An overview of measurement needs and developments for water treatment membranes

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INTRODUCTION

The figures-of-merit for the entire spectrum of membrane science and technology may be summarized as speed, selectivity, and stability. These are defined as: *speed*—how productive is the membrane (and the process using it); *selectivity*—how good is the membrane at making the desired separation; and *stability*—how long will the properties stay at their desired level. The challenge of characterization is to identify tractable, reproducible, and accurate measurements that are significant with respect to predicting a membrane's performance along these criteria. The "customers" for membrane characterization are: scientists, who are interested in developing new membranes; production engineers, who are optimizing the membrane production processes in order to make high quality, economical membrane products; and process developers, who are using membranes to achieve some desired end-use objective. They all need a variety of measurement methods to fit their various goals.

Researchers in the fields of polymers, materials, physics, and physical chemistry, as well as, membranologists, have developed and refined a variety of experimental approaches for probing bulk, surface, and phenomenological properties of membranes. In general, there are three broad divisions of characterization:

1. *Measurements that are made before you use the membrane.* These measurements describe what you are starting with and, for example, would include determination of the pore size distribution in a porous membrane, or free volume in a dense film.
2. *Measurements that are made while using a membrane.* Obtaining mass transfer figures-of-merit, or quantifying flux decline/fouling phenomena are examples of these characterization data.
3. *Measurements of material properties after using the membrane.* This category includes microscopic and/or spectroscopic measures of surface chemistry or absorbed species after a membrane is used.

Clearly, many of the same instruments and experimental methods can be applied in more than one of these categories, but the discerning practitioner will realize that, in such cases, the interpretation of the resulting data may not always be the same. For example, data obtained when measuring streaming potential on a "fresh" membrane in a well-defined electrolyte is more straightforward and "well-behaved" than data obtained from a "fouled" membrane where possible sorption/desorption phenomena at both the membrane and the electrodes are possible sources of measurement artifacts.

Water Treatment

It is well-recognized that the compositions of the permeate and retentate streams produced by any membrane process will depend on the operating conditions. Primarily, this relationship corresponds to the effects of fluid phase mass-transfer on the actual solute concentrations that are present at the membrane-fluid interface. Thus, an objective of *any*

standard method for characterizing membrane performance is to provide some parameters that can be reasonably incorporated into engineering design models, so that performance can be extrapolated to some other operating conditions, and/or feed stream compositions.

Membrane processes for water treatment accesses a subset of the general membrane characterization methods, in all three of the aforementioned divisions, though, in practice some specifics of the protocols change because of differences in the feed compositions involved. For example, an ultrafiltration process in water treatment might be concerned with the membrane's retention of water-borne bacteria or various colloidal species, while in the pharmaceutical industry the same membrane might be used but the solutes of interest would be specific therapeutic proteins. In either case though, retention measurements would be performed to identify a nominal relative molecular mass (MWCO) or size cut-off, but the solution compositions chosen would likely be different. This is not necessarily the best practice because it can lead to confusion and unnecessary lab and pilot scale tests. Thus, the development of "standard" characterization protocols can provide many advantages.

Technical Needs Assessments

A report by the AWWA Membrane Technology Research Committee (J. of AWWA, 90 (6), 91 – 105, 1998) found particular needs for research in four areas (the following points are excerpted directly from the Executive Summary):

- *Basic interactions between membranes and foulants.* Because the filtration properties of membranes are directly related to the materials making up the membrane, it may be possible to select or modify materials to produce membranes that will filter given foulants Attacking this problem will, in turn, foster research into the characteristics of membrane surfaces, the nature of natural organic matter, and processes involved in adsorptive fouling.

- *The mechanism that makes membrane cleaning practices effective.* Few reports document cleaning procedures that remove specific foulants or performance of membranes after cleaning. No published reports describe optimal cleaning frequency or the effect of cleaning on membrane life.

- *The removal efficiencies of specific compounds and pollutants.* A database that compiles this information would be used during investigations of many other topics.

- *The toxicity of membrane residuals.* Topics ripe for investigation include common-ion toxicity, possible hazards posed by high concentrations of pathogens in some residuals, and the recovery of contaminants (such as radium or fluoride) that may have commercial value.

It is clear that, in order to effectively conduct membrane technology research and development, it is imperative that the results of the many academic, government, and commercial groups be inter-comparable. Significantly, in the former report, the discussion on *Design And Scaleup Of Membrane Systems*, included a subsection on scaleup of pilot- and bench-scale results that contained a number of points of debate with respect to how these tests are conducted and the appropriate interpretation. For example, when performing rapid bench-scale membrane tests, points of protocol-inconsistency include the number of membrane samples needed in order to address membrane variability; membrane pretreatment; the length of time to run measurements; and the appropriate amount of concentrate recycle that may be used. In fact, the issue of concentrate recycle during both bench-scale and single-element tests, often brings up the question as to whether specific foulants are exhausted during the tests (e.g., adsorption onto the membrane surface or precipitation in the feed tank.)

As a simple example of the variability of the result of membrane pretreatment with pure DI water to remove the manufacturer's humectants (wetting agents), consider Fig.1. Fig. 1 presents the area normalized (g/m^2) total organic carbon (TOC) removed versus cumulative
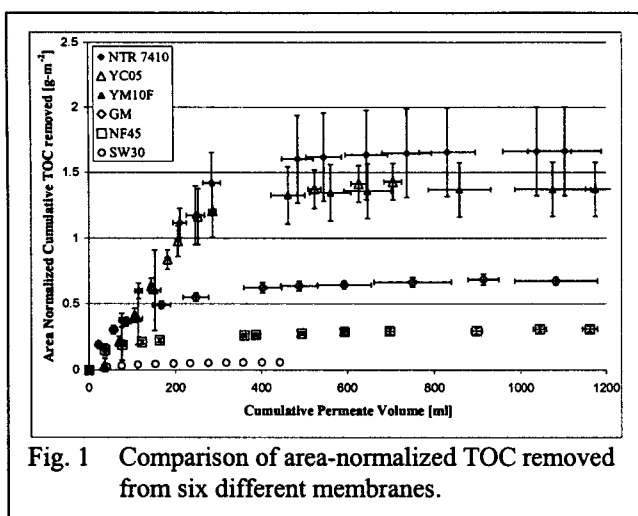
Fig. 1 Comparison of area-normalized TOC removed from six different membranes.

permeate volume collected for the six membranes studied under constant flux and temperature. Variations in membrane permeability are represented in the x-axis uncertainty bars while variations in the TOC removed are included in the y-uncertainty bars. These results show that different membrane materials (e.g., NTR 7410 vs. NF 45) require different volumes of DI water to remove carbon-based humectant so that it does not influence further studies relying on organic carbon measurements at the bench scale. The entire study confirmed that a thick membrane and/or a membrane with relatively high MWCO is capable of retaining a larger amount of humectant during membrane production. Clearly, any standard protocol must ensure that most of the carbon-based humectant is removed prior to transport and/or rejection studies.

European Activities (Charmme Network)

Members of the European Community recently completed a discussion group project entitled *"Harmonization of Characterization Methodologies of Porous Membranes"*. This group of 20+ organizations considered the membrane and membrane process properties that are important for "harmonization" or consistent standards. There were 4 working groups: (1) Porosimetry; (2) Flux and Retention; (3) Surface and Electrical Properties; and (4) Mechanical, Chemical, and Thermal Properties. The groups made recommendations for standard protocols in several (but not all) areas. Their plan going forward is for independent groups to take these recommendations and build upon them. A formal report of their activities is expected to be published sometime in 2003.

Standard Protocols Under-Development at NIST and Reclamation

NIST has supported a Membrane Science and Technology (in various forms) since the mid-1980's. Since the mid-1990's the group has worked closely with a variety of US government agencies but most-vigorously with the US Bureau of Reclamation to perform basic research and development on measurement techniques and models for characterizing membranes and membrane processes. At the current time, this collaboration has the following projects (in various states of activity) that are devoted to standard protocols that address issues in water treatment processes.

Standard test mixture. This is an ongoing project that has been conducted with additional support from the US Army and in cooperation with the University of Colorado-Boulder and the Colorado School of Mines. A synthetic, complex standard solute mixture was developed to facilitate reproducible measurements of flux decline and other important figures-of-merit relating to membrane processes. As a result of natural water quality changes from seasonal variations and weather events, and the large volume of water required to perform studies over time, there is a need for a standard fouling mixture that minimizes these variations. Thus, in general, an ideal synthetic complex feed solution would have some or all of the following characteristics: 1) readily available in large quantities; 2) known composition; 3) composition that does not change over time and is not susceptible to
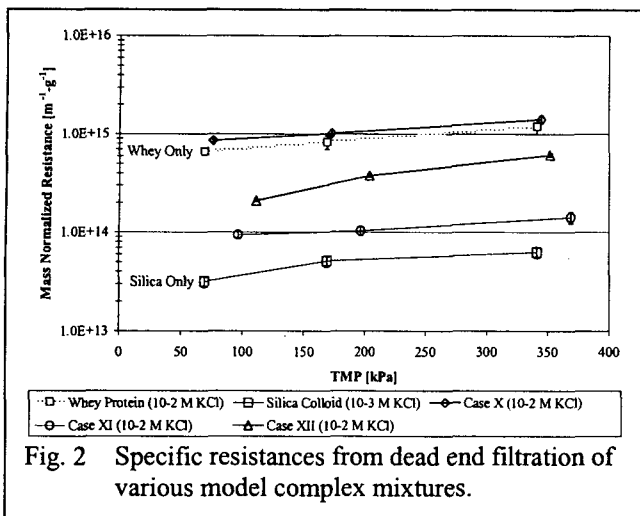
Fig. 2 Specific resistances from dead end filtration of various model complex mixtures.

microbial degradation or transformations; and 4) commercially available for use in laboratory investigations worldwide. Two different types of melange components have been initially selected for this investigation. A silica sol (Snowtex ZL, Nissan Chemicals Tokyo, Japan) is the colloidal component. Whey protein (PowerPro, Land O'Lakes, Arden Hills, MN, USA) was selected as a macromolecular protein component that also contains a variety of smaller molecules. inorganic salts and pH adjustment are the components that can be adjusted at will.

Table 1. The mixtures in Fig. 2

Case	Description	Molar Ratio (Whey:Silica) [x 10⁻⁴]
	Whey only	
X	Natural Water Analog	182
XI	Silica Dominant	0.045
XII	Protein Dominant	0.466
	Silica only	0

Fig. 2 illustrates some of data we have collected thus far. Using dead-end filtration the specific cake resistance has been carefully measured for several combinations of the components (as listed in Table 1.)

Pore Size Characterization Methodology and Standards for Ultrafiltration Membranes. This ongoing project was developed through the NAMS-facilitated R&D initiative. Presently, six organizations are part of the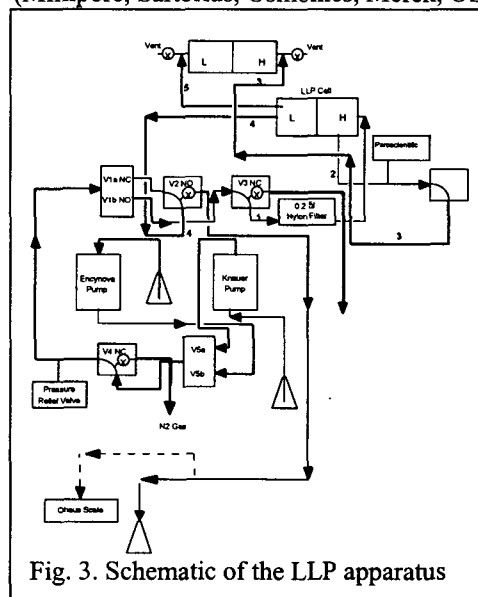 consortium (Millipore, Sartorius, Osmonics, Merck, US Bureau of Reclamation, and NIST) and the project focuses on protocol development for liquid-liquid porosimetry and standard solute retention (MWCO) measurements.

The two primary tasks are (1) to develop a "standards-quality" apparatus and protocols and analysis techniques for physical characterization of the pore size and distribution of ultrafiltration membranes using liquid-liquid porosimetry (LLP), and (2) to develop a standard protocol for a solute retention of the same membranes. The cross-correlation of the data from the two characterization tests should help membrane manufacturers and end-users to better communicate with each other about the expected mass transfer properties of the membranes. Our protocol for LLP involves using a very accurate positive displacement pump (e.g. an HPLC pump) to provide a "controlled" volumetric flow rate of the displacing

Fig. 3. Schematic of the LLP apparatus

fluid phase, and measuring the differential pressure across the membrane that the flow produces as it "opens" more pores from the wetting fluid phase. Fig. 3 presents a schematic of the apparatus and Fig. 4 illustrates the type of data that is collected.
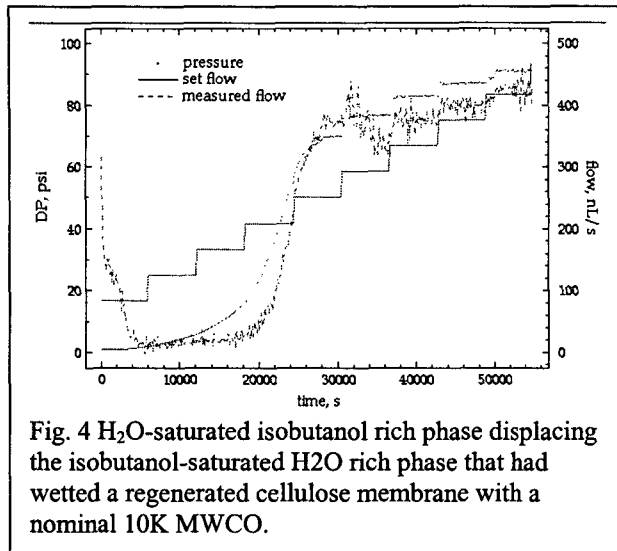

Fig. 4 H₂O-saturated isobutanol rich phase displacing the isobutanol-saturated H2O rich phase that had wetted a regenerated cellulose membrane with a nominal 10K MWCO.

In Fig. 4 there is an initial pressure spike until some pores are opened then the measured flow rate and differential pressure track one another. The measured flow does not follow the "stepwise" increases in the pump flowrate until the higher flowrates. At the present time we have not yet identified an operating protocol that yields self-consistent results

Membrane Integrity Test. An apparatus has been developed to measure the unsteady permeation of pure water through permselective reverse osmosis and nanofiltration membranes under an osmotic pressure gradient. The key component of the apparatus is a capacitance-based level sensor with a resolution of approximately 5 nL/s. The measurement protocol is based on the familiar time lead analysis that assumes the membrane is presaturated with water. Fig. 5 presents initial measurements of the unsteady water back-diffusion through a seawater RO membrane, that was exposed to varying levels of free chlorine illustrate the utility of the apparatus for monitoring subtle changes in a membrane's material properties. An appropriate unsteady diffusion model can be used to quantify the results in terms of two membrane parameters: one which relates to water mobility and another related to water solubility. Of course, "gross" damage to the membrane removes its capability of supporting the osmotic pressure gradient that is easily detected with this measurement.
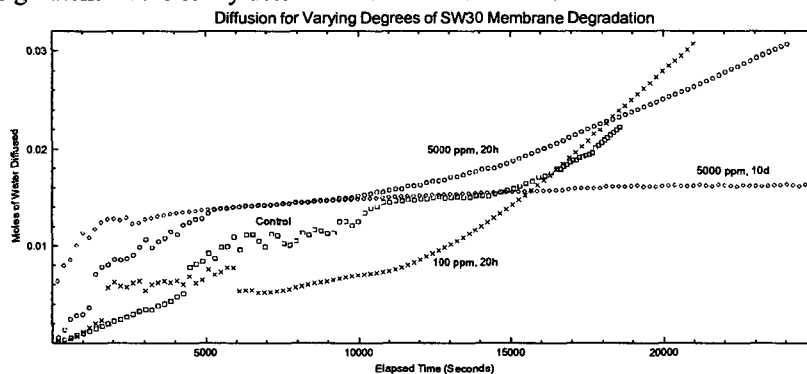

Fig. 5 Water diffusion through a seawater RO membrane exposed to various levels (time and concentration of hypochlorite.