Membrane filtration:

What’s new in membrane filtration?

In his series of articles covering progress in a number of broad classes of filtration and other separation equipment types, Ken Sutherland looks at developments in membrane media and membrane filtration systems.

The wide, and steadily less and less expensive, availability of the membrane, in all of its forms, as a filter medium has made a tremendous difference to the ability of the filtration industry to achieve very fine levels of separation. Improvements in membrane systems of all kinds have been made possible by the continual production of new materials from which membranes can be made. There is now a very wide range of materials with specific properties that can be utilised to make membranes with improved system performances.

In its early days as a separating medium, the membrane was a thin flexible sheet or a thin-walled flexible tube, rendered semi-permeable by its production process. This characteristic of flexibility has remained associated with the membrane, but the widespread existence of the rigid ceramic membrane makes it very difficult to provide a simple definition for a membrane. In fact it is probably better to define a membrane in terms of what it does, rather than what it is: so that a separation membrane is a semi-permeable material able to retain suspended or dissolved substances at levels in the region of a few micrometres, down to a few tenths of a nanometre.

The earlier applications for membranes covered reverse osmosis, primarily for the desalination of water (in the size range up to around 400 Dalton or about 1.5 nm), and ultrafiltration, widely used for the removal of dissolved organics and larger inorganic ions (in the size range 0.3 to 500 kD or about 1 to
200 nm). The two major liquid processing changes that have occurred have been the appearance of nanofiltration overlapping the top end of reverse osmosis and the lower end of ultrafiltration (covering around 50 D to 5 nm), and the extension of membrane separations into the microfiltration range (from around 50 nm up to 2 µm or more). This latter move, into microfiltration, has greatly increased the applicability of membrane media in separation processes, and microfiltration uses are approaching the largest component of the total membrane market place.

In addition to the better known liquid separation uses of membranes, they are also widely used for gas and vapour separations, which are rapidly growing as applications for membranes. The largest is in the separation of the components of air, such that small, on-site oxygen or nitrogen plants are now commonplace, enabling the local production of these gases. The growing emphasis in global warming abatement technology on carbon dioxide capture and storage is likely to provide a huge application for gas permeation, as will any major move into hydrogen systems for better energy economy.

The membrane business

The manufacture of membrane modules and systems for the various separation processes is a sizeable business. It represents (counted at the membrane module level only) 35-40% of the total filter media market, approaching $8 billion in 2009, and is the fastest growing of the media market segments. Not surprisingly, in a business of this size, there are some large players, such as Degrémont, Dow Chemical, DuPont, GE (including Ionics, Osmonics and Zenon), Koch, Pall and Toray. There are many other companies involved, often a lot smaller than these, but noteworthy for some specific feature of their product range, such as New Logic with its vibrating membrane array, and the steadily increasing number of makers of ceramic membranes and membrane bioreactors.

In common with every other segment of the filtration business, corporate acquisitions among membrane suppliers have been a feature of business life. Of the 30 companies featured in the last of Elsevier's Profiles of the membrane business, published in 2004, less than half have survived unaffected by take-over activity. The two largest centrifuge companies have each bought into the membrane business (Alfa Laval with DSS Nakskov, and GEA with Membrall), but a larger observable move is into the fresh and wastewater applications, for which membrane separation makes a very good entrée – well demonstrated by the recent acquisitions of GE and Siemens. Other business expansion moves can be seen in Pall’s purchase of several of the USFilter range of companies, including Mencor; Polypore’s acquisition of Membrana; and the sale of donnick hunter to Parker Hannifin, and of Cuno to 3M. The private equity houses have been busy in the membrane business, as elsewhere, as witness the purchase of Norit, and of the expanded Polypore, by investment funds, also the assisted buy-out of Novasep/Orelis.
Membrane operating problems

Most membrane processes are characterised by two key process parameters: flux and selectivity. The selectivity is governed by the intrinsic nature of the membrane material, built into it by its method of manufacture, and measured by its permeability to the species in question. The flux is determined by the specific resistance of the membrane material under a given differential pressure across the membrane, so that the flux increases with the operating area of the membrane and with the applied pressure.

On the face of it, the membrane is an ideal filter medium, able to meet the increasingly severe demands from its marketplace for ever finer degrees of separation. In practice, there are a number of operating problems affecting all types of membrane, and much of the work entailed in the recent developments in membrane media and systems has been designed to reduce the impact of these problems.

Fouling

The main operating problem of membrane separation processes remains the ease with which the membrane plugs, causing the resistance to flow to increase. This behaviour, fouling, is caused by the deposit of slimy solids, present in the feed, on the upstream membrane surface, which eventually blocks it. The plugging process is accentuated by the concentration polarisation that occurs in the relatively quiescent fluid zone close to the membrane surface, as the species separated from previously processed fluid build up in this zone and interfere with fresh material trying to get to the surface.

The problems of fouling and concentration polarisation have found some resolution in the process arrangement that causes the feed liquid to flow parallel to the membrane surface, rather than perpendicular to it, so scouring the surface as the flow moves across it, thinning the surface layer and removing deposited material. The consequent cross-flow filtration method has been one of the most important equipment developments in the filtration industry, especially when coupled with rotating or vibrating filter systems.

Throughput

Because the resistance to flow through most membranes is high, the consequent low throughput has needed large membrane areas, and high pressures, to achieve worthwhile fluid flow rates. The history of membrane material and process development is very largely one of reduction in flow resistance, first in the diffusion membranes from reverse osmosis to ultrafiltration, and then to the microporous materials of microfiltration. A similar relaxation occurred in the move from reverse osmosis to nanofiltration.

Mechanical strength

The first membranes were relatively weak materials, hence their use as hollow fibres, which are intrinsically strong. As new materials were developed, strength was often not the first priority, and modern membranes can be very thin, with low tensile strengths. The saving move from the point of view of strength has been the development of the composite membrane, in which the active separating layer is supported on one or more substrate layers, which give the necessary strength to the finished membrane.

Cost

The earliest membranes were expensive to make and lasted only a short time. Coupled with these operational costs was the cost of high pressure operation. Developments both in membrane materials and system design have resulted in a marked reduction in membrane cost, measured in filtration area or process throughput, which has reduced exponentially with passing time. The overall speed of reduction has, of course, been affected by the development of new and initially more expensive materials, both organic and inorganic, but these have in turn followed a similar cost reduction path.

Corrosion resistance

The majority of membrane applications feature relatively bland conditions, but increasingly, as membranes have found application in the chemicals and pharmaceutical sectors for example, corrosive environments have become involved in processing. This has provided an opportunity for ceramic and other inorganic membranes to take the place of less resistant polymeric membrane media, although newer membranes made of fluorinated polymers, such as PTFE and PVDF, show marked resistance to chemical corrosion.

Temperature resistance

Just as polymeric membranes are not well suited to highly acidic or alkaline environments, so too are they not well suited to higher temperature applications. Even with the use of fluorinated polymers, temperatures much above 150°C are not easily handled, and here again the ceramic membrane has found ready application, although the module must then take a form suited to ceramic materials, such as the monolith or...
coarse tube. More recently, ceramic materials made from fibres have enabled some flexibility to be built in, and hollow-fibre ceramics are now being made available.

Feed quality

The hollow fibre format is a very successful one, because the fine tube structure resists high trans-membrane pressures very well. A disadvantage of this format is the need for the fluid flow to occur in very fine passageways, and thus be prone to blockages caused by the presence of large particles. As a consequence, the finer the membrane separation process, the more carefully must the feed solution be filtered to ensure the absence of blockages. Good pre-filtration is also a help in controlling the effect of fouling, as the excess of solids that causes concentration polarization can be removed in the pre-filtration stages. It is not uncommon now for a membrane process to consist of a train of units, in order of diminishing cut-off points.

Solids handling

Membrane systems, especially in hollow fibre and spiral wound formats, are not well suited to the handling of feed suspensions with high suspended solids loadings – hence the need for efficient pre-filtration. However, other formats can accept more concentrated solids, and membrane systems are being used as thickeners as well as clarifiers.

Permeate treatment

One of the major effects of the wider use of membrane systems is that impurities that were quite dilute in the feed stream become concentrated in the retentate. This can create a toxic waste stream, which may require that a special retentate treatment process be built on to a membrane installation.

Energy conservation

Some membrane processes, reverse osmosis in particular, operate with high trans-membrane pressures. The need for high operating pressures means that high energy consumptions are involved – and the pressure in today’s world is for energy consumptions to be reduced. In the case of filtration, this drive to more efficient use of energy directly opposes the major driving force represented by the need to provide ever-finer degrees of separation. This dichotomy is not easily resolved, since filter media that separate more efficiently usually need higher pressure drops to do so. Much development activity is being put into the production of media with lower pressure drops, such as the membrane materials formed from a surface layer of fine fibres, like Donaldson’s ‘Ultra-Web’ and the ‘Nanoweb’ media supplied by Hollingsworth & Vose.

Recent developments

The membrane operational problems already discussed have been well known for some time, even in the relatively short lifetime of membrane separations, and the methods adopted for their control are well understood: composite materials, fluorinated and ceramic membranes, agitated cross-flow, efficient pre-filtration systems. Some more recent developments, all aimed at better membrane systems, are highlighted in the remainder of this article.

Recent developments in membrane materials and formats

Polymeric media are by far the most widely used materials for membranes, but other semi-permeable materials are also receiving considerable attention, and the ceramic membrane is growing rapidly in range of application. Particularly noticeable is the availability of ceramic membranes in hollow-fibre and flexible sheet formats. They are also being made by the sintering of very fine spherical particles, enabling the creation of pores as low as 0.3 nm in diameter, and from very finely spun fibres. An important development in membrane materials is the ability to make smart or functional membranes, such as those with appropriate chemicals grafted onto their surface, which can then be very selective for certain chemicals (such as enzymes), or which enable them to resist fouling more easily.

Although still at the small scale, the development that offers great promise is the rotating or vibrating membrane unit, with mechanical movement employed to reduce the thickness of the boundary layer at the membrane surface.

Recent developments in membrane applications

The standard membrane processes for liquids processing (RO, NF, UF and MF) are now reasonably commonplace in bulk industries, as well as their original niche applications. The demands for clean water, free of pathogens such as bacteria and viruses, have propelled membrane processes to the first level of consideration in fresh and recycled water processing. Sterilisation of a liquid flow is now possible by passage through a UF membrane.

Ultrafiltration is, in fact, becoming the pre-filter of choice ahead of reverse osmosis desalination plants, and membranes are being employed with great success in the microfiltration range, where until relatively recently, they could not have been considered. A prime example of the latter situation is the rapid spread of the microfiltration-based MBR (membrane bioreactor), combining a biological process to treat a waste liquid with a membrane separation process to clean the treated liquid. The membranes now available for use in MBRs operate satisfactorily with very low transmembrane pressures, and this has become an important component of the membrane market.

The expansion of membrane separations into the microfiltration range is being driven by the market’s wish for finer degrees of filtration of its products (or waste streams), to match its customers’ demands for cleaner final products or the demands of environmental regulators for less contaminating effluents. In whichever part of industry or commerce there exists a need for fine filtration, in the 1 µm region or below, then the chances are that it will now be met by a membrane separation process.

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