Technology Readiness Level: 4
Component and/or Breadboard Validation
in Laboratory Environment

Eltron Research
& Development

Tech Brief

High Stability Membranes for Nanofiltration and Reverse Osmosis

Today's state-of-the-art reverse osmosis (RO) and nanofiltration (NF) water filter membrane technology can provide excellent salt rejection (up to 99.8%) with moderate to good recovery at filter pressures below 600 psi.

One of the primary limitations of current membrane technology, however, is rapid degradation by strong oxidizers such as chlorine or transition metals. Current industry standards have settled with 1000−2000 ppm-h of chlorine exposure stability because the next level of stability that can be economically justified is on the order of a 50 to 100-fold increase, which cannot be achieved with current technology.

Standard thin film composite membrane, cross sectional SEM image (50µm scale)

Membrane fouling by sediments or microbial growth and delamination caused by intermittent use are also significant failure mechanisms in abusive environments. Significant advances in membrane stability have occurred slowly and incrementally over the past 30+ years of technology development, yet much greater advances are necessary to increase the economics and profitability of water filtration and desalination processes from the status quo.

Current Approaches

Spiral-wound and hollow-fiber membranes are the most widely used filter forms in membrane separation processes. Spiral-wound membranes utilize thin film composite membranes that incorporate a semipermeable barrier layer that provides their ion-rejecting properties. The best performing semipermeable barrier layers are based on highly crosslinked aromatic polyamide or polyimide materials that are generally common throughout the industry. Most advances in membrane performance for RO and NF applications are made by the use of additives in the general polymer formulations or incremental improvements in process conditions. In the case of polyamide membranes, the same base polymer discovered more than 25 years ago by Filmtec (soon after obtained by DOW) is still one of the primary industry standards used today with slight variations between manufacturers. Some of the best improvements recently have been increasing resistance to fouling by producing membranes with more hydrophilic surfaces.

Benefits

- Exceeding 19,000 ppm-h chlorine tolerance for sulfate rejection
- Stable to high concentrations of transition metal ions and catalytic metals
- High water recovery, approaching 60% at 600 psi feed pressure
- High rejections for both magnesium and calcium, as well as sulfate
- Similar performance under brackish water and seawater conditions
- Good fouling resistance to humic acid proteins
- Tolerant of abusive and intermittent use
- Materials costs are comparable to conventional technology
- Long shelf life—years

Issues

The most obvious ways to reduce the cost of membrane filtration processes are to decrease water pre-treatment requirements, eliminate membrane failure mechanisms, and increase process throughput. Approximately 30−60% of RO filtration cost is related to pre-treatment of the water prior to reaching the membrane filter plant. This is to minimize fouling, biofouling, and oxidative degradation of membrane performance as these are the most costly membrane failure mechanisms. Increasing water throughput, of course, increases the overall efficiency of filtration. Making significant steps towards any of these improvements will require a significantly different approach to membrane design at the molecular level. The ability to manipulate structure and stability of semipermeable membranes for NF and RO filter applications is very challenging with industry-standard technology. Membrane pore structure is currently an intimate part of the polymer backbone structure, which limits significant changes from being made to one without affecting the other. Dramatically new polymer design approaches and materials are necessary to break away from the constraints of current polymer technologies.

Eltron's Strategy

A new family of polymers has been developed at Eltron with a significantly different approach to polymer design. The result has been development of semipermeable membranes that are 10−20 times more tolerant to oxidizers such as chlorine, stable to continuous contact with transition metals, good mechanical durability, and increased filtered water production at low pressures (up to 50% greater than comparable membranes).

Comparison of sub-micron surface morphology, SEM surface images

Eltron's polymer systems are unique in that they partially decouple the polymers' supporting structure from the pore structure providing the chemical flexibility necessary for strategic design. Having the ability to manipulate electronic effects, charge density, pore size/structure and hydrogen bonding somewhat separately from the basic polymer backbone structure is a significant breakthrough in itself.

On the molecular scale, this has allowed us to examine a wide variety of membrane formulations and chemical substitutions to determine how to alter water permeability, manipulate electron density for structural stability, manipulate charge density for ion rejection, and examine new polymerization reaction mechanisms to improve processing and product consistency. On the microscopic scale Eltron's polymer membranes can also be made with smooth surface morphology, which has increased fouling resistance and makes them easier to clean.

These advancements have been made while keeping the process conditions compatible with current production methods and keeping material costs comparable to current technology. Eltron's membranes are compatible with a variety of substrate types, the most common being polysulfone and polyethersulfone. Membranes are produced on the demonstration scale (41 in2) and tested under a variety of application conditions using planar cross-flow filtration systems common to the industry.

Recent studies of these materials have demonstrated several approaches for improving membrane performance even further. Work is currently underway to implement several significant improvements in stability, salt rejection, and water permeability.

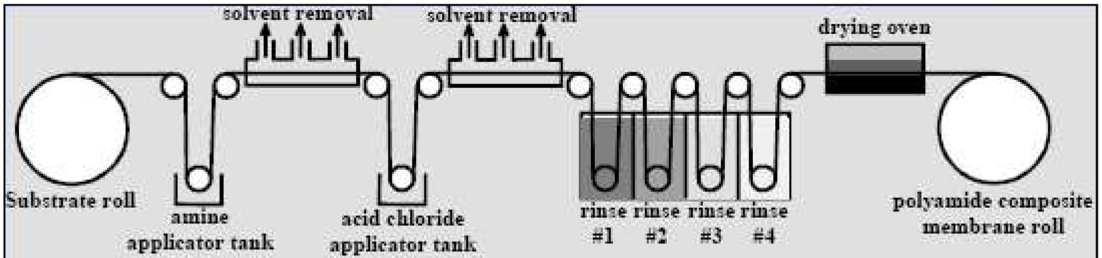

Diagram of the general polyamide thin film composite membrane fabrication process

Examples
Membrane performance specifications have been established for two of Eltron's new membranes. One example is given here illustrating ion rejections and estimated water recovery under a variety of conditions. The most significant differences from current industry performance standards are indicated in bold.

<u>Operating Limits</u>			
Membrane Type:		ER-HF2, thin film composite	
Operating pressure:		75-200 psi	
Maximum operating pressure:		600 psi	
Free Chlorine Tolerance:		**10,000 ppm-h** (overall rejection)	
		>**19,000 ppm-h** ($MgSO_4$)	
Maximum Feed SDI:		5 (humic acid, cheese whey)	
pH Range:		2-11	
Minimum Feed Flow Velocity:		0.5 m/s at 100 psi	
Shelf Life:		**years**	
<u>Stabilized Salt Rejection</u> (200 psi, 20°C)			
$MgSO_4$ (2000 ppm):		Mg^{2+}	92-96 %
		SO_4^{2-}	97-99.4 %
$CaCl_2$ (2000 ppm):		Ca^{2+}	96-97 %
		Cl^-	94-96 %
NaCl (2000 ppm):		Na^+	52-65 %
		Cl^-	58-68 %
$CuSO_4$ (200 ppm, pH 5.1):		Cu^{2+}	77-81 %
		SO_4^{2-}	73-75 %
<u>Seawater (4% salinity, 400 psi)</u>:			
	15% recovery*	SO_4^{2-}	97-98 %
		Cl^-	45-47 %
		Mg^{2+}	82-84 %
		Ca^{2+}	78-83 %
<u>Stabilized Permeate Flow</u> (2000 ppm $MgSO_4$, 20°C)			
200 psi	135 L/h/m^2	(79.5 gfd)	19% recovery*
100 psi	68.1 L/h/m^2	(40.1 gfd)	9% recovery*
75 psi	51.5 L/h/m^2	(30.3 gfd)	7% recovery*

* % Recovery estimated for a standard 40 in. spiral wound module with 34 mil feed spacer and 38 inch feed flow path length.

The water permeation rate of the ER-HF2 membrane above is near 51 L/h/m2 (30 gfd) at 75 psi feed pressure and has recently been improved to as much as 70 L/h/m2 (41 gfd) at 75 psi feed pressure (approximately 10% recovery) **without loss of salt rejection**. This is a 37% increase in water permeability obtained by strategic alteration of the hydrogen bonding strength around the membrane pore structure.

Recent discoveries about the polymerization reaction mechanism have greatly improved the consistency of process conditions and repeatability of membrane performance. This has also opened the door to a vast number of new possibilities for improvements in polymer formulations. One of them to be implemented in the near future is further stabilization of the ER-HF2 membrane material to strong oxidizers such as chlorine, hydrogen peroxide, and ozone. **This is likely to result in stabilities approaching the 50 to 100-fold improvements sought** by the filter membrane industry.

Increasing the salt rejection capabilities of this new family of membranes for desalination applications is also underway. Several design approaches are being used to decrease pore size and increase charge density around the pores in this family of membranes.

In summary, many new opportunities exist for advancing semipermeable membrane filtration technology for NF and RO applications using Eltron's successful revolutionary approach to polymer structure engineering. The ER-HF series of membranes are a solid foundation on which to further develop membranes with an unprecedented **combination of stability *and* salt rejection *and* water permeability**.

Stage of Development
Prototype systems are currently being tested and fabricated.

Eltron has a related patent application filed with the USPTO 12/170,036 *Semipermeable Polymers and Method for Producing the Same.*

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