ultrafiltration and reverse osmosis, followed by a deep bed demineralizer [97]. The plant needed to process two tanks containing a total of 1440 m^3 (380 000 Gal (US)) of LRW that was also contaminated by TRU elements. The objective was to reduce the waste volume to a level that would be practical for further processing and conversion to a final waste form. The waste feed was directed to the ultrafiltration unit and the ultrafiltration permeate was fed to the reverse osmosis unit. Both the ultrafiltration and the reverse osmosis concentrate streams were returned to the feed tanks. The reverse osmosis permeate, after passing through deep bed demineralizing units, was collected in product water tanks and then, after confirmation that release criteria were met, discharged from the plant. By using an ultrafiltration/reverse osmosis system, the feed tank contents were reduced by a factor of 10, minimizing the residual volume requiring treatment for final disposal. The product water met the 1×10^{-6} μCi/mL total activity and 1×10^{-8} μCi/mL TRU activity limit requirements for discharge.

Example 4

Facility name:	River Bend nuclear power plant (USA)
Membrane system:	Ultrafiltration
Objectives:	— Select a technology based on pilot testing — Reduce the contribution of organics from walnut shell filtration media — Reduce fouling of ion exchange resins

The River Bend nuclear power plant is a BWR plant that began commercial operation in June 1986 [97]. The plant uses walnut shells as filter media. These increase the total organic carbon of the water and contribute to secondary waste generation. A pilot study using advanced processing technology was carried out to determine the possibility of using a back-flushable dead end filter (BFF) or ultrafiltration as a replacement for the current system. The advantages of using a BFF or ultrafiltration unit are that there is no contribution of organics from the filtration system itself and the volume of waste generated is less than that of the walnut shells. The ion exchange resin efficiency was also expected to increase since fouling of the resin by the walnut shells would be eliminated.

Initial pilot testing utilized the BFF unit to process floor drain water. However, the rapid plugging of the BFF filters and the short operating cycles proved not to be practical for full scale application. Pilot testing was then resumed with an ultrafiltration unit for five weeks. Again, floor drain water was processed through the unit. The concentrate was routed to a plant sump and the ultrafiltration permeate was directed through two demineralizer vessels charged with carbon and mixed bed ion exchange resin. The demineralizers were able to remove the dissolved contaminants in the stream and the water produced was suitable for recycling to the plant. In addition, the pilot unit was able to process feedwater with a turbidity range of 20–150 NTU and routinely produced ultrafiltration permeate with turbidity values of <0.1 NTU. The ultrafiltration unit essentially removed all suspended solids. In addition, the membranes were backwashed with clean water, which eliminated the need for chemical cleaning. Table 12 shows the DF values and radioisotopic activities for the BFF and ultrafiltration tests.

TABLE 12. RIVER BEND ACTIVITY REDUCTION RESULTS (COMPARISON OF BFF AND ULTRAFILTRATION)

Equipment type	Feed (mCi/mL)	Demin effluent (mCi/mL)	Overall DF
BFF	5.7×10^{-4}	1.5×10^{-5}	39
BFF	6.7×10^{-4}	4.5×10^{-6}	147
BFF	5.8×10^{-4}	1.9×10^{-5}	31
Ultrafiltration	3.7×10^{-4}	4.9×10^{-7}	750
Ultrafiltration	2.9×10^{-4}	5.7×10^{-7}	510
Ultrafiltration	4.9×10^{-4}	4.8×10^{-7}	1030
Ultrafiltration	4.7×10^{-4}	2.2×10^{-7}	2110
Ultrafiltration	4.3×10^{-3}	6.0×10^{-7}	7260

Example 5

Facility name:	Salem nuclear power plant (USA)
Membrane system:	TUF™ ultrafiltration
Objective:	Reduction of activity in the plant's discharges

The Salem nuclear power plant was one of the first PWRs to use ultrafiltration in their LRW system. The plant consists of twin Westinghouse 1100 MW(e) PWR units [98]. The first unit began commercial operation in June 1977, the second in October 1981. In the 1980s, Salem's primary LRW processing goal centred on reducing costs through volume reduction of contaminated secondary wastes resulting from processing of the LRWs. However, these goals shifted in the 1990s from an emphasis on volume reduction to reduction of activity in plant discharges. In 1995, management set a goal of discharging <0.5 Ci/a while preserving their industry-leading volume reduction performance in LRW processing.

The LRW system in Salem is a collection of liquids from floor drains, sample points, laboratories, primary and auxiliary equipment drains, containment, and other miscellaneous source points. The plant's two principal sources of water are service water and deionized water. The service water is mechanically filtered brackish Delaware Bay water that is high in sodium, conductivity and organics, while the deionized water is high quality demineralized water. The waste collection system provided limited opportunity for segregation of incoming liquids based on water quality. The resulting high conductivity water lessened the efficiency of demineralization with ordinary organic ion exchangers.

By August 1997 the plant completed installation of an LRW processing system that consisted of a tubular ultrafiltration unit and a demineralization system. A WPS™ (waste processing system) was installed and began operation in April 1991 while a TUF system was installed in August 1997 (both from Diversified Technologies Services, Inc., Knoxville, Tennessee).

The ultrafiltration system was the key to reducing effluent discharges while maintaining favourable waste generation rates. The TUF system was designed to provide filtration down to 0.05 μm, thus protecting the downstream ion exchange beds by removing fouling agents such as suspended solids, oils, greases, and most colloids and metal complexes. The removal of these agents was expected to promote longer bed life and improve the DF. As part of the process of solids removal, a fraction of $^{58/60}$Co, ^{54}Mg and ^{100}Ag activity is also removed. This fraction was found particularly important since the removed activity is, by definition, insoluble and not subject to removal by ion exchange. This insoluble activity has chronically plagued demineralizer operations in the past by readily passing through standard filter/demineralizer systems [98]. The WPS demineralizer system was employed downstream of the ultrafiltration and utilized a cascade logic that allowed for utilization of fresh polishing beds downstream of the process beds when an isotopic leakage occured. This configuration allowed production of the highest quality water.

Approximately 31 200 m^3 (8.24 million Gal (US)) were processed from April 1991 to August 1997, representing 50–75% of the total water generated and released by the plant. The unprocessed water was generally low activity water that was sampled and discharged if regulatory specifications were met. Since the installation of the ultrafiltration upstream of the demineralizer, water containing hydrazine at concentrations as high as 300 ppb has been successfully processed without addition of hydrogen peroxide, with no detrimental effects on cobalt DFs. In addition, the ultrafiltration removed virtually 100% of the insoluble radioactive species while permitting the bulk of the ionic material to pass through for removal by the demineralizer system.

The introduction of ultrafiltration has minimized or eliminated the need for activated carbon, thereby further reducing the waste disposal volume and cost. From 1991 to 1998, DFs for total activity across the processing system ranged from 10 to 14. With the ultrafiltration removing particulate isotopes upstream of the demineralizer system, the total DFs have increased by approximately 2.5 times. Another measure of system performance and the impact of system changes are the water volumes processed versus Ci released [79]. From 1992 to 1997, prior to ultrafiltration, approximately 10 070 m^3 (282 000 Gal (US)) were processed per Ci released. In 1998, with the installation of TUF, volume/Ci released improved 15 times to 16 120 m^3/Ci (4 259 048 Gal (US)/Ci). In 1999, this further increased to 21 180 m^3/Ci (5 594 937 Gal (US)/Ci). Through June 2000, the Salem nuclear power plant was averaging 78 000 m^3/Ci (20 592 965 Gal (US)/Ci) released.

Example 6

Facility name:	Seabrook nuclear power plant (USA)
Membrane system:	ultrafiltration
Objectives:	— Remove colloidal ^{58}Co to below discharge limits — Reduce all other TSSs — Improve overall performance

An ultrafiltration system was installed and tested at the PWR of the Seabrook nuclear power plant with the goal of removing colloidal ^{58}Co to below discharge limits of 1×10^{-5} mCi/mL. The plant management was also interested in removing all other TSSs and improving the overall performance of their LRW processing system [97].

The ultrafiltration/demineralization pilot unit was operated in parallel with Seabrook's processing system by taking a sidestream from the wastewater feed line. The spent resin tank drain-down water and the water from the two floor drain tanks were tested.

The processing configuration for testing at Seabrook was similar to that used at the River Bend nuclear power plant (see Example 4), with two exceptions. Only cation resin was used in the demineralizer vessel because the Seabrook nuclear power plant was focused on the removal of ^{58}Co. In addition, the ultrafiltration reject was routed through a solids collection system (SCS^{TM}) and returned for recirculation. The purpose of the SCS is to collect and contain the solids separated from the feed wastewater by the ultrafiltration. Therefore, with the SCS in service, no reject stream that would require additional treatment was discharged from the ultrafiltration plant during pilot unit testing.

The pilot test results showed that the ^{58}Co activity in the ultrafiltration effluent was consistently at or below Seabrook's discharge limit of 1×10^{-5} mCi/mL. The ^{58}Co activity in the product water taken from the sidestream was also consistently equal to or less than that in the plant system effluent. It was also demonstrated that more than 90% of the total activity was removed with TSS by the ultrafiltration system. No chemical cleaning of the membranes was required. In addition, no coagulants were needed or added, and no pH adjustments were made to the waste stream.

Example 7

Facility name:	Callaway nuclear power plant (USA)
Membrane system:	Ultrafiltration
Objectives:	— Reduce the plant's liquid effluent mixed fission and activation product activity — Reduce the occupational radiation dose

The Callaway nuclear power plant's management was interested in reducing the plant's liquid effluent mixed fission and activation product activity to less than 0.25 Ci/a and in lowering the radiation dose to less than 1% of specified annual limits. For an annual generation of 4540–6060 m^3 (1.2–1.6 million Gal (US)) at the Callaway nuclear power plant, 0.25 Ci/a corresponds to an average of 4.1×10^{-5} mCi/mL in the plant's liquid effluent [99].

Using advanced processing technologies such as ultrafiltration, ion exchange, and SCS, 757 m^3 (200 000 Gal (US)) of waste were processed from March to June 2001. The processed waste was taken from the FDT, the equipment drain tank (WHUT) and the reactor coolant system waste tank (RHUT). Table 13 gives the averages for the chemical and radiological characteristics of the waste.

Four ultrafiltration modules were used to process the RHUT wastes. The flow rate was limited to about 5.7 m^3/h (25 gal/min) because of a high pressure drop through the plant's ion exchange system. The testing unit processed 760 m^3 (200 000 Gal (US)) of this waste. No fouling of the ultrafiltration membranes was observed and thus no back-flushing or chemical cleaning of the membranes was required. The ultrafiltration unit removed about 70% of the total activity as suspended solids. The remaining activity was then removed to minimum detectable activity (MDA) by the test ion exchange system. The ^{58}Co was always removed to MDA levels.

One ultrafiltration module was used to process the FDT water. The ultrafiltration permeate was discharged to the floor drain for recycling into the plant rather than routing it through the plant's ion exchange system. This unusual step was requested by the plant management because of previous unsuccessful attempts at processing this waste through the plant's ion exchange system. The FDT waste was processed successfully, with 89% of the total activity removed as suspended solids by the ultrafiltration unit. Again, the remaining activity was reduced to MDA or to low 1×10^{-8} mCi/mL levels by the differently configured test ion exchange system. As in the case of the RHUT runs, ^{58}Co was removed to MDA. Complete recovery of the permeate flow was achieved by back-flushing. No chemical cleaning was required.

TABLE 13. CALLAWAY LIQUID WASTE: AVERAGE CHARACTERISTICS

	RHUT	FDT	WHUT
Annual volume (m^3 (Gal (US))	2250–30308 (600 000–800 000)	1140–1510 (300 000–400 000)	1140–1510 (300 000–400 000)
Average conductivity (mS/cm)	90	660	300
Average activity (mCi/mL)	1.30×10^{-3}	3.60×10^{-3}	7.50×10^{-3}
Co-58 (mCi/mL)	5.77×10^{-4}	2.4×10^{-3}	3.11×10^{-3}
Co-60 (mCi/mL)	5.90×10^{-4}	1.10×10^{-3}	1.60×10^{-3}
Cs-134 (mCi/mL)	1.29×10^{-5}	1.20×10^{-5}	5.76×10^{-5}
Cs-137 (mCi/mL)	2.80×10^{-5}	4.50×10^{-5}	1.80×10^{-4}

In June 2001 a new correctly configured ion exchange system and other components were added to the original system. This full scale system is capable of processing the waste at a higher rate of 115 L/m (30 gal/min). Including the test period, as of November 2001 more than 1890 m^3 (500 000 Gal (US)) of various waste streams had been processed. The performance of the full scale system has confirmed the results reported above. The 530 L (18.8 ft^3) of SCS waste contained all the TSSs. Approximately 90% of the activity from the wastewater was also present in the SCS waste. The SCS waste has been certified for direct disposal at the radioactive waste disposal site.

In summary, the ultrafiltration unit was highly effective in removing virtually 100% of suspended solids, thereby preventing fouling of the resin beds as well as causing colloidal particles to bypass the beds. The unit eliminated the use of chemical injection that would shorten the life of the resin beds and consequently increase the secondary waste volume. The unit has also successfully processed high conductivity wastes and reduced radioactive isotopes to undetectable levels.

Example 8

Facility name:	Diablo Canyon nuclear power plant (USA)
Membrane system:	TUF ultrafiltration
Objective:	Select technology for spent media transfer liquids

The Diablo Canyon nuclear power plant has tested two ultrafiltration systems to process separate batches of spent media transfer liquid (sluice water). The liquid was high in sub-micrometre particulate activity and has proved to be the most difficult liquid for the in-plant system to process [81].

Diablo Canyon's current LRW system features segregated collection tanks, an in-plant filtration and ion exchange treatment subsystem, provisions for the use of mobile liquid treatment systems, and a filtered discharge subsystem. However, the in-plant subsystem is not capable of processing spent media transfer liquids from letdown, shutdown and spent fuel pool demineralizers high in sub-micrometre particulate activity. The LRW system routinely receives 3785–5677 m^3 (1–1.5 million Gal (US)) of LRW per year containing 15–30 Ci.

The in-plant treatment subsystem consisted of a layered carbon bed followed by three deep bed vessels and a polishing cartridge filter. The carbon bed serves as a pre-filter and can remove organics and particulates down to about 3 mm. The carbon bed was followed by a zeolite bed, a cation bed and an anion bed. However, sub-micrometre particulate activity could not be removed effectively with the carbon bed as a pre-filter or by the sub-micrometre cartridge in the downstream polishing vessel. Addition of polymers to agglomerate the particles for removal on the carbon was not practical because the entire carbon bed must be disposed of when it becomes fouled. Therefore other technologies were considered.

In 1999 a mobile TUF system service was installed at Diablo Canyon. The TUF unit collected waste liquid in a shielded conical bottom feed tank. Liquid was metered from the tank to the TUF modules. The filtered product liquid was then sent to the plant for further ion exchange treatment. The reject was recycled back to the shielded feed tank. The flow in the reject loop was maintained at about 378 L/m (100 gal/min) to prevent activity from adhering to the TUF modules. The ultrafiltration reject was metered from the shielded feed tank onto a spent carbon medium in a steel shuttle liner for future processing.

A total of 45 m^3 (11 910 Gal (US)) of sluice water containing 5.3 Ci of gamma activity were processed in three days and 4.7 Ci of particulate activity were removed. The TUF liquid was then routed back to the plant for treatment by ion exchange. All of the liquid was successfully treated in-plant and discharged. At the end of the testing period the membranes were removed, press packed into a 0.13 m^3 (4.7 ft^3) drum and disposed of at the Barnwell site.

In 2001, the Diablo Canyon nuclear power plant also tested a second ultrafiltration module. This 57 L/m (15 gal/min) modular system consisted of a waste feed pump skid, an ultrafiltration module skid, a recirculation pump skid, a clean in-place tank, a control console and an SCS. It was used to process 60 m^3 (16 000 Gal (US)) of sluice water containing 5 Ci of gamma activity.

Waste liquid was metered to the ultrafiltration modules by the feed pump. The filtered product liquid was sent to the plant for further treatment by ion exchange. The reject was recycled to the ultrafiltration modules at a very high flow rate of more than 1515 L/m (400 gal/min). This high flow rate was used to prevent fouling of the membranes. All of the effluent from the ultrafiltration system was successfully treated in-plant by ion exchange and discharged. It should be noted that due to the SCS technology deployed no ultrafiltration reject effluent that would require additional processing was produced. The system did not appear to have intrinsic hot spots other than low point drains and could be transported, including the membranes, to the next project. No chemical cleaning was required before the system was shipped from the plant site.

Based on this experience, both ultrafiltration systems provided a product liquid that was free of particulate activity for the in-plant exchange system. However, innovative design characteristics such as membrane reusability, much lower secondary waste produced, elimination of reject that requires additional treatment (SCS), hot spot prevention and improved operability showed that the ultrafiltration technology for nuclear applications had significantly improved between the tests.

Example 9

Facility name:	Mound Laboratory (USA)
Membrane system:	Ultrafiltration
Objectives:	Process alpha contaminated waste from fuel reprocessing

An ultrafiltration system was tested to treat LRW from the reprocessing of irradiated nuclear fuel at the Mound Laboratory (USA) [34, 100]. The content of radionuclides in the initial waste stream did not exceed 16 000 Bq/L (the main radionuclide being ^{238}Pu). The waste feed had a mild alkaline reaction (e.g. pH of 7.2–8.5) and a suspended matter content of 5–100 mg/L. The ultrafiltration system used tubular membrane elements. The pilot installation consisted of a bank of 32 three metre long tubular elements with a total membrane surface of 6.5 m^2. The initial productivity of the installation was 4.5 m^3/h. More than 450 m^3 of LRW were processed. In the test operation, approximately 80–99% of alpha radionuclides were retained. In the subsequent full scale installation, the retention of various radionuclides was as follows:

- ^{241}Am: 98.9%;
- ^{237}Np: 69.1%;
- ^{233}U: 93.7%;
- ^{238}Pu: 98.6%.

Example 10

Facility name:	AECL Chalk River Laboratory (Canada)
Membrane system:	Microfiltration and reverse osmosis
Objectives:	— Investigate and verify the application of membrane technology for treatment of LRWs — Treat the laboratory's LRWs

Most of the detailed information on performance of a reverse osmosis system applied for cleaning liquid radioactive effluents has been reported in Refs [57, 58, 81–83]. Development of a membrane installation for cleaning LRW at AECL Research Laboratories at Chalk River, Canada, began in the 1970s [81]. The objective was development and acquisition of a two stage reverse osmosis system with a productivity of 28 000 m^3/a. The concentrated reject from the reverse osmosis system (e.g. up to 5 wt%) was to be bitumenized.

The LRWs at the AECL nuclear research centre are characterized by a salinity of up to 5 g/L and specific radioactivity of up to 2×10^5 Bq/L (^{50}Mn, ^{51}Cr, ^{60}Co, ^{95}Zr, ^{103}Ru, ^{144}Ce). Research and exploratory work was conducted in the 1980s which enabled design of a full scale system consisting of cross-flow microfiltration, spirally wound reverse osmosis (first stage) and tubular reverse osmosis (second stage), as shown in Fig. 45 [81].

The feed, that is the LRW to be treated, is collected in a fresh feed tank then pumped into the hollow fibre microfiltration apparatus. The microfiltration concentrates and the products of the gas membrane backwash are routed into the thin-film evaporator, representing the first evaporation stage. The evaporator bottoms are then processed, together with other concentrates, in the second stage evaporator/bitumenizer to produce a bituminized product. The microfiltration permeate is routed into a collection tank (spirally wound reverse osmosis feed tank), becoming the reverse osmosis feedwater.

The spirally wound reverse osmosis apparatus consists of nine modules, arranged as a three stage cascade in the proportion 5:3:1, as the flow rate of feedwater is reduced because of the permeate withdrawal. Each module (with a diameter of 100 mm and a length of 6 m) contains six spirally wound Filmtec SW30HR RO elements. The membrane packing density in the element is 1000 m^3/m^2. The operating pressure at the inlet of the cascade is 2.7 MPa. The total flow rate of the treated solution through the cascade is up to 3 m^3/h. The permeate, almost completely cleaned from all toxic impurities, including radionuclides, $R > 0.99$, is accumulated in a discharge tank and then discharged into the environment (Table 14) Alternatively, the concentrate from the spirally wound reverse osmosis apparatus could be directed to the SWRO feed tank for recirculation or into tubular reverse osmosis feed tanks for further treatment by the tubular reverse osmosis system.

The tubular reverse osmosis system consists of three successively connected banks of eight tubular modules arranged in parallel. Each module (length 4 m, diameter 0.1 m) has 18 tubular membranes with a diameter of 1.3 cm. A working pressure of 4 MPa is used. The general content of salts and suspensions in the final concentrate is as high as 40 g/L. This concentrate was then directed to the thin-film evaporator and treated together with the concentrates arriving from the microfiltration pretreatment system. The concentrates fed to the thin-film evaporator are bituminized in 200 L galvanized steel drums furnished with an anti-corrosive layer. The system processes approximately 2200 m^3 of LRW annually.

TABLE 14. CONTAMINANT REMOVAL EFFICIENCIES

Radionuclide	Microfiltration	Spirally wound reverse osmosis	Tubular reverse osmosis	Plant efficiency
α	81.2 ± 15.5	97.3 ± 4.3	98.5 ± 2.2	99.9
β, γ	55.6 ± 20.8	99.3 ± 1.2	~99.9	99.6
^{144}Ce	75.7 ± 20.8	99.4 ± 0.7	~100.0	99.6
^{60}Co	55.1 ± 26.6	99.7 ± 0.2	~100.0	99.6
^{137}Cs	17.5 ± 14.6	98.6 ± 2.1	99.8 ± 0.4	98.6
Total solids	16.0 ± 14.4	98.5 ± 4.0	98.7 ± 3.5	99.5
Ca	12.7 ± 13.1	97.3 ± 1.3	~100.0	99.5
Fe	69.6 ± 26.4	98.2 ± 1.6	~100.0	99.5
Mg	21.6 ± 16.3	98.2 ± 1.1	~100.0	99.5
SO^{2-}	—	99.5 ± 0.8	~100.0	99.5
PO_4^{3-}	10.0 ± 7.3	99.8 ± 0.1	~99.99	99.8

Example 11

Facility name:	AECL Chalk River Laboratory (Canada)
Membrane system:	Microfiltration
Objective:	Demonstrate cleaning of contaminated groundwaters and soils

Noticeable progress in the use of microfiltration for cleaning contaminated groundwaters and soils has been made by AECL's Chalk River Laboratory [57, 58, 82, 83, 89–92]. In the systems developed and introduced by AECL, microfiltration can work as a self-contained process for cleaning radioactive groundwaters [92] and also as a pretreatment step prior to reverse osmosis, as shown in Fig. 45. Since the overall system has been described elsewhere, only the microfiltration experience is addressed in the following.

A hollow fibre microfiltration system (model 40M1) with a nominal pore size of 0.2 μm was introduced at Chalk River in 1988. The membrane elements had to be completely replaced in 1992. The cross-flow microfiltration system contains 40 filtration modules, approximately 6 cm in diameter and 50 cm long. Each filter module contains polypropylene hollow fibre membranes arranged in a shell and tube geometry. The total membrane surface area available for filtration in each module is about 1 m^2. The system is configured as two individual banks of 20 modules operating in parallel from a common surge tank. Each bank of 20 modules is further divided into two stages of 10 modules operating in series.

Feed flows tangentially across, over, and around the hollow fibre membranes at a sufficient cross-flow velocity to keep the solids in suspension, thus minimizing deposition and fouling. A small fraction (about 10%) of the total feed flow passes through the membrane into the centre of the tube or lumen and exits as a filtrate. The unfiltered portion of the feed is recycled to the system surge tank. The inlet feed pressure to the first stage is normally 300 kPa. The differential pressure across each stage is normally 40–50 kPa at a cross-flow rate of 245–285 L/min. At a filtrate production rate of 25 L/min per bank, the TMP drop, which is the average feed pressure minus the filtrate pressure, is in the range of 20–100 kPa.

To maintain productivity and performance of the membranes at the design values, the membranes are periodically backwashed by gas. Air at high pressure (e.g. 700 kPa) is periodically introduced into the filtrate side of the system and instantaneously expanded through the hollow fibre into the feed, thereby releasing accumulated solids from the membrane surface. Feedwater is then used to flush the remaining solids from the system. The duration of the backwash sequence is approximately 90 seconds. Backwash is started automatically by a panel mounted timer, or manually by a push button. The system is chemically cleaned periodically, usually with an alkaline detergent. Chemical cleaning is required when the TMP exceeds 100 kPa at normal filtrate production rates of 15–25 L/min or if the cross-flow pressure drop across the feed channel exceeds 80 kPa.

In the early 1990s it was demonstrated on this system that microfiltration can successfully compete with ultrafiltration as long as the correct selection of reagents for the sedimentation of toxic impurities (including radionuclides) from the radioactive groundwaters and soil leachate is ensured. Based on the research work, a process flow diagram of the application of microfiltration to treat groundwaters and contaminated soils is given in Fig. 47.

During the 7-month pilot plant demonstration in 1991, about 120 m^3 of radioactive groundwaters contaminated with ^{90}Sr were cleaned. The concentration of ^{90}Sr was reduced from 1700–3900 Bq/L to 2 Bq/L. These concentrations were lower by a factor of 5 than the Canadian drinking water standards for ^{90}Sr. Since 1991 the groundwater treatment system has processed over 20 000 m^3.

In another test of the microfiltration installation, with pH adjustment of the treated solution the following retention factors of radionuclides in radioactive groundwaters were reached:

— Up to 70% for α radionuclides;
— Up to 45% for β/γ radionuclides;
— Up to 98% for Fe (e.g. from 50 to 1 mg/L).

It must be noted that up to 60% of the β radioactivity in the permeate was from ^{137}Cs [58, 92].

Appendix II

OTHER MEMBRANE SEPARATION METHODS

This appendix provides information on membrane separation methods other than those utilizing pressure as their process driving force. The process driving forces in the methods described below are based on an electrical potential gradient, temperature gradient or concentration gradient. In some cases the process driving force may be a combination of gradients. It should be noted, however, that the processes described here do not cover all existing membrane separation methods.

Some of the processes described have been used in laboratory or pilot scale experiments and are in development. Other processes have been used in non-radioactive applications but may have potential for the treatment of radioactive waste liquids. Another group has been used for the treatment of radioactive liquids. In this group the process has either been used far less than pressure driven membrane methods (and would require further significant development to become truly practical or a method of choice) or a process has been used to treat a specific radioactive liquid rather than LRWs in general.

MEMBRANE TYPES

The separation processes addressed in this appendix usually use different types of membrane than those used in pressure driven processes. This specifically applies to processes utilizing electrical potential gradient as the process driving force, which use ion exchange type membranes.

Ion exchange (ion selective) membranes

Ion exchange (ion selective) membranes allow the selective transport through the membrane of ions or molecules carrying a certain electric charge. The properties of ion exchange membranes are closely related to those of ion exchange resins but the purpose of these membranes, when used in processes driven by electrical potential gradient, is not the exchange of ions but rather the controlled and selective transport of ions through the membrane.

An ion exchange membrane is a foil or a plate made of an ion exchange substance, which is usually a synthetic resin or a macromolecular substance, containing firmly bound (fixed) functional groups with a charge that dissociates when in contact with water or ions. These ion exchangers have the characteristics of a polyelectrolyte with ionized groups bound to the polymeric structure of the membrane.

The charge of fixed functional groups in the membrane must be compensated by an equivalent number of oppositely charged ions. They are not fixed by means of covalent bonds and can move freely through the polymeric network until an equilibrium of charges is reached. These mobile ions are called 'counter-ions' and the membrane is selectively permeable for them.

Irregular distribution of bound functional groups in a polymeric skeleton of the membrane causes irregularities in the uniformity of spatial charge. These irregularities allow a passage of 'co-ions', i.e. ions with a charge identical to that of functional groups in the membrane.

From the perspective of the physical structure of the membrane, these polymeric ion exchange membranes are heterogeneous and their structure is characterized by ion exchange materials dispersed in an inert polymeric carrier. This offers a broad scope of possible production technologies. An important factor in the attainment of high efficiency of the membranes is the uniform distribution of the ion exchange materials in the inert binder. An n ion exchange membrane can be represented in a simple way by a homogeneous model, as shown in Fig. 48.

Three basic types of ion exchange membrane can be distinguished relative to the nature of the fixed functional groups:

(1) Cation exchange membranes (CMs) containing firmly bonded acid anionic groups such as $–SO_3^-$, $–COO^-$, $–PO_3^{2-}$, $–AsO_3^{2-}$, etc., that allow passage of positively charged ions only, since passage of negatively charged ions is considerably restricted.
(2) Anion exchange membranes (AMs) containing fixed basic cationic groups based on quaternary ammonium groups $–NR^{3+}$ (where R is the hydrogen or alkyl group) that allow free passage for negatively charged ions only, since passage of positively charged ions is highly restricted.
(3) Bipolar membranes (BMs) that are a combination of CMs and AMs, thus containing both functional groups. Bipolar membranes are composed of two layers of membrane materials, each containing one type of functional group. The membrane layers are bound together using a suitable 2–5 μm thick 'intermediate zone' between the layers of. The BMs are a source of H^+ and OH^- ions that are produced in the intermediate zone by water dissociation.

The majority of ion exchange membranes have low selectivity for ions of one specific (i.e. positive, or negative) charge. To increase the membrane's ion selectivity, the thin (0.1–1 μm) layer of a membrane surface can be modified to

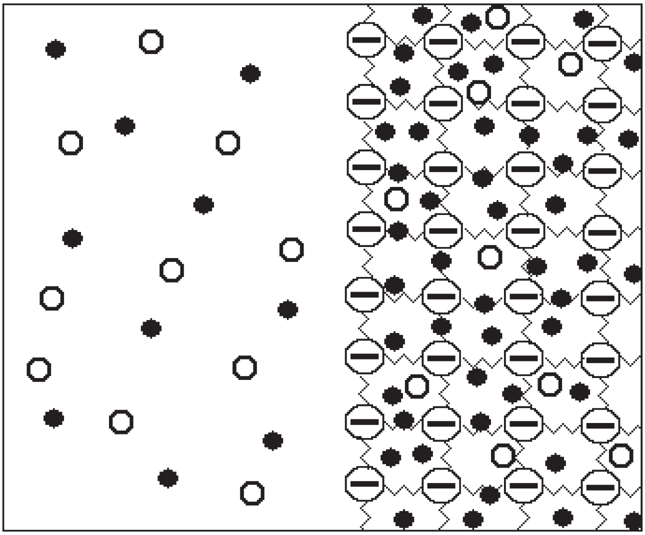

FIG. 48. Homogeneous ion exchange charged membrane immersed in a solution of binary electrolyte (⊖: fixed charges (in this case negatively charged), ●: cations, ○: anions).

act as an energy barrier, which enhances passage of similarly charged counter-ions [101]. Modification of the membrane surface may include etching, deposition of a polymeric ion exchange layer with an opposite electric charge, and various other methods.

Ion exchange membranes with hydrophobic structure

Some processes, such as membrane electrolysis, utilize ion exchange membranes with hydrophobic structures. The water content in such membranes does not exceed 3–4 molecules of water for each ion exchange group. Such membranes have strong electrical resistance, but can separate solutions containing various water dissociation products (H_3O^+ and OH^-). An example of such membranes is the NAFION type of membrane [102].

Inorganic ion exchange membranes

While the use of polymeric ion exchange membranes is subject to similar restrictions to those for the polymeric pressure driven membranes, there have been efforts by the industry to develop inorganic ion exchange membranes having high ionic selectivity.

References [103, 104] describe a method of inorganic ion exchange membrane preparation by precipitation of barium phosphosilicate on a porous ceramic substrate made of alumosilicate materials with average pore sizes ranging from 0.3 to 2.5 μm. The tests have shown that these membranes can withstand radiation exposures of 7.5×10^6 Gy without deterioration of their frame. This method of membrane preparation and the verification of their performance are still in the early stages of development.

Development and fabrication of tubular membranes based on the composite material NASICON has been reported from the USA [105, 106]. The membranes are characterized by a high diffusion rate of Na^+ ions in the matrix of the material, but other single charged cations have diffusion coefficients orders of magnitude lower. NASICON ($Na_3Zr_2Si_2PO_{12}$) is also claimed to have high radiation resistance. The specific ion transport properties of NASICON are assumed to permit the following potential radioactive applications:

(a) Regeneration of ion exchange resins;
(b) Regulation of pH and an increase of sodium removal from radioactive solutions before extraction of ^{137}Cs;
(c) Extraction of sodium from high level radioactive sludges;
(d) Extraction of sodium from acidic LRWs.

Liquid organic membranes

There are three basic types of liquid organic membrane, as shown in Fig. 49:

(1) Volumetric (or ‘bulk’) liquid membranes;
(2) Membrane emulsions;
(3) SLMs.

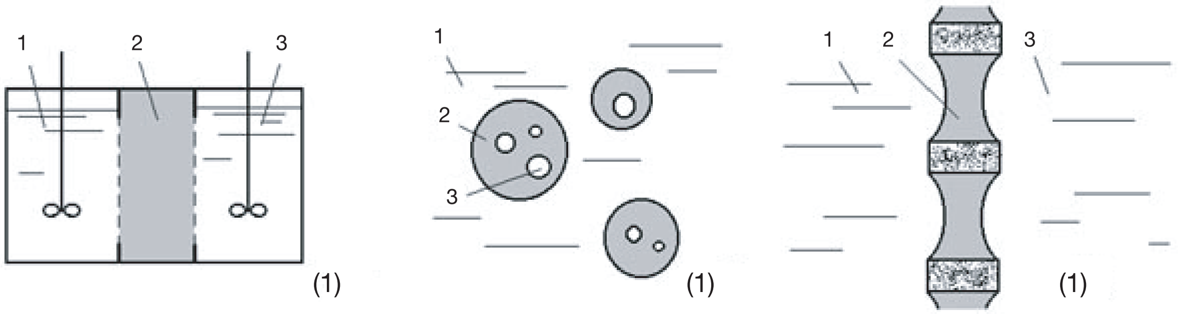

FIG. 49. *Main types of liquid organic membrane: (1) volumetric liquid membranes, (2) membrane emulsions, (3) SLMs (1: treated water solution, 2: liquid membrane, 3: receiving water solution).*

ELECTRICAL POTENTIAL (ΔE) DRIVEN PROCESSES

Some membrane processes use an electric field as the process driving force. These processes separate ions from solution by transferring ions through membranes under the influence of an electric field differential. They differ from pressure driven processes in that the ionic species are transported through the membrane rather than the solvent. The processes invariably use ion exchange membranes.

Three main processes in this category have been tested or utilized on a limited scale for processing LRWs:

(1) Electrodialysis;
(2) Electro-osmotic concentration;
(3) Membrane electrolysis.

These may be complemented in the future by such processes as electrofiltration, electrosorption, electrochemical ion exchange and electro-osmofiltration. General information on processes utilizing electrical potential gradient (ΔE) as a driving process force can be found in Refs [1, 38, 107].

Electrodialysis

The electrodialysis process

Electrodialysis is a well established membrane technology that has been used widely for the desalination of brackish water. It is also used to separate monovalent ions from multivalent ions.

Electrodialysis systems are generally stacks of multiple compartments placed between two electrodes, separated by alternating cation and anion permeable membranes. The process feedwater flows through all the compartments (channels are available for water flow on either side of each membrane). A direct current electrical charge is applied to the electrodes. Positively charged ions are drawn through the cation permeable membranes to the cathode, whereas the negatively charged ions are drawn through the anode permeable membranes to the anode. The ions migrate to the appropriate electrode until a membrane that is permeable only to the opposite charge stops them. Under the influence of the electrical field, every other flow channel becomes ion depleted and the adjacent channels become ion enriched. Both positive and negative ions are concentrated in the ion enriched compartments [33]. The principle of ion transport in electrodialysis is shown in Fig. 50 [108].

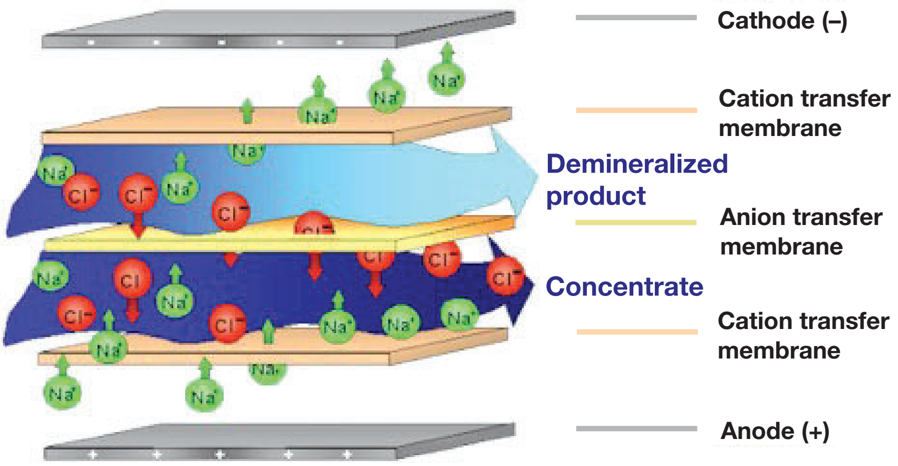

FIG. 50. Principle of electrodialysis.

To reduce membrane fouling, most new electrodialysis systems use reversible electrodialysis. By reversing the polarity in the cells, ionic flow in the concentrating and depleting cells is reversed. Fouling, precipitates and surface films tend to either re-dissolve or are physically dislodged. Reversible electrodialysis is possible by using BMs that can operate in either anion or cation selective modes.

Electrodialysis is predominantly used in a plate and frame type of processing equipment. Some electrodialysers also utilize tubular membranes [38, 109]. Both arrangements exhibit low specific membrane surfaces (e.g. less than 300 m^2/m^3). Patents on the use of electrodialysis for cleaning LRWs are described in Refs [110–115].

Advantages and disadvantages of electrodialysis

The advantages of electrodialysis include the following [33]:

(a) Electrodialysis cells can operate at nominal pressures and temperatures;
(b) The ion enriched stream can be concentrated to salt levels of 20% or more, which is higher than the level achievable by other membrane treatment processes;
(c) With proper feedwater pretreatment and regular cleaning, the membranes exhibit reasonable useful lifetimes.

Electrodialysis also has the following disadvantages:

1. The electrolysis products which evolve on the electrodes, i.e. water, hydrogen and oxygen, can form an explosive admixture;
2. Electrodialysis does not remove uncharged impurities such as suspensions and emulsions, hydrolysing cation forms, molecular impurities, neutrally charged complexes and the majority of organic compounds from treated solutions;
3. Ion exchange membranes can be 'poisoned' with multiple charged ions (i.e. iron ions) and organic ions (including surfactants), which are frequently present in treated radioactive wastes;
4. An overflow of electric current can cause the formation of precipitates of hydroxides, carbonates and other compounds (in some cases the crystalline sludge is immediately formed in the membrane body);
5. Concentration polarization of ion exchange membranes frequently invokes precipitation of slightly soluble compounds in the concentrate pathways of the equipment;
6. Transport of significant quantities of ions through a membrane (for example, in desalination of high salinity liquids) results in excessive power consumption;
7. Suspended solids or high organic levels can clog or foul the membranes;
8. Oxidizing materials and ferrous or manganous ion concentrations greater than 0.3 ppm (0.3 mg/L) can damage the membrane;
9. At alkaline pH values, membrane life may be reduced;
10. Calcium concentrations above 400 ppm (400 mg/L) can cause precipitation of calcium sulphate scale.

Electrodialysis utilization

Electrodialysis is most suitable for acidic streams containing a single principal metal ion, but can also be used for treating alkaline feedwaters. Electrodialysis is used in a number of industries and applications, including salt removal from brine and demineralization of brackish waters. New applications have been developed for electrodialysis in the food and pharmaceutical industry because the relatively gentle separation does not damage or thermally decompose the products.

Electrodialysis has been used to a limited extent on waste streams in the nuclear industry. New developments in membrane materials and production technologies are increasing the potential applications of electrodialysis, but large scale application for the treatment of radioactive wastes has not been achieved. The following is a brief overview of some applications of electrodialysis in the nuclear industry:

(a) An experimental electrodialysis facility [116] was started in 1964 at a Moscow plant for LRW treatment (Fig. 50). It had a productivity of up to 100 m^3/d of treated LRW. In the first stage of the electrodialyser, the DF for LRW was 2–4 and for beta nuclides the DF was 2–5. After the second stage of the electrodialyser, the DF for radioactive wastes was 20–40, and for beta nuclides 100–30 000. The study indicated that the process scheme described was 70% more cost effective than that provided by ion exchange. Further development in 1987 of the scheme depicted in Fig. 51 is shown in Fig. 52. [117, 118]. The main difference is the use of dead end

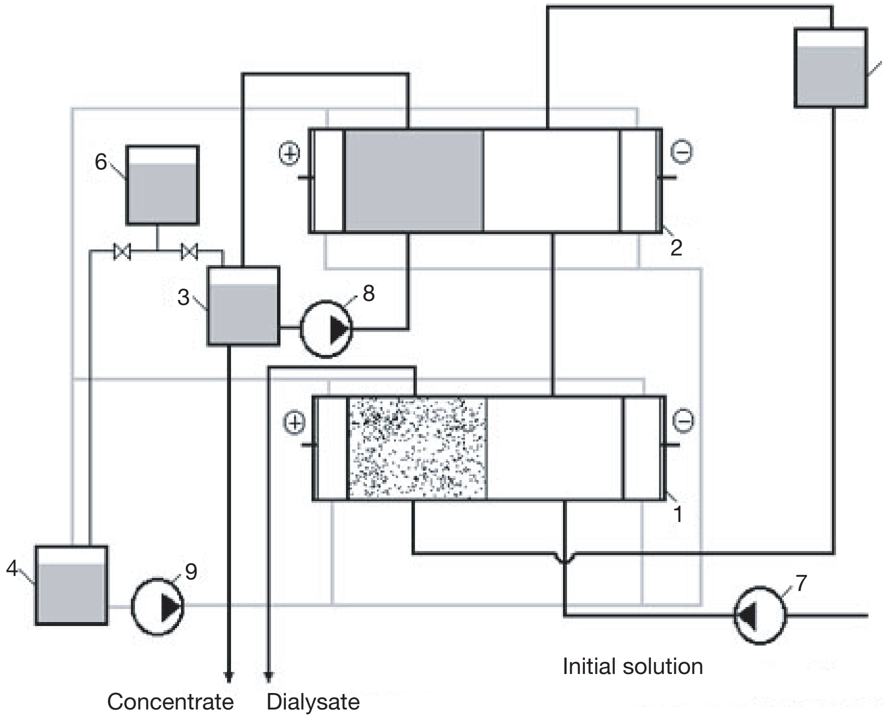

FIG. 51. Flow diagram of a radioactive water cleaning system in an experimental industrial electrodialysis application: (1) second stage electrodialyser, (2) first stage electrodialyser, (3) tank of concentrate, (4) tank of electrode washing solution, (5) tank for separation of gases, (6) tank with 20% HNO_3, (7–9) pumps.

flow concentrate chambers for further concentrating brines produced in the first electrodialysis stage.

(b) Test data from 1986 for a pilot electrodialysis facility [119] that processed low level radioactive acidic waters showed that electrodialysis can successfully remove ^{90}Sr, ^{137}Cs, ^{129}I, ^{106}Ru and Hg. For radionuclides the DF equalled 10.

(c) Liquid mercury was used as a cathode in an electrodialysis unit used in Armenia [120] in 1987, and an electrodialysis apparatus was installed at the Armenian nuclear power plant.

(d) Electrodialysis was examined for treatment of radioactive wastes between 1979 and 1987 in Japan [121–123].

(e) Laboratory research [121, 124] has demonstrated that electrodialysis is capable of removing radionuclides, producing a clean water product.

(f) An experimental industrial electrodialysis facility (on a scale of 1:100 to the designed plant) was tested on low level LRW in 1984 [125]. The concentrated liquid waste after treatment contained ^{106}Ru, ^{51}Cr, ^{131}I, ^{137}Cs and other toxic non-radioactive components up to 10% of the initial volume. The production rate of the installation was 18 L/h.

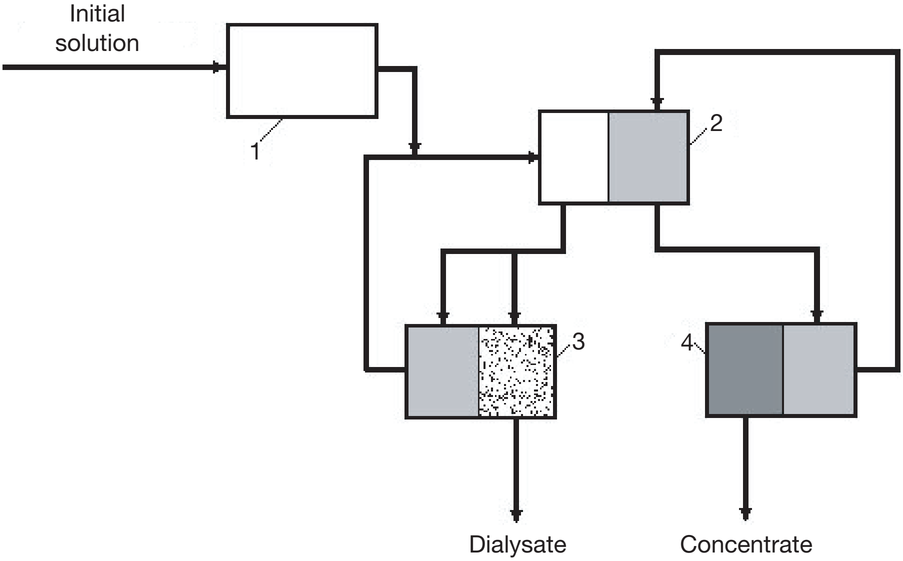

FIG. 52. Block diagram of an electrodialysis installation for cleaning radioactive liquids: (1) feedwater pretreatment, (2) first stage electrodialyser, (3) second stage electrodialyser, (4) electrodialyser concentrator.

(g) A facility for cleaning LRW generated in the operation of Russian nuclear powered ice-breakers and submarines has been described in Refs [126, 127]. The facility, implemented in 1994, has the capability to process up to 5000 m^3/a of LRW. This stationary system includes a cascade of seven water cleaning modules, one of which is electrodialysis and includes four regular electrodialysers and two electrodialyser concentrators with dead end flow concentrate chambers. The scheme of the electrolysis modules is a simplified variant of the flow diagram in Fig. 51.

(h) Reference [128] describes another variant of an electrolysis based system for treatment of LRW. The results of experimental tests with this 100 L/h system are described. A DF of 140 was reached in this electrodialysis application.

(i) Electrodialysis has been installed in an existing membrane treatment facility at Los Alamos National Laboratory, USA, in order to reduce the volume of reverse osmosis concentrate prior to evaporation [56]. Approximately 24 000 L/d of reverse osmosis concentrate are processed in an electrodialysis reversal unit to reduce the feed volume to the evaporator to 4800 L/d. The product stream is recycled to the existing reverse osmosis plant.

Electrodialysis using liquid organic membranes

This method does not differ fundamentally from conventional electrodialysis. The main difference is that instead of a firm polymeric membrane, either SLMs [129] or ‘bulk’ liquid membranes [130] are used. The use of an electric field to intensify ionic transport through liquid membranes was described in the 1970s [131, 132] However, difficulties have been encountered in the use of liquid organic membranes that have prevented their utilization in industrial applications.

Membrane electrolysis

Membrane electrolysis utilizes ion exchange membranes with hydrophobic structures. Membrane electrolysis is carried out in an electrolyser, which has electrodes separated by a membrane. A membrane electrolyser may be of a two chamber design (i.e. electrode chambers are separated by one membrane) or a three chamber design (i.e. each electrode chamber is separated by a membrane, while the treated solution occupies the inter-membrane space in the central chamber).

A three chamber membrane electrolyser has been used in nuclear fuel fabrication activities for obtaining HNO_3 and NH_4OH from a NH_4NO_3 solution

[133]. In another application [134], a method of regenerating acid electrolyte used for decontamination of equipment surfaces has been considered. In this application, the membrane electrolyser was divided into two chambers by an AM. The treated solution was introduced into the cathodic chamber. While anions pass into the anodic chamber under the influence of electric current, where an accumulation of acid occurs the cations, including radionuclides, precipitate on the cathode.

Electrosorption, electrofiltration and electrochemical ion exchange

In electrosorption [38], simultaneous use of sorbents and electric current was tried to increase efficiency of the electrodialyser chambers by introducing ion exchange materials into them [135]. However, the construction of such electrodialysers using ion exchange fillers became complicated and constrained broader utilization of this developing technology. However, efforts continued through the 1990s [136, 137]. A number of variants on the basic process have been developed, defined as ‘contact electrosorption’, ‘non-contact electrosorption’, ‘true electrosorption’, etc. [138]. Examples of these applications, including processes such as electrosorption, electrofiltration and electrochemical ion exchange, can be found in Refs [62, 139–143].

CONCENTRATION GRADIENT (ΔC) DRIVEN PROCESSES

Some membrane processes operate solely on the basis of a concentrated driving force between a feed and a receiving solution. Solutes can be transferred in both directions, depending on the concentration difference. The most common of these processes is dialysis, which has been developed as an artificial kidney replacement. Several other processes (e.g. membrane solvent extraction (MSX), ELMs) use concentration and other liquid properties together as the driving force for separation. Some of these processes are described in this appendix.

Dialysis

Dialysis is a rate governed membrane process in which a microsolute is driven across a membrane by means of a concentration gradient. The membrane separates solutes by size, and the process relies solely on diffusion. Both phases on each side of the membrane consist of aqueous solutions. Dialysis has not been used in the nuclear industry, although other concentration gradient processes that are descended from dialysis have been tested experimentally.

Membrane solvent extraction

Membrane solvent extraction relies on concentration differences and different solubilities of species in an organic extractant. It consists of a microporous membrane separating an organic and an aqueous phase, and is essentially the same process as conventional solvent extraction except that the interfacial area is known in MSX.

Recently developed MSX processes using microporous hollow fibres are of particular interest because of their versatility and the fact that they overcome problems encountered in conventional liquid–liquid extraction [144]. Non-dispersive membrane solvent extraction (NDMSX) is simply liquid–liquid extraction in a hollow fibre contactor which involves the use of a standard commercial hollow fibre module to contact an aqueous phase without dispersion, which minimizes the possibility of forming emulsion/third phase or crud formation with extractant; a second module would be used to strip the solute from the loaded organic phase.

The hollow fibre modules may also be connected in series or in parallel and the length and diameters of the fibres and modules can be varied to provide the required interfacial area. Such membrane processes not only remove the required components from the streams but can also concentrate the species on the product side simultaneously for further processing. Compared to conventional systems, membrane contactors provide various advantages such as non-dispersion of the phases in contact; independently variable flow rates without flooding limitations; lack of phase density difference limitations; lack of phase separation requirements; higher surface area per unit volume values, which may be up to 10^4 m^2/m^3; and direct scale-up due to a modular design. These advantages may be offset, however, by an increased mass transfer resistance because of the need for diffusion through the membrane pores. However, recent results indicate that with careful design this resistance can be minimized.

In another study [145] a hollow fibre contactor was fabricated and experiments were conducted for extraction of macro amounts of uranium from reprocessing waste using a TBP/n-dodecane system. In an integrated membrane system, U(VI) (116 g/L) was extracted into an organic phase and subsequently re-extracted using 0.05M HNO_3. Some of the important results obtained established the potential for recovering high concentrations of uranium from low concentration feed stock.

Nuclear fuel reprocessing plants generating large amounts of radioactive wastes, such as condensate waste, could be treated with the NDMSX technique under suitable chemical conditions [146]. Preliminary tests were conducted [147] with a microporous hollow-filter membrane module for the liquid–liquid extraction of actinides to evaluate the feasibility of recovering actinides or processing radioactive wastes. This work involved analysis of the potential for using these modules for process scale metal separation such as radioactive waste stream cleaning and environmental remediation. Similarly, Rogers and Lang [148] predicted the performance of shallow filter membrane contactor modules for extracting compounds with interfacial chemical reactions.

Supported liquid membrane

In a SLM an organic liquid is immobilized in the pores of a microporous membrane. Feed solution is contacted on one side of the membrane, extracted into the trapped organic phase, and stripped on the other side of the membrane by a strip solution. As an alternative to conventional solvent extraction or MSX the SLM has the advantage of very low solvent inventories. However, the membranes often suffer from poor stability. This has led to the development of the hollow fibre contained liquid membrane, which consists of a bundle of hollow fibres immersed in a stationary organic (contained liquid membrane). Feed and strip solution flow through the lumen of adjacent fibres and liquid separation is achieved.

Research in this field is continuing with the use of flat supported membranes and with membranes based on thin, hydrophobic, porous, hollow fibres. It has been reported that most of the research is being carried out in:

(a) The USA, on recovery of Am, Pu, lanthanide and I-II group metals;
(b) South Africa, on isolation of ^{134,137}Cs and ^{90}Sr from storage pool water;
(c) France, on consecutive recovery of the most radiotoxic components (^{134,137}Cs, ^{90}Sr, actinides).

The processes of uranium compounds transported through SLMs have also been studied on a smaller scale in Japan, Pakistan, South Africa, Taiwan and the Republic of Korea. In France, research on membrane extraction with SLMs is a part of the French radioactive waste management programme ACTINEX [149].

Industrial scale modules were used at the Hanford site in the USA to test SLM separation of uranium (VI) from actual contaminated groundwater [150]. The uranium concentration was reduced by a factor of approximately 3500. The apparatus for membrane extraction consisted of polypropylene microporous fibres with a total surface of 3.6 m^2 [151]. Trilauryl amine dissolved in N-dodecane was used as a liquid membrane. Another example of the use of an apparatus with hollow fibre SLMs is given in Ref. [152], but the results are irrelevant from the viewpoint of radionuclide extraction. Further research in this field has been reported in Refs [153–161].

TEMPERATURE GRADIENT DRIVEN PROCESSES

Temperature can be used as a driving force for membrane separation of the components of a liquid. Membrane distillation and pervaporation are the most common of these processes.

Membrane distillation is a thermally driven evaporation process for separating volatile solvent (or solvents) from solution on one side of a non-wetted microporous membrane. It is a method for desalination and removal of a broad spectrum of impurities from water [162], utilizing low temperature heat fluxes. In membrane distillation, the 'hot' feed solution (30–70°C) is introduced onto one side of a hydrophobic thin porous membrane, and a colder 'cool' distillate onto the other side of the membrane. The membrane is hydrophobic, with a small pore size (e.g. less than 1 μm), and so the liquid phase does not permeate through the membrane. However, the vapour phase from the 'hot' solution permeates into the membrane pores, diffuses through an air layer in the pore and condenses on the cool side of the membrane. The process is non-isothermal and is applied to hydrophobic porous membranes developed for concentrations of water solutions or for the production of pure water [163–169]. As the process is characterized by high retention of non-volatile solutes, large DFs are expected in the separation of radionuclides that are present in liquid radioactive effluents in ionic form. Laboratory tests have shown that membrane distillation can be used to concentrate radioactive solutions [52, 170].

The feasibility of removing ^{137}Cs, ^{90}Sr and ^{90}Y from water by membrane distillation and their solution concentration limits have been studied and reported [167]. The average pore size of the membrane was between 0.15 and 0.65 μm. Decontamination factors for various radionuclides were measured as follows: 90–11 000 for ^{137}Cs, 140–15 000 for ^{90}Sr and 180–18 000 for ^{90}Y. Special attention was given to the examination of surfactant influence on membrane distillation, which can result in hydrophilization of a membrane surface and loss of its water repellent properties [171–174].

Similar data were obtained from testing an apparatus for membrane distillation with flat membranes made of polytetrafluoroethylene on hot condensate from a nuclear power plant. The tests demonstrated highly efficient membrane distillation compared to traditional evaporation technology for radioisotope removal [174].

In pervaporation, liquid is maintained at atmospheric pressure on the feed or upstream side of the membrane while the permeate is removed as a vapour because of a low vapour pressure existing on the permeate or downstream side. This low (partial) vapour pressure can be achieved by employing a carrier gas or using a vacuum pump. The (partial) downstream pressure must be lower than the saturation pressure, as a minimum. In its simplest form pervaporation separates one component from another by the difference in the permeation (diffusion) rate of one component through a membrane compared to another. Pervaporation is most often used for the separation of such volatile components as hexane, toluene and trichloroethylene from water.

PROCESSES WITH COMBINED DRIVING FORCES

Various membrane processes exist that combine several driving forces to achieve separation. These will continue to be developed in the future. A typical process in this category that is worth mentioning is electro-osmofiltration (P + E). This is a process of directional separation of ions in the reverse osmosis condition under the influence of electric current running through a reverse

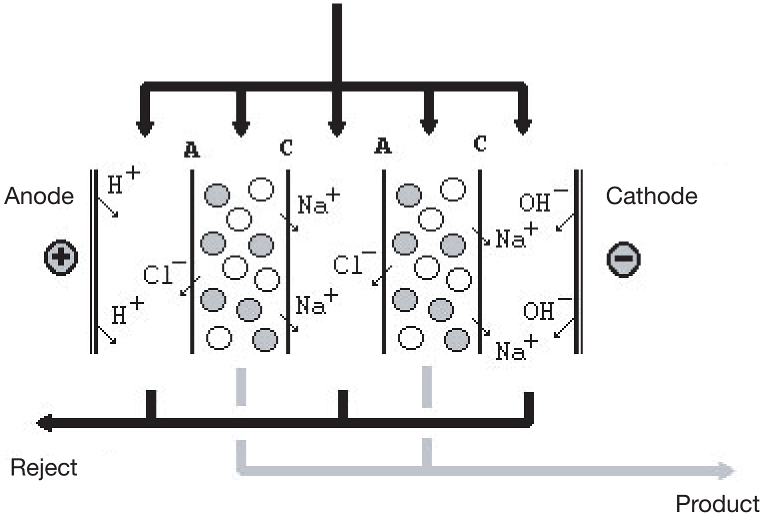

FIG. 53. The ELIX technology membrane apparatus: (A) reverse osmosis AM, (C) reverse osmosis cation exchange membrane.

osmosis membrane [8]. It has been shown in laboratory experiments that by passing a constant electric current through reverse osmosis membranes during contact electro-osmofiltration, the DF could be increased 3–5 times [175].

A commercial vendor in the USA [176] speaks of the availability of reverse osmosis ELIX^{TM} technology which combines electro-osmofiltration and electrodialysis by filling the desalinating chambers with granulated ion exchange material. While a detailed description of the technology is not available, the operating principle of the apparatus is shown in Fig. 53.

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