Outcomes of membrane research: Impacts on the Australian and international water industry

Impact study - Membranes

Water for the wellbeing of all Australians
Outcomes of Membrane Research: Impacts on the Australian and International Water Industry

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1. INTRODUCTION

A healthy and prosperous membrane technology industry has developed in response to the needs of the water industry to supply greater quantities of water and to use poor quality raw water sources. This growth in the membrane technology industry has been underpinned by research that has progressively improved membrane treatment processes, making them more effective and affordable, thus allowing the water industry to meet increased demand for water.

The rapid growth of membrane technology in the past 20 years is testament to the benefit of past research efforts. Membrane processes are now more effective and less costly than in previous years, and implementation of the current technology is increasing. What need is there, then, for future funding of research into membrane technology? What are their current shortcomings and how much better can the technology become? What are the expected returns on investment for such funding? These are difficult questions to answer because they rely on a forecast of research findings and human ingenuity. At best, we can make an informed prediction. This report supplies the information for an informed judgment regarding future membrane research investments.

This report aims to provide a brief history of membrane development to demonstrate the benefits and impact of past membrane research for the water industry, draw out specific case studies that highlight the benefits of membrane research, and finally point to future directions in membrane research, thereby putting into context the Australian R&D efforts in the area of membrane research, particularly through the CRC for Water Quality and Treatment and WQRA (Water Quality Research Australia) / WaterRA (Water Research Australia) to assess the benefits of this research portfolio.

Figure 1: Research themes and major contributors to the development of today’s’ economically viable membrane technologies
2. A BRIEF HISTORY OF MEMBRANE DEVELOPMENT

Development of now widely implemented membrane based technologies provides a significant research and development success story with measureable benefits. Membrane technology is now a mature, economically competitive technology with widespread application. The water industry uses membrane technology to improve the quality of water for use, reuse, or discharge to the environment. This improvement is achieved by removal of particles, biological contaminants such as protozoans, bacteria or viruses, or by the removal of dissolved contaminants such as salt. The advantages of modern membrane technology include its modular design, the high quality of the product water and the relatively small environmental footprint [Fane, 2011].

The six major contributors to the development of today’s economically viable and mature membrane technology are shown in Figure 1. These can be classified as largely social in nature (in orange) or largely scientific in nature (in blue). The social contributing factors - increasing water demand, the broadening of the water resource management regime brought about by the use of new water sources to help meet the greater water demand, and the increasingly stringent regulatory environments - have been drivers for investment in membrane technology. The scientific contributing factors - improvements in membrane performance, process design, and membrane operations - have improved the effectiveness and economic viability of membrane processes. The rapid growth in low-pressure membrane water treatment (UF and MF) since the early 1990’s, for example, can largely be attributed to changes in regulatory requirements, process design, and energy requirement. The combination of tighter treatment standards in the US, prompted by a serious cryptosporidium outbreak in 1993, a reduction in membrane plant costs and the adoption of dead-end mode with backwash operation, resulting in lower energy demand [Fane, 2011] have greatly contributed to the rapid growth in low pressure membrane water treatment.

The research themes that have underpinned scientific contributing factors are also shown in Figure 1 (in boxes). Much of the early work on membranes performance was focused on rejection and permeability, and the quest to achieve high rejection without loss of permeability, or to improve permeability without loss of rejection continues. These research themes were joined by other themes such as resistance to chemicals (mainly chlorine) and resistance to fouling. Research themes related to process design include inorganic fouling mitigation for high recovery RO operation - scalant removal or operation under conditions that do not favour scale formation – and the continued developments in membrane module design. The use of dead end mode operation with backwash for low pressure membrane processes has led to lower energy requirement, and the more recent development of energy recovery technology has reduced the energy required for desalination. Stimulated by forecasts of water shortages and increasingly stringent regulatory environments, research within these areas has progressively improved membrane performance, process design and energy use, improving commercial operations.

2.1 Ion exchange membranes

Early membrane studies were performed using natural materials such as animal bladders. Nollet in 1752, for example, found that a pig’s bladder allowed preferential passage of ethanol from ethanol-water mixtures. These early studies, however, did not translate to commercial applications. The first commercial use of membranes was with synthetic ion exchange membranes in electrodialysis and began with the development of the first reliable ion-exchange membranes that had both good electrolyte conductivity and ion-permselectivity [Juda, 1953]. Electrodialysis was first commercially exploited for desalination of brackish water by Ionics Inc. This membrane process was attractive due to its relatively small footprint arising from compact membrane stacking, and because of its mode of operation, electrodialysis reversal, which provided periodic self-cleaning of the membrane stack allowing long-term continuous operation at high concentrations of scaling materials without mechanical cleaning of the stack [Katz, 1979]. More recently, in the early 1980’s, a new area for the application of electrodialysis was opened up with the development of bipolar ion selective membranes for the recovery of acids and bases from the corresponding salt [Nagasubramanian, 1977]. Such systems are able to separate monovalent ions from divalent ions. While such processes hold promise in applications such as lowering the Sodium Adsorption Ratio (SAR) of recycled water, they have not been used within the water industry because they are currently economically uncompetitive. Changes arising from water availability, however, may change the economics for such processes, making them of greater interest.
More recently, Strathmann (2010) has identified the limitations and key problems in ED, highlighting the need for membranes with higher permselectivity, lower electrical resistance, and better chemical and thermal stability at lower costs. According to Strathmann, electrodialysis currently has an economic advantage over reverse osmosis for brackish water desalination in a certain range of feed water salt composition. It is mainly used in small to medium size plants with capacities of less than a few 100 m$^3$.d$^{-1}$ to more than 20,000 m$^3$.d$^{-1}$ with a brackish water salinity of 1000 to 5000 mg.L$^{-1}$ total dissolved solids. Reverse osmosis is considered to have an economic advantage for the desalination of water with total dissolved salts in excess of 10,000 mg.L$^{-1}$. Other advantages of electrodialysis are high water recovery rates, long useful life of membranes, operation at elevated temperatures up to 50 °C, and less membrane fouling or scaling due to process reversal. The potential disadvantages of electrodialysis are that neutral toxic components such as viruses or bacteria are not removed from a feed stream, but this property is advantageous for treatment of high silica containing waters as silica is not removed and does not scale the membranes.

A cross sectional SEM image of a modern commercial ion exchange membrane (Neosepta, Tokuyama Co-Astom of Japan) is shown in Figure 2. Key features shown are the polymer cloth support and the active layer consisting of functionalised polystyrene that has been cross linked with divinyl benzene (DVB) and polyvinyl chloride (PVC).

![Figure 2: SEM micrograph of a cross-section of a Neosepta electrodialysis membrane. From Ghalloussi, 2013](image)

The main manufacturers of ion exchange membranes are Asahi Chemical Industry Co. of Japan (Aciplex brand), Asahi Glass Col. Ltd Japan (Selecion brand), DuPont Co.of USA (Nafion brand), FuMA-Tech GmbH of Germany (Fumasep brand), GE Water & Process of USA (AR, CR, brands), LanXess Sybron Chemicals of Germany (Ionac brand), MEGA a.s. of Czech Republic (Ralex brand), PCA GmbH of Germany (PC brand), Tianwei Membrane Co. Ltd. of China (TWAED brand) and Tokuyama Co-Astom of Japan (Neosepta brand) [Valero, 2012]
2.2 Reverse osmosis and nanofiltration membranes

The invention of the pressure driven, cellulose acetate RO membrane by Loeb and Sourirajan in 1964 [Loeb, 1964] sparked interest in the technical utilisation of membrane processes on a larger scale as an alternative to thermal desalination of seawater and brackish water to provide drinking water. The membrane developed by Loeb and Sourirajan had an asymmetric structure with a dense skin at the surface which determined the membrane selectivity and flux, and a highly porous substructure which provided mechanical strength and fast mass transport. The permeation rate is inversely proportional to the thickness of the actual barrier layer and thus asymmetric membranes show a much higher permeation rate (water flux) than symmetric (homogeneous) membranes of a comparable thickness [Mulder, 1991]. Soon after the development of asymmetric cellulose acetate membranes, other synthetic polymers such as aromatic polyamides, poly(piperazine-amides) and polysulphone were used as basic material for the preparation of synthetic membranes. These polymers often showed better mechanical strength, chemical stability, and thermal stability than the cellulose esters, but suffered from lower than desired salt rejection [Lee, 2011].

A cross section SEM image of an asymmetric cellulose acetate film prepared at various casting shear rates is shown in Figure 3. These images clearly show the dense outer skin that determines the selectivity and flux, as well as the underlying porous substructure which also determines the flux.

Cellulose acetate remained the dominant material for the preparation of reverse osmosis membranes until the development of the interfacial-polymerised composite membrane [Cadotte, 1977]. These membranes showed significantly higher fluxes, higher rejection, and better chemical and mechanical stability than the cellulose acetate membranes. Steady improvements in performance resulted from the fine tuning of the chemistry of the different layers. Thin film composite membranes are used in RO, NF and some UF applications, and can be manufactured in flat sheet, hollow fibre or tubular configurations. Thin film RO/NF membranes are now the dominant market format for RO/NF membranes because of their energy efficiency advantage compared to other membrane formats, coupled with their high salt rejection performance and range of chemistries possible.

A cross sectional SEM images of a poly(piperazine amide) – polyethersulfone thin film composite membrane and the polyethersulfone support on which the thin film was applied are shown in Figure 4. This thin composite membrane’s solute rejection properties make it suitable for nanofiltration.

Figure 3: Asymmetric cellulose acetate NF membranes produced at different shear rates during casting. Note decrease in large pore diameter with increasing in shear rate (a) to (d). Highest rejection and flux was achieved with membrane (c). From Ismail, 2004
2.3 RO and NF module design

The development of membrane modules followed shortly behind the development of membranes with industrially useful properties. In the early days of RO, modules existed in both flat sheet spiral wound configuration and in hollow fibre configuration. The industrial requirements for high packing density, ease of cleaning, good flow distribution and low cost were met by these modules. The DuPont hollow fibre, had been leading the RO market in the 1980s and early 1990s, but started to lose ground to polyamide spiral wound modules in the 1990s [Johnson, 2009]. The DuPont concept lost its appeal and the business became increasingly unattractive, which led to the exit of DuPont from hollow fine fibre module production. The hollow fibre module continues to be used today in limited applications. The Toyobo Hollsep® RO membrane module uses cellulose triacetate membranes and is able to withstand pressures of 70-80 atmospheres when extracting fresh water from seawater, and has a high water recovery rate of 40-60%, and strong chlorine tolerance, allowing chlorine disinfection which facilitates easy maintenance and biofouling mitigation. Most modern RO membranes, however, are predominantly produced in continuous flat sheets, and they are housed in spiral wound modules of standard sizes, typically 8 inch (203 mm) diameter and 40 inch (1016 mm) long (see Figure 5), which allows interchange between products and replacement. For large scale operations the 16 inch diameter RO elements (and 18 inch elements from Koch) have potential for considerable economies of scale once demand for this format increases [Johnson, 2009]. The Sorek seawater desalination plant in Israel, currently the world’s largest desalination plant, has installed 16” RO elements in a vertical configuration to reduce the plants footprint and to reduce piping costs [Lokiec, 2012]. Over the 30-year period from 1978 to 2008, the spiral wound module design has steadily improved, with a drop in real cost (1/12), an increased life (2.3 times), an improved water production rate (2.5 times), and a reduced salt transmission (1/7) [Birkett, 2007]. The spiral wound module design is now extensively used for RO, NF, and some large-scale UF applications, and this standardisation of format has allowed decreased membrane costs to be achieved via market competition between membrane suppliers.

2.4 High-efficiency energy recovery devices in RO

Energy demand and costs for SWRO have steadily declined, largely due to the introduction of high-efficiency energy recovery devices that recover the pressure energy in the RO concentrate stream (see Figure 6). Turbines were initially used for energy recovery and were replaced by Pelton turbines in the 1980’s, and hydraulic turbocharger devices in the 1990’s. From the 1990s onward, isobaric pressure exchangers have been used [Penate, 2011]. The Dual Work Exchanger Energy Recovery (DWEER) [Flowserv] and ERI Pressure Exchanger Energy Recovery [Energy Recovery] devices are
able to recover >97% of energy in the brine reject streams, so little further improvement of these devices is possible.

**Figure 5:** Spiral wound membrane module. Adapted from Li 2008

**Figure 6:** Integration of energy recovery devices into RO process (Left, from Mirza 2008), and Energy consumption improvements since 1970 (Right, from Lee, 2011)
2.5 **Widespread large scale use of membrane technology in the water industry**

Prior to the early 1990’s, membranes were considered too expensive for the production of a low-cost product such as water, with the possible exception of seawater RO in niche areas. The rapid growth in low-pressure membrane water treatment (UF and MF) since the early 90’s was largely brought about by the combined effect of tighter treatment standards in the US prompted by a serious *cryptosporidium* outbreak in 1993, a reduction in membrane plant costs and the adoption of dead-end mode with backwash operation resulting in lower energy demand [Fane, 2011]. This was brought about by growth in the market (see Figure 7(a)) leading to reduced costs due to economy of scale, and the operational experience and research that led to increase water flux recoveries [Le-Clech, 2006]. The rapid growth of desalination membrane processes (NF and RO) since the early 90’s (Figure 7(b) was largely brought about by the combined effects of a growing world demand for low salt water, lower membrane costs (see Figure 7(d)), higher rejection efficiency membranes (see Figure 7(c)) and lower power requirements due to the use of efficient energy recovery technologies (see Section 2.1). The research that led to today’s high solute rejection and high permeability RO membranes is discussed in Section 3.1. The research that has led to the development of the modern membrane bioreactor is discussed in Section 3.2.

2.6 **Brine management**

A pressing issue that has emerged from the widespread use of membrane technology since the early 90’s is the management of waste streams from membrane processes [Mickley, 2006]. The environmental effects of waste brine disposal for seawater desalination have been the focus of
community resistance to the investment of taxpayer funds into seawater desalination. This issue, however, seems to have been largely resolved by putting in place environmental safeguards that ensure efficient dispersal of the concentrate during its return to the sea such that it does not adversely affect the organisms in the vicinity of the waste brine outlet. For inland desalination processes such as wastewater reclamation or groundwater treatment, however, brine management looms as a major impediment to use of membrane technology to meet the growing demand for water in inland regions. Increasingly stringent environmental safeguards have put pressure on proponents of desalination processes to look for alternatives to disposal as a management option. To this end, a number of research groups (UCLA, UTEP, VU, Desalitech) have a concerted research effort to decrease the volume of waste brine by operating the plants at higher water recoveries [Bond, 2007], thus facilitating the evaporation of the water to obtain a salt product that can be more easily disposed of or utilised. This research involves the removal of certain components from the water that give rise to solid materials, such as calcium carbonate, calcium sulfate or silica, which foul the membranes at high water recoveries [McCool, 2013] (see Figure 8).

![Figure 8: Waste brine volume reduction by removal of scale precursors prior to further RO treatment. From McCool, 2013](image)

### 2.7 Further refinement of membrane properties

The water industry is well positioned to take advantage of current research into membrane chemistry and structure. The development of the thin film composite membrane has opened up an enormous range of possibilities for the production of membranes which have the required flux and structural strength, as well as selectivity and resistance to fouling. For membranes which are ultimately intended for large scale applications, and for which the current membrane formation processes via phase separation have already been optimised at large expense, the existing processes are quite flexible and still offer considerable room for innovative adaptation via easy and efficient post-treatment [Ulbricht, 2006] (see also Section 3.1). There are also a wide range of variations in polymer chemistry that can improve selectivity. It is, for example, possible to design a membrane with an active surface layer with the desired packing of chain segments in the solid state, creating selectivity by interconnected free volume, or to create predetermined regular ‘nanoporous’ morphologies from a range of techniques such as: i) phase separated block or graft copolymers (see Figure 9 left), ii) polymeric hydrogels with controlled mesh structure, iii) micro- or macropore structures created by using templates during membrane synthesis or formation (see Figure 9 right), iv) functional grafted macromolecular layers to facilitate binding to pore walls or to protect the membrane barrier from unwanted interactions, v) give the membrane affinity binding sites by immobilisation through macromolecular crosslinkers or vi) by in-situ synthesis via molecular imprinting of polymers [Ulbricht, 2006]. These are just some of the areas that are currently being investigated by membrane chemists, and some of these may stand up to the rigors of larger scale testing, and industrial implementation to yield better performance at an affordable price for the water industry. Such innovations will come from membrane suppliers, and NanoH2O has released a range of nanocomposite RO membranes. The use of such membranes for new applications or for improved operations will require further verification.
Identifying and quantifying the impacts of membrane research on the Australian water industry

Figure 9: Images showing the level of control that can now be achieved over membrane pore size and shape: The left image shows a nanoporous membranes from phase separated polystyrene-block-poly lactide copolymers with varied copolymer structure. The right image shows a thin-film macroporous membrane prepared via ‘particle-assisted wetting’ of an aqueous sub-phase by a dispersion of nanoparticles in a monomer mixture, followed by in situ crosslinking copolymerisation and subsequent removal of the nanoparticle templates. From Ulbricht, 2006

The future may also hold promise for the water industry from emerging membrane processes such as membrane distillation [Alkhudhiri, 2012] (see Figure 10 right) and forward osmosis [Subramani, 2011] (see Figure 10 left). These technologies have the potential to complement conventional membrane treatment processes for waste brine from RO processes [Perez-Gonzalez, 2012, Martinetti, 2009] and difficult to treat feedwaters. Forward osmosis is also being actively considered for energy recovery using concentration differences associated with brines and fresh water, in a process termed Pressure Retarded Osmosis (PRO). Further developments in membrane chemistry and structure are likely to maximise this potential, and already Modern Water has sold a forward osmosis plant for seawater treatment in the Middle East and companies such as Samsung and Woonjin have developed or purchased forward osmosis membrane businesses.

Figure 10: Laboratory scale study of forward osmosis (left) and direct contact membrane distillation (right) for the treatment of feedwaters with high scale forming potential (such as waste RO brine). From Martinetti, 2009
2.8 Membrane bioreactors

The idea of using membranes in activated sludge treatment was first reported by research conducted at Rensselaer Polytechnic Institute in New York, and at Dorr-Oliver [Radjenovic, 2008], and the first commercially available membrane bioreactors (MBR) were developed by Dorr–Oliver in the late 1960s. In the early period, a major incentive for the use of membranes was to increase the biomass of the mixed liquor to high levels to reduce excess sludge production. The commercial development in North America was pioneered in the mid-1980s by Zenon Environmental Inc. (now part of GE Water & Process Technologies) with a tubular pressurised membrane [Benedek, 2011]. The high solids, however, led to increased fouling and reduced oxygen transfer. In addition, the high cost of membranes required relatively high fluxes that, in turn, required vigorous crossflow and high-energy input to control fouling. As a result, the MBR remained a niche membrane application until the early 1990s, after which, the cost of membranes decreased sufficiently for plants to have large membrane areas and lower specific fluxes, resulting in lower intrinsic fouling.

Other major developments such as the immersion of the membranes directly into the activated sludge tanks [Yamamoto, 1989] and the use of air scouring to control fouling, allowed retrofitting the technology into existing plants and relatively low energy control of fouling. More recently, modified aeration systems have reduced energy requirements and subsequent operating costs. The use of MBR is now becoming widespread in industry and for municipal use. Immersed membranes were developed starting in the early-1990s by Zenon with the ZeeWeed hollow fibre (see Figure 11), and by Kubota Corporation with a flat sheet membrane [Cote, 2012]. Today, there are dozens of suppliers offering products using both immersed technology platforms. Mitsubishi, Zenon, Memcor, Pentair and Kubota are the major membrane manufacturers [Le-Clech, 2005]. Flat sheet membranes are mostly used in small plants (<5,000 m³/d); hollow fibres are used across the entire flow range and dominate for larger plants (>10,000 m³/d). It is estimated that about 75% of the total MBR installed capacity employs hollow fibres [Cote, 2012]. The implementation of MBR has been growing at an average of 12-13% per annum since 2000, slightly higher than the growth in the use of RO (9-10%) [Santos, 2011].

![ZeeWeed ZW500D cassette](image11)

Figure 11: ZeeWeed ZW500D cassette From Cote, 2012.
3. CASE STUDIES THAT HIGHLIGHT THE BENEFITS OF MEMBRANE RESEARCH

Membrane research can broadly be divided into two major areas – research into membrane materials and research into process design. Here, two case studies that illustrate how these two major areas of research have contributed to the success of two different modern membrane treatment processes are presented. The first case study deals with the evolution of modern reverse osmosis membranes and the continuing efforts to achieve higher permeability without loss of salt rejection. The second case study deals with how a decrease in membrane cost and optimisation in process parameters have contributed to the evolution and success of the modern MBR process.

3.1 Evolution of modern TFC RO membranes

The development of modern thin film composite (TFC) RO membranes was recently summarised by Lee et al (2011) as shown in Figure 12.

Figure 12: Development of modern thin film composite membranes. From Lee, 2011

The first cellulose acetate membranes developed in the 1960’s had high salt rejection but low water permeability. Attempts to improve the permeability by having a very thin active layer on top of a microporous support of the same material (cellulose acetate) achieved higher permeability but were also found to have a decreased salt rejection [Francis, 1966]. The use of a polysulfone support further improved permeability, but did little to improve salt rejection. Polysulfone also had better resistance to compaction and stability in acid and alkaline environments, allowing a wide range of interfacial polymerisation reactions. The next major steps were the development of the NS-100 polyamide membrane [Cadotte, 1977], and NS-200 polyfuranene membrane [Rozelle, 1968]. These membranes had high salt rejection and good permeability, coupled with good rejection of organic compounds and good stability at high temperatures. Their major weaknesses, however, were their low resistance to chlorine attack and high surface brittleness due to the highly cross linked structure. Subsequent
developments of structures with less cross linking led to the polyamide PA300, RC100 [Riley, 1976] and polyvinylamine WFX-X006 [Naaktgeboren, 1988] membranes which had good salt rejection and further improved permeability and lowered brittleness. The RC-100 has also been found to have a high resistance to biofouling. The low resistance of polyamide membranes to chlorine attack led to the development of the NS300 semi-aromatic polypiperazine-amide [Eriksson, 1988] which had better chlorine resistance but had very low monovalent salt rejection. The presence of anionic functional groups such as carboxyl on the surface, however, provided Donnan exclusion effects, allowing rejection of divalent anions such as sulfate. This led to the commercial production of NF membranes. Further improvements in permeability and salt rejection were later achieved by the use of monomeric aromatic amines and aromatic acyl halides to give the fully aromatic polyamide FT30 [Cadotte, 1981] membrane. This membrane chemistry gives rise to membranes with high resistance to compaction, thermal and chemical resistance, a wide pH operational range and a degree of tolerance to chlorine attack which is sufficient to withstand accidental exposure to chlorine. A series of current membrane products based on the FT30 fully aromatic polyamide structure are commercially available from Dow Filmtech. Similarly, current commercial membrane products that are based on the fully aromatic polyamide membrane developed by other manufacturers (UTC - Toray Industries and X-20 - Tricep Corporation) are available. Subsequent to the early 1990’s, further improvements in salt rejection and permeability has been achieved through membrane surface modification, optimisation of interfacial polymerisation reaction parameters, and more effective design of the module structure.

Figure 13: The development of RO membrane by reaction optimisation and post-synthesis surface modifications: (a) Dow Filmtec seawater series and (b) Toray brackish water series. From Lee, 2011
The Hydranautics LFC-LC-LD membrane launched in 1995, for example, has a poly(vinyl alcohol) (PVA) coating on the surface of conventional fully aromatic polyamide membranes to give it low surface charge and greater resistance to chemical attack. They are designed to minimise the adsorption of organic foulants and resist chlorine attack, and are suited to wastewater treatment and reclamation applications [Lee, 2011]. These developments in commercially important RO membranes are now difficult to identify due to greatly reduced patenting activity by membrane manufacturers. Some of the improvements in rejection and flow for the Dow-Filmtec and Toray line of membranes are shown in Figure 13.

Review of the scientific literature on the subject, however, reveals the level of sophistication of control of the desired membrane properties that is now possible, and may have been used by membrane manufacturers. Membrane properties can be modified via the use of additives to control the rate of polymerisation. There are also a host of post-synthesis membrane modifications that can be used to improve membrane properties [Lee, 2011]. Manufacturers can, for example, increase permeability and chlorine resistance by making the membrane more hydrophilic after the membrane has been cast. Mixtures of alcohol (ethanol and iso-propanol) and acid (hydrofluoric and hydrochloric acid) in water have also been used to improve flux and rejection due to the partial hydrolysis and skin modification initiated by the alcohol and acid [Mukherjee, 1996]. Similarly, 70% flux improvement has been attained by soaking composite membranes in solutions containing various organic species, e.g. glycerol, sodium lauryl sulphate, and the triethylamine salt of camphorsulfonic acid. Post-treatment of membranes using an aqueous solution of PVA and a buffer solution have been use to improve the abrasion resistance as well as the flux stability of the membrane [Pinnau, 1999]. Manufacturers can also alter membrane properties by inclusion of additives into the casting solution that can optimise membrane properties by altering the monomer solubility, hydrolysis, protonation, and can act to scavenge inhibitory reaction byproducts [Song, 2005]. Generally there is a trade off in salt rejection with permeability or operating pressure as increased cross linking required for improved salt rejection also acts to decrease the permeability (or increase the operating pressure). Figure 14 shows the improvements made over more than a decade in this tradeoff between salt rejection and operating pressure. It appears that further improvements of membrane performance are possible. Recent press releases by NanoH20 have claimed that the pilot testing of new nanostructured QuantuFlux RO membranes has achieved high salt rejection (99.85%), with 50% more water being produced at the same operating pressure than the currently used membranes [Membrane Technology, 2012]. This is interesting to note as nanocomposite membranes have also shown promise in improving the separation and flux of gases and similar improvements may also be possible for water treatment.

Figure 14: Improvement of RO salt rejection and operating pressure over time. Adapted from Casañas, 2012
Research into new membrane materials has led to dramatic improvements to membranes used within the water industry, and further development seems likely. Given that such developments are the basis for highly successful businesses, such research is likely to be supported by membrane suppliers to focus on improved salt rejection, higher flux and improved selectivity of species (e.g. greater separation of monovalent and divalent ions etc).
3.2 Evolution of modern MBR processes

The major role of membranes in membrane bioreactors is to allow operation of the activated sludge process at higher biomass concentration, thereby minimising plant size. The original process was introduced by Dorr-Oliver Inc and used a cross-flow flat sheet membrane filtration loop attached to a conventional activated sludge bioreactor [Smith, 1969]. Due to the high cost of membranes, however, the system relied on relatively low active membrane areas with high cross flow velocity to mitigate fouling. The high energy demand required to generate these high cross flow velocities (of the order of 10 kWh/m³ [Le-Clech, 2006]) made the process unattractive. A milestone in MBR technology was the idea to use dead end filtration and submerge the membrane in the bioreactor [Yamamoto, 1989]. The use of dead-end filtration mode with backwashing and later relaxation rather than cross flow mode resulted in large energy savings [Fane, 2011]. Another key development was the use of air scouring to mitigate fouling, which also serves as a means of aeration of the activated sludge in aerobic MBR operations. The decrease in membrane prices also allowed the use of more membrane area and lower specific fluxes, allowing further reduction of fouling. One of the key benefits from MBR technology is the beneficial effect the membrane process can have on the microbial community in the reactor. Munz et al (2008), for example, compared the microbial communities in MBR to that of a conventional activated sludge process (CASP) run under the same operating conditions and found that the microbial community in the MBR process was able to achieve higher removal of chemical oxygen demand (COD) and a more stable and complete nitrification than the CASP process. The better performance of the MBR reactor was attributed to a higher abundance of α and γ Proteobacteria in the MBR reactor, and the presence of ammonia oxidising bacteria on the surface of the MBR flocs only. These authors suggested that the difference between the two microbial communities was due to different biomass selection in the two processes. Subsequent developments and improvements of MBR performance have tended to come from less expensive membranes and optimisation of process parameters rather than from improved membrane performance. In early days, for example, MBRs were operated at high solid retention times (SRT), as high as 100 days with mixed liquor suspended solids up to 30 g/l. The recent trend is to apply a lower SRT (around 10–20 days), resulting in more manageable mixed liquor suspended solids (MLSS) levels (10–15 g/l), and lower fouling propensity and overall lower maintenance requirements and membrane cleaning. Further cost reduction is now being sought from better fouling mitigation [Le-Clech, 2006].

In the early 1990’s, MBR was largely used for industrial applications, and in 2009 the number of MBR industrial applications greater than 20 m³/d was estimated to be growing at 50 per year in Europe. The uptake of MBR technology for municipal wastewater applications greater than 100 m³/d was very low in the 1990’s, and was estimated to be growing at 20 per year in 2006 in Europe (see Figure 15) [Lesjean, 2008]. The use of MBR is now becoming widespread in industry and for municipal use. The volume of water treated by MBR has been estimated to be growing at 20% per annum [Le-Clech, 2005].

![Figure 15: Number of MBR installations in Europe. From Lesjean, 2008](image-url)
The MBR process is now cost competitive with conventional activated sludge bioreactor technology and provides a more reliable water quality. Mitsubishi, Zenon, Memcor, Pentair and Kubota are the major membrane manufacturers [Le-Clech, 2005]. Future challenges to be met by manufacturers and operators of membrane technology include the reduction and detection of the incidence of membrane integrity loss and the optimisation of process control systems [Le Clech, 2005]. Also, control of micro-contaminant removal through MBR has the potential to reduce water recycling process units and costs.

The success of membrane bioreactors in wastewater treatment via aerobic digestion has recently raised interest from the research community for the application of membranes technology to anaerobic wastewater digestion processes. One of the prime motivations is the potential for combination of wastewater treatment with energy production. Other advantages of anaerobic digestion are total biomass retention, excellent effluent quality, low sludge production and small footprint. Current research is largely focused on the challenge posed by the higher membrane fouling potential of anaerobic digestion liquor than aerobic digestion liquor [Lin, 2013], suggesting the need for research into low fouling membranes and process improvements to mitigate fouling. Pilot plant implementation of anaerobic MBR remains limited and no industrial-scale anaerobic MBR plants have to date been trialed [Skouteris, 2012], although both Pentair and Veolia supply anaerobic membrane systems.
4 FUTURE DIRECTIONS IN MEMBRANE RESEARCH AND EMERGING MEMBRANE TECHNOLOGIES

4.1 Emerging areas of research

Three of the major challenges that are being addressed in emergent research areas are membrane fouling, the management of waste streams, and the application of membrane treatment to poorer quality water. The need to operate in a high energy cost environment is another challenge that is being addressed in emergent research.

**Membrane Fouling**

The successful control and minimisation of membrane fouling is one of the many contributing factors to the success of the membrane technology to date, but this control and minimisation requires considerable effort and expense. It is, therefore, not surprising to see that many emergent areas of research are somehow motivated by and related to minimising or delaying fouling.

One emerging area of research is that of reduction of cost of membranes. The motivation is now, however, not only to lower the cost of treatment systems, but to give the added option of lowering the running costs by allowing the use of higher membrane surface areas, thus reducing fouling by operating at lower flux.

Another emerging research area that is largely aimed at fouling control is that of development of nanocomposite UF membranes. The incorporation of nanoparticles into the membrane can alter the porosity of the skin and the macrovoid structure, thus having the potential to improve product water quality, improve mechanical performance and the membrane’s ability to withstand harsh chemicals and fouling. For PVDF and PES membranes, however, polymer additives that are added during the manufacture such as poly (vinyl pyrrolidone) (PVP) and poly (ethylene glycol ) PEG, can themselves act as antifouling agents and negate the influence of nanoparticles on the surface properties.

The potential for lower fouling is also one of the major motivators for research into forward osmosis (FO). The driving force for the movement of water across FO membranes is the natural tendency for water to flow from a low salt concentration solution to a high concentration solution. The foulant layer formed on forward osmosis membranes is subject to less compaction and is looser than that formed in pressure driven processes such as RO, resulting in lower flux decline and allowing physical control of the foulant layer using high cross flow velocity. The expense and practicality associated with regeneration of the draw solution, however, is FO’s current weakness, and its low fouling potential is exploited by combining it with RO to regenerate the draw solution and thus treat waters that exhibit high fouling in RO operation (see Figure 10). Research to understand and minimise the mechanisms of fouling in these combined FO/RO systems in the treatment of these recalcitrant feedwaters is an emergent area of research.

Other fouling related emergent areas of research include the development of scaling monitors to allow better process control to prevent scaling, and reverse flow control for RO systems to reduce or eliminate anti-scalant use and to prevent scaling.

**Management of waste streams**

As RO has become more widely implemented, the issue of brine management of the waste brine in order to avoid environmental impacts, and to avoid the high cost required to meet increasingly stringent regulatory requirements has emerged as a major issue. This has, together with the need to make the most of scarce water resources, motivated research into high recovery reverse osmosis. Research into interstage treatment to remove of scale precursors such as calcium from brackish surface waters has shown that this is possible, and emergent areas of research involve interstage treatment of other water sources such as municipal wastewater, groundwater and coal seam gas product water.
Treatment of poorer quality feedwaters
The motivation to treat poorer quality water that would rapidly foul organic membranes is the major driver for emerging research into ceramic and sintered metal membranes. These membranes have the ability to withstand harsher abrasive environments and robust cleaning regimes without lumen breakage, and the potential to act as a catalytic site for foulant breakdown. Ceramic membranes can be used with ozone to keep the membrane clean and assist in catalytic removal of organic compounds. They also have potential for cost reduction via improved module design; (Potential use in small scale treatment systems where the membrane cost is a small component of the system and where reduced operator intervention is required (e.g. small scale recycling systems)). Sintered metal membranes also have potential to use electrical properties to improve fouling and may allow backwashing of difficult streams (e.g. sludge treatment).

High energy costs
Membrane distillation is another low pressure membrane based process that has received recent attention due to the potential to use waste heat rather than electrical energy. The driving force for the movement of water across an MD membrane is the water vapour pressure difference at different temperatures. If the water to be treated can be heated using waste heat, passing this heated water over an MD membrane that is in contact with a colder air or liquid phase will result in the establishment of a vapour phase within the hydrophobic membrane pores and condensation of clean water on the cold side of the membrane. The emergent aspects of MD research is based on gaining a better understanding of the process, in the design of better membrane materials, and in its application to new feed streams such as dairy.

Anaerobic MBR is also being studied as a technology that may help meet the challenges of rising energy costs. Its advantages over the more commonly implemented aerobic process are the ability to operate with little operator experience, higher energy recovery, longer solids retention, smaller footprint, and higher COD removal.

4.2 Emerging membrane technologies
4.2.1 Ceramic membranes
Low pressure ceramic membrane processes (MF/UF) are a rapidly emerging technology for water treatment. The motivation for the use of ceramic membranes rather than the accepted, tried and tested organic polymeric membrane processes is their greater chemical resistance and robust performance, making them more suitable for harsher cleaning processes for application to feedwaters with high fouling potential, corrosive composition or abrasive particles. Their strength also results in negligible integrity problems (caused only by inappropriate handling during maintenance), leading to reduced operational issues. Ceramic membranes are also making inroads into areas where organic polymeric membranes are widely used. There are, for example, 50 small ceramic membrane drinking water facilities in Japan that have been constructed in the last decade, and a study using a 2.5 MGD capacity pilot plant is planned for Colorado [Lee, 2013]. On a capital cost basis, it appears that ceramic membranes are becoming increasingly competitive particularly since PWN Technologies has developed a module to contain up to 200 elements rather than individual elements.

The cost competitiveness of ceramic filtration when compared to conventional polymeric systems depends largely on the fouling potential of the feedwater. For low fouling water, ceramic filtration is the more expensive option. Recent economic modeling from the US Bureau of Reclamation, however, found that ceramic filtration becomes competitive when the fouling is such that the lifetime of the polymeric membrane is 3 years or less [Guerra, 2011]. Similarly, cost estimates for a recent U.S. surface water treatment application requiring powdered activated carbon (PAC) pre-treatment of surface water to remove high levels of dissolved organic carbon, found that ceramic filtration with recirculating PAC can achieve the required treatment goals with similar cost to a conventional polymeric system with dissolved air flotation pretreatment to remove the PAC [Parker Water and Sanitation District, 2010]. The negligible integrity issues experienced by ceramic membranes may also make them suitable for applications where remote, unattended operation is preferred, as the need for repair of membrane modules (pinning) is dramatically reduced or eliminated. Furthermore,
with an estimated life of up to 20 years, and with sustainability becoming increasingly important to industry, ceramic membranes are also increasingly been seen as more attractive option for their potential for lower environmental impact [Water and Waste Digest, 2013].

**Figure 16:** SEM micrograph of silica/γ-alumina/α-alumina NF membrane. From de Lint 2006

As the water industry gains more experience with pilot-testing and full-scale plants are commissioned and start producing water, ceramic membrane implementation is likely to increase in the United States and internationally [Freeman, 2011]. ITN Nanovation have recently received 2 orders for flat sheet ceramic membranes to treat a difficult groundwater in Saudi Arabia [Roplan Membrane &Desalination Industry portal].

Ceramic membrane structure closely mirrors that of organic polymer membranes. They are asymmetric structures with a porous support layer for mechanical strength with a thin top layer that provides the membrane its filtration properties (see Figure 16). The pore size distribution of ceramic membranes, however, is generally narrower than that of polymeric membranes.

As with organic polymeric membranes, the understanding of fouling mechanisms and fouling mitigation is a major area of research that attracts attention. Research performed by Lee et al. (2013), compared the fouling of ceramic membranes with that of organic polymer membranes in the treatment of solutions containing polyethylene glycol and humic acids as model compounds of natural organic matter (NOM). Lee et al found that ceramic membranes appeared to have much less reversible and irreversible fouling after chemical cleaning than polymeric membranes, i.e. they fouled less and were easier to clean. This was attributed to weaker interaction of the foulant with ceramic membranes than with polymeric membranes due to the more hydrophilic nature of the ceramic membranes. However, polysaccharides may have been a better model synthetic compound to use, as polysaccharides such as alginites interact strongly with metals and may be more representative of fouling compounds for ceramic membranes. Ceramic membrane’s ability to withstand harsh conditions has also prompted research into the use of ozone to mitigate fouling by NOM [Lehman, 2009]. Doping of the membrane with iron oxide [Park, 2012] or with a layer of TiO₂ [Zhu, 2011] has been found to enhance the ozone degradation of NOM.

Another research area in ceramic filtration is the preparation of less expensive ceramic membranes through the use of cheaper raw materials. Nandi et al (2008) investigated the characterised ceramic membranes prepared from kaolin, quartz, calcium carbonate, boric acid and sodium metasilicate, including the estimated cost of manufacture of these membranes, and found that they had good mechanical strength, chemical stability and filtration performance. They estimated a cost of $130-200/m² of active area, comparing favourably with organic polymeric membranes ($50-200/m²), α-Alumina ceramic membranes ($500/m²) and stainless steel asymmetric membranes ($3,000/m²).

More recently, Emani (2013) estimated that a low cost ceramic membrane for juice clarification could be manufactured for $78/m².
Research into ceramic desalination membranes is also being undertaken [Duke, 2007], and ceramic membranes have been used for purifying alcohols via pervaporation for many years [Verkerk, 2001]. Currently, ceramic membranes for desalination are not competitive with organic membranes and do not offer any major advantages over polymeric systems for most applications. However, the pore structure and mode of separation is different to that of polymeric membranes, and different separation characteristics to those of polymeric membranes may result.

### 4.2.2 Membrane distillation

The first patent for membrane distillation was filed in 1963 and the first paper was published by Findlay in 1967. More than 5 decades later, MD has still not reached widespread commercial implementation for water treatment. The number of research publications on MD has, however, increased considerably in the last 6 years [Khayet, 2011] and there are now a number of commercially available membrane modules – Fraunhofer ISE, Memstill, Aquastill, Scarab and Memsys. Although the niché markets for the use of MD still remain unclear, MD appears to be poised for commercial implementation [Mar Camacho, 2013]. A recent press release by Memsys [Memsys, 2013] declared that GE and Memsys have entered into an Agreement in 2012 to jointly develop membrane distillation (MD) technology for the fast-growing unconventional resources marketplace, including shale gas, coal seam gas, and other unconventional fuels recovered by hydraulic fracturing. Under the terms of the agreement, GE will invest in testing the technology and in return receive an exclusive license for the use of the technology in these applications.

A recent review of MD literature [Mar Comacho, 2013], has highlighted that a major obstacle to implementation of MD technology is its high energy requirement compared to RO. The Fraunhofer ISE MD system is claimed to have achieved thermal energy consumptions of 140 to 200 kWh/m³ (Gain Output Ratios (GOR) up to 4.5), and are available in spiral wound configuration that provide 5 to 14 m² of membrane area per module. They have recently been reported to have achieved 130 kWh/m³, representing a Gain Output Ratio of 4.8 [Winter, 2011]. The Memstill MD system is claimed to be able to achieve thermal energy requirements as low as 56 to 100 kWh/m³ water produced (GOR up to 11.2). This is the lowest value reported from real testing (or highest GOR), but to achieve this, the water must be heated to 80–90 °C. The electrical energy required was assumed to be 0.75 kWh/m³. The Scarab AB system features plate and frame modules and has been trialed in numerous projects worldwide. A recent (2011) trial has reported flux of 6.5 LMH and thermal energy consumption of 810 kWh/m³ (GOR 0.78) [Guillén-Burrieza, 2011]. By comparison, the energy requirements for RO range from 3 kWh/m³ to 17 kWh/m³ depending on the scale, incoming salinity (fresh to brackish to seawater) and use of energy recovery devices [Mar Camacho, 2013].

The Memsys system is regarded as the state of the art in MD technology and pilot plants have been installed in Singapore, Australia and India to test the technology. Memsys promises thermal energy requirements of 175–350 kWh/m³ (GOR up to 3.6) and electrical energy requirement of 0.75–1.75 kWh/m³. These high energy requirements make it clear that MD can only compete with RO where it can utilise waste heat (e.g. in power stations and chemical plants), or in situations where current established technologies are unable to operate, e.g., RO waste brine treatment in situations where discharge is problematic [Mar Camacho, 2013, Kesieme, 2013]. With available waste heat, however, MD could outcompete RO as it has low electrical energy requirement (e.g. 0.75–1.75 kWh/m³ for the Memsys system) and requires less expensive equipment due to the lower pressures involved [Kasieme, 2013]. The higher quality of the product water from MD of highly saline feedwaters also make it an attractive option. Another major limitation of MD over RO is the relatively lower fluxes and the potential for membrane wetting. These are dependent on a wide range of membrane characteristics such as hydrophobicity, surface morphology, thickness, thermal conductivity, pore size and porosity, as well as module characteristics. The level of knowledge of the importance of these and other process variables has grown considerably over recent years, and has translated to better MD membranes. The membranes used in early days of MD were simply microfiltration membranes that were made of very hydrophobic materials such as PTFE. A cross section SEM image of a PTFE membrane is shown in Figure17.
The membranes being marketed specifically for MD applications are much better than the conventional MF membranes for this application. Zhang et al (2010), for example, compared a number of new membranes with older MF membranes and found that the new membranes achieved significantly higher flux and had better energy efficiency under the same conditions. The new membranes were more hydrophobic, had liquid entry pressures (LEP) twice those of the older membranes, and greater salt rejection (100%) than the older membranes (96%). More recently, the understanding of the MD process has been expanded by mathematical modeling [Zhang, 2013] which showed good agreement with experimental results and allowed prediction of optimum MD operating parameters. Such models are required for design of membrane distillation systems, particularly if localised waste heat is to be used as the quality and availability of heat will vary from site to site. Recent inroads into understanding how fouling decreases flux have also been made [Goh, 2013]. This study showed that the hydrophilicity of the sludge can affect the particle size and hence, the pore-size distribution of a biofouling layer. More hydrophilic sludges tended to form fouling layers with significantly smaller pore sizes that result in an enhanced vapor-pressure depression relative to less hydrophilic sludges. Another example of the level of advanced MD development is the very recent work of Liao (2013), which showed that it is possible to emulate the hydrophobic properties of lotus leaves and thus produce highly hydrophobic (superhydrophobic) MD membranes which have superior flux to that achieved with unmodified commercially available MD membranes. The modified PVDF membrane achieved a high and stable MD water flux of 31.6 L.m\(^{-2}.h^{-1}\) while the unmodified commercially available membrane achieved 10 L.m\(^{-2}.h^{-1}\), using a 3.5 wt% NaCl solution as the feed, with the feed and permeate temperatures fixed at 60 °C and 20°C respectively.

Another obstacle to the implementation of MD is the susceptibility of the membrane to amphipathic substances such as detergents, fats and oils. The presence of these substances in the feed can decrease the liquid entry pressure to the point that water enters and wets the membrane [Goh, 2013, Gryta, 2008].

The incidence of membrane wetting limits the applicability of the technology, and also the available options for cleaning the MD membrane. As with all membrane processes, membrane fouling and cleaning is of great importance. The difference with MD membranes, however, is that the interaction of cleaning solution with the foulant can be detrimental. The dissolution of the foulant in the cleaning solution can form amphiphilic substances that lower the surface tension of the air/liquid interface, thereby decreasing the hydrophobicity of the membrane and the liquid entry pressure, resulting in entry of liquid into the pores of the membrane (i.e. “wetting” of the membrane) [Gryta, 2008]. While the hydrophobicity loss resulting from cleaning can be restored by drying the membrane after rinsing.
with clean water, this is impractical on a large scale. It is, therefore, of paramount importance to avoid wetting during cleaning, and this severely limits the range of chemical agents that can be deployed for the cleaning of MD membranes.
5 WATER QUALITY RESEARCH AUSTRALIA (WQRA) / WATER RESEARCH AUSTRALIA (WATERRA) RESEARCH

The research strategy adopted by WaterRA and its predecessors has addressed the critical water quality research needs of Australia’s water industry with an emphasis on public health outcomes related to public health risk in both current water sources and in new and alternative water products and services, primarily in urban areas. WQRA has recently changed name to WaterRA to reflect a broader research scope – to lead and facilitate high quality and collaborative research of national significance and to ensure implementation outcomes to address current and emerging issues in water.

Since membranes have become a standard treatment process, WQRA began to focus on operational issues associated with membrane technology. Issues such as membrane integrity monitoring, membrane bioreactor (MBR) robustness particularly associated with the removal of micro-contaminants, membrane ageing and chemical pre-treatment for high pressure membranes, and the use of coagulants in MBRs to control phosphorus concentrations, have been funded. Application of ultrafiltration membranes in point of use applications was also the subject of research within the CRC for Water Quality and Treatment [Gray, 2007], while treatment of RO concentrate for removal of organic compounds has also been considered.

Membrane integrity of both low pressure (MF/UF) and high pressure (NF/RO) membranes has been considered, with UNSW completing a comprehensive literature review (Project 2006/08). The review identified the current state of membrane integrity testing and as well as new approaches for improved integrity testing such as Limulus Amebocyte (LAL) assay test for endotoxin, high performance size exclusion chromatography, the pulse integrity test and fluorescence spectroscopy.

Subsequently, two projects on RO integrity monitoring were funded (Projects 2013/10 and 2018/10). This is considered a high priority area as currently on-line validation of RO membranes restricts the credited log reduction value (LRV) for pathogens to 1.5 or 2, although actual LRV for pathogens may be >4. Therefore, additional treatment stages maybe required to obtain the necessary LRV credits for recycled waters. These projects have investigated the use of fluorescent particles and dyes and the effect of membrane ageing on these approaches. While fluorescent dyes have been used industrially (eg. Rhodamine WT), they provide a conservative estimate of membrane integrity due to their size being significantly smaller than that of virus particles. Fluorescent nanoparticles of size similar to that of virus have been fabricated, but the limit of detection has increased to higher concentrations than for dyes and on-line monitoring for LRV >2.5 cannot be achieved using this approach. Alternative light scattering techniques are being investigated and have shown promise in laboratory tests for on-line monitoring for LRV >4. These techniques and other novel approaches will be studied in greater detail in a WaterReuse Research Foundation project (MW and Victoria University) and the AWRCoE NatVal project (University of Queensland, UNSW, Curtin University: Project 3018/12). These two projects will be funded separately, but informal collaboration will see them focus on complimentary approaches. Success in this project may also bring direct potable reuse a step closer, as on-line integrity monitoring would improve the reliability of such systems.

Membranes degrade during operation and ultimately need to be replaced, and this is a significant expense for membrane systems. Development of predictive tools for membrane ageing of low pressure membranes (Project 2008/09) has included the effect of different cleaning chemicals on ageing of various common MF/UF membrane materials and assessed the effects on membrane ageing and integrity. Generally, the pore size increased and the membrane resistance reduced due to ageing of membranes, and the membrane lifetime exposures to chlorine was identified. This work has culminated in it being released as an IWA book “Development of predictive tools for membrane ageing”.

Chemical pre-treatment for high pressure membranes (UNSW, Project 2009/09) has conducted a comprehensive literature review on high pressure membrane scaling [Antony, 2011] and is developing a scaling sensor to detect the on-set of scaling so that preventative actions can be taken.
The application of UF as a point of entry treatment process was assessed against conventional sand filtration and UV disinfection for delivery of potable water in small, remote communities [Gray, 2007]. One of the simple point-of-entry units used in this trial is shown in Figure 18. The trials were successful at demonstrating the ability of these systems to produce potable quality water over a period of approximately 3 months. GWMWater and Coliban Water have recently received funding from the Department of Environment and Primary Industries (DEPI), Victoria to undertaken a management costing project to assess the economic viability of such systems, and the use of pressure decay tests (PDT) will be used to assure water quality and for alarming if faults are detected. The project is investigating the economic feasibility of this approach to provision of potable water in remote communities.

Membrane bioreactors (MBR) are becoming more common in the water industry, particularly for producing recycled water. Therefore, operational issues surrounding this technology are now more significant and WQRA began research on MBR robustness with respect to water quality and transient operational upsets (UNSW, Project 4038/11) and is developing projects on MBR optimisation for water recycling (University of Wollongong awaiting ARC Linkage outcome, Project 3024/12) and MBR integrity monitoring (AWRCoE NatVal, UNSW, Victoria University: Project 3018/12). Successful outcomes would reduce the number of subsequent treatment steps required for validation of MBR based recycling schemes. The use of coagulants in MBRs for control of phosphorus concentrations was also considered in a WQRA supported ARC Linkage project (UNSW, WQRA, Sydney Water, Origin Water), and the key operational variables for efficient phosphorus removal, control of coagulant dosing and cleaning of membranes were identified.

Reverse osmosis concentrate from water recycling applications contains concentrated organic compounds that may be problematic for discharge to sensitive receiving waters. Reduction of the organics concentration from RO concentrate has been the focus of a WQRA - Smart Water funded project (RMIT, City West Water) with an emphasis on the use of UV/H₂O₂ for oxidation of this material. Oxidation is possible with little production of oxidation by-products, and further analysis of these results is being undertaken.
5.1 Case study: Organic fouling of low pressure membranes

The first membrane projects funded by the CRC for Water Quality and Treatment were focused on organic fouling of low pressure membranes and techniques to reduce the rate of fouling [Booker, 2007, Occasional Paper 6, 2003, Fabris, 2008]. A survey of water treatment plants [Booker, 2000] had shown that low pressure membrane plants were increasingly being installed for the provision of drinking water, particularly in small regional locations. This project was undertaken early in the development and installation of membrane filtration plants when fouling and pre-treatment before MF and UF plants was a significant issue. For instance, an Amicon plant was installed in Victoria but was later removed because of poor performance related to fouling and pretreatment.

These initial CRC Water Quality and Treatment projects assisted in changing the international opinion of membrane fouling from being humic acid controlled to fouling being dominated by polysaccharides and proteins, and identified which of the pre-treatment strategies were most likely to succeed. Research on fouling as a function of flux also demonstrated improved performance at lower flux, and thus the importance of design criteria on operating performance. Additionally, laboratory techniques for membrane fouling testing changed as a result of these projects, with a move to the use of backwashable fibre systems that provide information on backwashing as well as fouling build up.

The industry settled on coagulation – MF/UF and during the life of these CRC projects, smaller pore size UF membranes with hydrophilic surface coatings that were chlorine tolerant became available and are now the industry standard (PVDF, PES). While organic fouling is still an issue for these MF/UF membranes, the hydrophilic coatings and chemically enhanced backwashing (regular chlorine cleaning) has reduced the importance of fouling as an operational issue, along with greater operating experience and the subsequent expectation of regularly cleaning requirements.

Prior to these projects, UNSW (through Prof Tony Fane) was a leading international membrane research group, but there was little other membrane research capacity within Australia. These projects included researchers from UNSW, CSIRO and RMIT and assisted in increasing Australia’s membrane research capacity. PhD students were supported through both UNSW (Andrea Schæfer, Andrew Lee, Eun Kung Lee) and RMIT (Cunli Xiang, Farhana Malek and Linhua Fan), and several have remained in academia (Linhua Fan, Andrea Schæfer) or moved to industry (Eun Kung Lee – Siemens Water Technologies).

Organic fouling research continues with WQRA having supported a Smart Water Fund project (RMIT) on fouling by cyanobacteria blooms that sought to provide an understanding of the key variables that lead to increased fouling rates for cyanobacteria blooms. Fundamental research issues (not funded by WQRA/WaterRA) associated with membrane fouling are now concerned with interactions between organic compounds, as the presence of smaller molecular weight compounds appears to increase fouling via providing adhesion with the hydrophilically coated membranes [Gary, 2008, Henderson, 2011]. Additionally, there is some evidence that greatly improved membrane fouling performance can be achieved by targeting the removal of specific organic compounds and matching the pre-treatment process to the membrane material [Tran, 2006]. Organic fouling is also re-emerging as an issue in seawater treatment where biofouling issues can be significant, and there are several projects within the National Centre of Excellence for Desalination Australia (NCEDA) on this topic. Reduced costs of membranes may also enable lower flux operation (ie. purchase more membrane area) with improved fouling outcomes, and understanding this trade off in greater detail may lead to improved economic performance.

5.2 Case study: Membrane distillation

Research into membrane distillation was funded towards the end of the CRC Water Quality and Treatment and the reporting occurred via WQRA [Dow, 2008]. This small, short term project (6 months) undertaken by Victoria University investigated the use of direct contact membrane distillation to treat brines streams from brackish water RO systems, and built on modeling work from the CSIRO Cluster Project on Advanced Membrane Technologies for Water Treatment. This project demonstrated the ability of membrane distillation to treat conventional RO brine streams to increase the recovery of desalination systems and reduce the amount of brine for disposal. The PTFE membranes used in membrane distillation were also shown not to be prone to organic fouling from these streams and there was evidence that scaling of membranes could be readily managed through acid cleaning or hydraulic removal of the scale.
This project was followed by a GWMWater funded project to scaling up the direct contact membrane distillation process using solar energy to provide the heat (see Figure 19). The pilot plant was shown to perform as predicted from the direct contact membrane distillation model, although the production rate was lower than planned because of cloudy and rainy weather. Scaling of the membrane was also demonstrated to be an issue rather than organic fouling, and possible improvements in the pilot plant design to reduce scaling were identified.

![Solar heated direct contact membrane distillation pilot plant at Edenhope. From Dow, 2008](image)

A subsequent WQRA project on membrane distillation was co-funded with the Smart Water Fund and City West Water (Recycling water at the Newport Power station: WQRA Project 2016/09) (see Figure 20), and demonstrated reliable process performance at Newport power station where there was sufficient waste heat even at low energy efficiency to recycle all of their wastewater. The process performed well over a three month period, and was able to utilise low grade waste heat (30-40 °C).

Further projects are being undertaken by Victoria University to identify suitable applications for membrane distillation for industrial water recycling, including commercialisation of the technology. Additionally, the NCEDA is funding several membrane distillation projects for provision of water in remote communities utilising either waste heat from generators or solar energy, as well as for treatment of coal seam gas brines. The NCEDA projects are being undertaken by a number of Australian universities and utilise commercially available air gap membrane distillation or vacuum enhanced air gap membrane distillation systems that are more thermally efficient. The applications research for membrane distillation is well regarded internationally, and is focusing on finding industrial outcomes for this new technology.

![Direct contact membrane distillation pilot plant at Newport Power Station](image)
6 CONCLUSIONS

Increasing water demand and the need for new water sources to help meet the greater water demand, coupled with increasingly stringent regulatory environments, have been drivers for investment in membrane research. Research to date has improved membrane performance, process design, and chemical and energy use, and made membrane technology an economically competitive technology with widespread application.

Through its evolution, from the CRC for Water Quality, to Water Quality Research Australia (WQRA), to the present organisation, Water Research Australia (WaterRA) has been a key player in membrane research in Australia. Since membranes became a standard treatment process, WQRA began to focus on operational issues associated with membrane technology. Issues such as membrane integrity monitoring, membrane bioreactor (MBR) robustness (particularly associated with the removal of micro-contaminants), membrane ageing and chemical pre-treatment for high pressure membranes have been funded. Application of ultrafiltration membranes in point of use applications was also the subject of research within the CRC for Water Quality and Treatment. Current research projects funded by WaterRA include projects on chemical pretreatment requirements for high pressure membranes, hybrid coagulation/submerged MBR treatment, membrane integrity monitoring for virus removal, and ceramic membrane treatment.

Despite the enormous advances made in membrane technology, and the considerable contribution of WaterRA to these advances, the potential for membrane technology has not yet been fully realised. The quest for improved membrane materials with higher permeability and no loss of rejection for RO membranes continues. Smaller pore size UF membranes capable of colour and organics rejection are under development. The need to find methods for treatment of RO concentrate to improve its management is increasingly becoming evident. More research into reduction and detection of the incidence of membrane integrity loss is required. There is also more research required into optimisation of process control systems in MBR continues. The search for more chemically and physically resistant membrane materials also continues. Research successes in any one of these areas stand to make what is now an economically competitive technology more competitive and profitable. Furthermore, research into emerging technologies such as MD and FO stand to open up new applications and markets. The future holds great promise for membrane technology and membrane research.
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