MEMBRANE SEPARATIONS-100 YEARS OF ACHIEVEMENTS AND CHALLENGES

Tony Fane: UNESCO Centre for Membrane Science & Technology, UNSW, Australia
Singapore Membrane Technology Centre, NTU, Singapore

Over the past 100 years membrane technology has grown from separations techniques of largely theoretical interest to a multibillion dollar industry covering a vast spectrum of applications. Today membrane technology has multiple uses in biomedicine, pharmaceuticals, food and biotechnology industries, the water industry, gas separations including carbon capture, electrochemical applications, analytical and diagnostic uses and other miscellaneous applications. This presentation provides a brief over view of the development of membrane technology and then focuses on the last few decades of membranes in water and wastewater.

In a comprehensive history of membranes up to 1981 Harry Lonsdale[1] estimated at that time the membrane market to be about $1.5bn (corrected to 2008 $) compared with about $ 10m in 1950. Today the market probably exceeds $ 6bn/yr, a 4 fold increase over the past 25 years. The following early history is a précis of the account by Lonsdale and Table 1 is adapted from his text.

Table 1. Early membrane milestones (adapted from [1])

Event	Scientist	Year
Osmosis	Abbe Nollet	1748
Laws of diffusion	Fick	1855
Dialysis, gas permeation	Graham	1861,1866
Osmotic pressure	Traube, van't Hoff	1860-1887
Microporous membranes	Zsigmondy	1907-1918
Distribution law	Donnan	1911
Membrane potential	Teorell, Sievers	1930s
Hemodialysis	Kolff	1944
Gaseous Diffusion	Urey	1940s

It is over 250 years since the Abbe Nollet observed osmosis through a membrane in the form of a pigs bladder. About 100 years later Fick framed his laws of diffusion providing a framework for mass transfer separations. Shortly after this (1860s) Thomas Graham provided us with laws of diffusion in gases and showed early examples of gas separations through rubber; he also demonstrated dialysis. Microporous membranes (MF and UF) were studied by Zsigmondy and Bechold (who introduced the term ultrafiltration) in the early 1900s. Other pioneering developments were demonstrations of 'reverse osmosis' by Manegold and others in the 1920s, Donnans distribution law for charged species and the theory of fixed charge membranes by Teorel et al. in the 1930s. In the early 1940s Kolff demonstrated that dialysis could be used as an artificial kidney. At the same time the gas diffusion process was being developed for UF_6 enrichment). As noted by Lonsdale, by 1950 all the basic principles of membrane transport had been revealed. It is interesting to note that most of this work had been done in Europe, with exception of uranium enrichment, and the pioneers were chemists and physicists. In terms of industrial and environmental separations membranes in the early 1950s were not competitive with alternative processes, such as distillation. The reasons [1] are summarized in Table 2.

Table 2. The non-competitive nature of membrane separations up to 1950-1960.

Non-competitive nature of membranes up to 1950-60
Fluxes were low due to membrane thickness.
Selectivity (separation factor) was relatively poor.
Effective modularization was yet to be developed.
Cheap energy limited benefit of energy efficient membranes.

From about 1960 the modern era of membranes commenced. It is probably no coincidence that from this time Chemical Engineers became significantly involved in membrane process development. It is convenient to discuss recent membrane history as 3 phases, I (1960-1980) the 'beginning of the modern era', II (1980-2000) the 'age of maturation' and III (2000-) the 'age of new challenges'. The invention of the asymmetric integrally skinned cellulose acetate RO desalination membrane by Loeb and Sourirajan [2] in the Engineering School of UCLA was arguably the key event that started academic and commercial interest in membrane separations. Once Loeb and Sourirajan had shown that it was possible to make membranes that were capable of desalting seawater with reasonable fluxes (a 2 order of magnitude improvement on previous membranes) the concept was rapidly taken up by commercial producers. The major applications were in water-scarce regions, such as the Middle East and the Caribbean, and the new RO technology had to compete with more established thermal processes. Significantly the development of a practical RO desalination membrane was a spin off from substantial targeted funding by the US Government through the Office of Saline Water. Towards the end of phase I, a major improvement was made in RO membrane preparation using interfacial polymerization to produce thin film composite (TFC) membranes; John Cadotte (a polymer chemist) patented this in 1997 [3]. The TFC remains the major RO membrane concept today, although it continues to be improved.

The discovery of the L-S RO membrane prompted the development of highly effective UF membranes by chemical engineers, such as Alan Michaels who founded Amicon and also trained many 'membranologists' for the growing industry. It was found that UF membranes could be produced with a wide range of pore sizes, and importantly these membranes could efficiently 'filter' macrosolutes and fine colloids. Two early applications promoted the growth of UF and continue to be major uses today; they are good examples of 'cleaner production'. The first application is the recovery of electrocoat paint colloids in the automotive industry. The evolution of the electrocoat process and UF technology in the 1960s was synergistic. The other important application for UF has been in the dairy industry, with UF used to recover whey proteins, converting a polluting waste into a valuable resource.

The successful development of commercial membrane technology during the 'beginning of the modern era' has relied on many disciplines, but the role of chemical engineers has been central, involving chemical engineers specializing in materials, mass transfer, fluid mechanics, surface phenomena, modeling and process engineering etc. One of the fundamental issues recognized early on by chemical engineers at MIT and elsewhere was the importance of concentration polarization in controlling membrane performance. The need to influence boundary layer conditions close to the membrane required good ‘fluid management’. An important example of this was the development of the spiral-wound membrane module (SWM) now the ‘work horse’ for RO desalination plant and many NF and UF applications. In addition to the SWM the other major concepts are based on cylindrical geometry, either tubes or as hollow fibres (HF). Membranes in HF form have been produced since the 1960s for the range of pressure-driven membrane processes (including RO), as well as for hemodialysis (and other biomedical applications) and gas separations. The largest production until recently has been for hemodialysis.

Hollow fibres are well-suited to gas separations requiring high driving pressures and in this case the feed is applied to the shell with product from the lumen. An important development occurred in the late 1970s when Henis and Tripodi [4] invented a composite HF with a polysulphone (PS) substrate and a thin silicone rubber skin layer; this thin layer effectively plugged imperfections in the PS and produced a fibre of high selectivity and acceptable flux. Gas separation applications include hydrogen recovery (the major use), nitrogen production and CO_2 from methane.

Harry Lonsdale’s membrane history [1] ends in 1981 and this covers the ‘beginning of the modern era’. It is illuminating to summarize the topics and applications featured in the review (Table 3). The ‘future’ included Liquid Membranes (coupled and facilitated transport) which has not lived up to expectations. Similarly the elegant immobilized enzyme Membrane Reactors are not in the main stream. There were some notable absentees during this phase I period, and from the anticipated future including membranes applied widely to the water industry, except for RO (and ED) applied to saline waters. However membranes and water has been a major theme in Phase II and III.

Table 3. The status of membranes around 1980 (based on [1])

Process	*Developments*	*Applications*	*Engineering*
MF	Phase inversion membranes Track-etched membranes Stretched membranes	Sterile filtration is ‘most important’.	Deadend, but with trend to Cross-Flow filtration, for fluid management.
UF	Hollow fibres, tubular and SWM modules	Pollution control (recover values) Foods, biotech.	Fouling control and fluid management.
Dialysis	Hollow fibre hemodialysis	Disposable artificial kidney.	Mass transfer analysis.
ED	Ion exchange membranes Nafion-type membranes	Desal brackish water. Chlor-alkali in place of Hg cells.	ED Reversal
RO	TFC in SWM Hollow fibres(ar polyamide) SWM & HF in competition.	Desalination. SWM RO about 50% of RO capacity.	Energy recovery devices ‘just being introduced’.
Gas Seps	HF compsite (plugged). SWM	H_2, N_2, CO_2	Cascade design
Other Applications		*Comment*	
Blood oxygenation			

Membrane electrodes Controlled-release technology	Health-care and agri-food
Future (from 1980 perspective)	
Liquid membranes (couple-facilitated) transport	High selectivity and flux. Pumping 'up hill'.
Membrane reactors (immobilized enzyme type)	Simultaneous conversion and separation.
Pervaporation	Alternative to distillation

The remainder of this brief history will focus on the evolution of membrane technology for water and wastewater in phase II (1980-2000) and on current activities and possible futures in this area (2000 and beyond).

In the period 1960-1980 salty water desalting by RO was the major use of membranes in the water cycle, although it was viewed as a relatively expensive technology best suited to water-scare, energy-rich locations. The prevailing consensus during this period was that membrane technology should only be applied where relatively high value products were involved, such as in the food and biotechnology industries, or in effluent processing to recover values, such as whey proteins or electrocoat colloids. Water was not perceived as a high value product per se.

However in Phase II (1980-2000) a number of factors or drivers have come into play that have significantly changed the perspective. The drivers include tighter regulations on water for consumption, for example based on out breaks of cryptosporidiosis in the early 1990s, and on more regulation of discharge quality. Also we have seen increasing pressures on water resources due to population increase and drought. These challenges have been met by notable developments in membrane technology, so that today membranes play a central role in Water Supply. Sea water desalination, raw water treatment, and water reclamation for reuse all rely on advanced membrane technology to augment our water resources. At this point in time membranes can produce potable water from sea water at US$ 0.5 to 0.7 per m^3, and can produce indirect potable water from municipal effluent for about half this cost, and low pressure (LP) membranes can process raw water at costs similar to conventional treatment [5] with a better quality product. A recent survey of LP membranes shows > 12,000 ML/d installed of which 60% are for water treatment [6]

One of the key developments has been the wide use of the thin film composite membranes in SWM modules for high pressure RO and NF, a trend starting in the late 1980s, and the proliferation of very effective hollow fiber membranes for low pressure UF and MF. There has also been some rationalization of module designs, for example the virtual 'standardisation' of the spiral-wound module (SWM) for high pressure processes. Over the past 10 to 15 years the Submerged Membrane module (in a tank and under suction) has evolved from curiosity to mainstream for low pressure processing and it is of particular interest in water treatment, pretreatment prior to RO and in the membrane bioreactor (MBR). However it has not replaced the contained pressurized hollow fibre module which has some benefits due smaller footprint. Another important paradigm shift has occurred in the application of dead-end operation for membranes processing dilute feeds, such as raw water or settled secondary effluents. This recognizes that energy-demanding crossflow (a feature of 'crossflow-filtration' for fluid management) is not a prerequisite in membrane applications if there are other effective means, such as backflushing with liquid or gas, to periodically remove surface deposits. Water treatment using low pressure UF or MF typically uses hollow fibre membranes with external feed (submerged and some contained) or lumen feed (some contained and pressurized).

The membrane bioreactor (MBR) for waste water treatment was initially developed in Phase I (the late 1960s/ early 70s) but tended to be a 'niche' application due to high pumping energy costs (about 10 kWh/m^3). However the combination of submerged membranes and air sparging has shown that the energy costs can be dramatically reduced to < 1 kWh/m^3 providing the user accepts lower operating fluxes which can be accommodated with lower cost submerged modules (hollow fibres or flat sheet). Major savings have occurred due to improved means of air sparging. Over the past 15 years the implementation of the submerged MBR has been dramatic [7] and the technology continues to grow at >10% per annum. The other major trend in wastewater and membranes has been in reclamation using dual membrane processes, with LP membranes as pretreatment to RO. Major applications can be found in Kuwait (the largest at about 400 Ml/d), Singapore (NeWater) and California (Groundwater Recharge). This approach acknowledges that treated wastewater is a valuable water resource, provided due diligence is applied to its use.

Phase III (2000- and beyond). The challenges facing the future of membrane technology in the water industry relate to product quality, productivity (in terms of fouling and its control), and energy usage and green house gas (GHG) emissions. In the light of these challenges let us look at potential developments in the use of membrane technology in the water cycle, from desalting, water treatment, water reclamation to MBRs.

Desalination. RO is the predominant method of membrane desalting and was a paradigm shift when introduced in the 1960s. The SWM was an early development and has been evolving over the years. The SWM 'Figure of Merit' (FOM) has been defined [8] to illustrate how , over the period 1978 to 2006, improvements in membrane permeability (2.25x) and membrane life (2.3x) and decreases in price per unit area (12x) and salt passage (7x) translate to a 'FOM' increase from 1 to 480. The FOM continues to rise and will be improved by use of Mega modules (16 to 18 inch) and improved thin film composite membranes (see below). Other benefits may come from better spacer design (improved mass transfer with lower pressure drop) as an outcome of CFD analysis (Schwinge et al. [9]). However it seems unlikely that the SWM is the end of the line in module development for SWRO. For several decades RO desalination also used hollow fibres, but this technology is currently sidelined. Nevertheless HF RO could bring intrinsic advantages if revisited, for example with greatly improved (membrane) pretreatment and modules with better fluid management.

Recently there have been significant new developments out of UCLA involving thin film nanocomposite (TFN) RO membranes [10]. These mixed matrix membranes incorporate nanoparticles in the thin polyamide separating film which impart greater hydrophilicity, as well as improving water permeability without loss of retention properties. The TFN concept offers immediate additional routes to improved RO membranes. Longer term 'new generation' RO membranes could come from the carbon nanotubes which promises orders of magnitude increase in permeability [11].

Desalination ~ Energy issues. Significant reductions in energy demand for SWRO have been demonstrated recently in the Affordable Desalination Collaboration project [12]. Using state-of-the-art RO and pressure exchangers the energy has been reduced to as low as 1.58 kWh/m^3, down from the more typical 3 kWh/m^3. The minimum water cost occurs at a recovery of about 50% whereas the minimum energy, and thus minimum GHG impact, occurs at a recovery of about 40%, so GHG minimization comes at a capital cost penalty for SWRO: a paradigm shift will be needed to adopt GHG minimization as the new optimum. There may also be opportunities for further energy reduction if the novel high permeability RO membranes under development are used optimally. Using a 'close to osmotic pressure' feed-side profile it may be possible to save about 35% of the energy. A potential adjunct to SWRO is concentrate processing by Membrane Distillation (MD), but this is only viable in GHG terms if low grade heat (waste or solar) is available. MD has the advantage that flux can be maintained to very high salt concentrations [13] so that overall recoveries > 90% may be feasible. Although MD has been studied for 2 or 3 decades it still awaits a major application, but its potential is attractive. Another membrane process with a long gestation time is Forward Osmosis (FO) which is having a surge of interest [14] as a potentially lower energy approach to desalination. In principle FO could desalinate water at < 1.5 kWh/m^3, provided a suitable membrane can be produced and an easily regenerated draw solute can be identified. Alternatively engineering heuristics suggest that an optimal separation process removes the least abundant species first, so that desalination should involve removal of salt from water rather than vice versa. One membrane process capable of this is electrodialysis, and recent developments are in place to refine this option

Water Treatment. A recent 'membrane' development is the commercial scale application of ceramic MF to water treatment at capacities upto 40 ML/day in Japan. The 15 m^2 modules from NGK have 0.1 micron pore size, and it is claimed that the higher cost of ceramics is offset by much longer lifetime (2 to 5x), greater chemical resistance as well as reportedly higher sustainable fluxes and recovery. For the removal of low concentrations of organics in water treatment the options include NF or low pressure 'hybrid' processes such as MF or UF with adsorbents or photocatalysis. The low pressure hybrid is potentially the lower energy option [15]. In water treatment with low pressure membranes using upstream chemical coagulation the process is typically dead-end with batch cycles and backwash. Cycle time is proportional to $1/(\text{flux})^2$. Each backwash consumes energy and consequently a high flux operation is more energy demanding, although it would require less membrane area. In one comparison conventional economics (minimum costs) suggest a flux in the range 70 to 80 l/m^2hr whereas the minimum energy criteria (minimum GHGs) requires a flux of only 10 to 20 l/m^2hr [15]. In a carbon constrained future there may be a trend to lower fluxes with more investment in membrane area.

Reclamation. Membranes have become the enabling technology for safe and cost effective wastewater reclamation. One of the challenges to RO in this application is biofouling and a future development that may help to combat biofilm development is the thin film nanocomposite (TFN) described earlier [10] but with the incorporation of TiO_2 or similar nanoparticles to reduce biofilms. An alternative approach to reclamation is to incorporate a 'tight' membrane in a membrane bioreactor to achieve higher quality permeate. A radical concept is to use membrane distillation as the separation stage [16].

The MDBR requires the reactor to operate at elevated temperature, such as 50 C, to provide sufficient driving force, so it uses thermophilic bacteria. A limitation of the MDBR process is that to avoid high energy penalty and GHG emissions it must be operated on waste heat. However if waste heat is available the MDBR provides a low GHG approach to reclamation.

Membrane Bioreactors. The MBR is now well established, but improvements may be possible by optimization of bubble size in air sparging. A more radical approach could be to replace or supplement the air scour my mechanical vibrations [17]. In the context of MBRs there are several approaches to 'lower carbon' solutions. The overall wastewater process provides conversion of the biodegradable organic carbon to CO_2 and the conventional aerobic MBR requires net energy input for aeration and membrane fouling control. The incentive to reduce net GHG emissions makes anaerobic processing more attractive if the methane generated can be captured and used to off-set the energy required to run the process. For municipal wastewaters this is more challenging due to the lower carbon load, and potentially lower yield of methane per unit carbon. An interesting option is to combine anaerobic processing (UASB or AnMBR) with polishing in an 'engineered' algal-bacterial MBR that treats the CO_2 and residual carbon. Clearly there are many technical challenges in harnessing the potential energy off-sets in anaerobic processing as well as opportunities for membrane technology. It will be important to quantify the benefits by LCA of the GHG emissions. Finally the direct production of electrical power from biodegradable carbon has been demonstrated in the microbial fuel cell (MFC) [18]. Improved membrane technology will be part of this development.

Decentralization. Decentralized membrane systems, such as water filters and MBRs, can provide benefits from a sustainability perspective [19] as well as potentially tackling the Millenium Development Goals for developing regions. However to apply membranes successfully in decentralized systems we need to make advances in several areas including lower system costs and affordability, minimization of energy demand, maximization of nutrient removal for beneficial use, and developing integrity monitors that are low cost, reliable and remotely accessible.

In Conclusion: the future for membrane separations is very strong. It can be anticipated that membranes will play a key role in a vast range of applications and particularly in critical areas such as the Water Industry (possibly in combination with nanoparticles, engineered biofilms etc), in GHG abatement including CO_2 management and energy (fuel cells etc).

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