INTRODUCTION

Membranes are selective barriers normally used to separate two homogeneous phases at least one of them being a fluid (Fig. 1.1). They can be porous or non porous, the former being more common. In case of porous membranes pore size is the key parameter which determines the effectiveness and efficiency of the membrane. Separation occurs under a pressure gradient or sometimes under an electrical potential gradient, associated with or without a catalytic reaction. Systems which can be separated, are solid particles suspended in a fluid medium and mixtures of two different liquids or gases. Separation through a membrane is schematically shown in Fig. 1.1. Porous membranes are typically classified according to their pore sizes in the following manner:

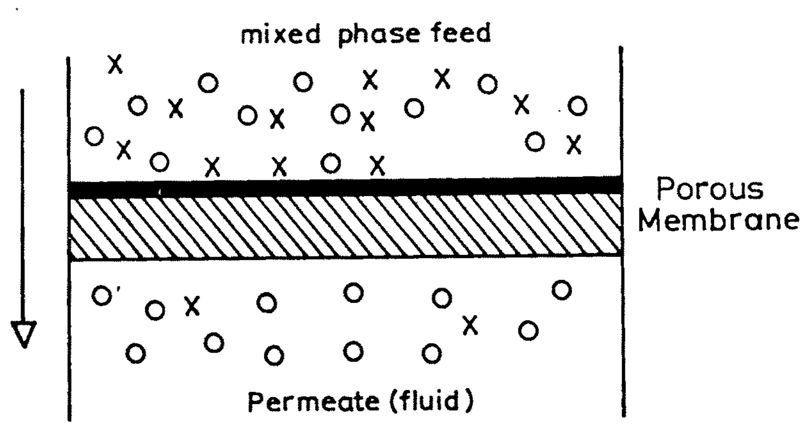

Fig. 1.1 A membrane as a selective barrier between two homogeneous phases (ref. 16)

1. Reverse osmosis (RO) and gas separation membranes have pore sizes of less than 1nm and are used to separate species in the molecular or ionic level.

2. Ultrafiltration (UF) membranes have pore sizes in the range

of 0.001 to 0.02 μm and are used to separate various macro-molecules from a liquid medium.

3. Microfiltration (MF) membranes have pore sizes in the range of 0.02 to 2 μm and are normally used to remove suspended solids from a fluid medium.

4. Membranes with pore sizes 2 to 10μm are used for fine filtration.

This classification of membrane separation processes is pictorially represented in Fig. 1.2.

Reverse osmosis and ultrafiltration are perhaps the first known continuous molecular separation process that does not involve a phase change or interphase mass transfer. The removal of solvent such as water is accomplished without a change in its state from liquid to vapour (as in evaporation) or liquid to solid (as in freeze concentration). Membrane processes can thus also be operated at ambient temperatures if necessary. This avoids product degradation problems associated with thermal processes, thus resulting in products with better functional and nutritional properties particularly in case of food processing.

For these reasons, energy requirement is also low compared to other dewatering processes. Typically, while open pan evaporation may need over 600 KWH/ 1000kg water removed and a 5-7 effect evaporator requires 37-53 KWH /1000 kg, reverse osmosis for desalination requires 5-20 KWH /1000 kg water removed. In addition, no complicated heat transfer or heat generating equipment is needed for membrane separation, electrical energy is required only electrical energy to drive the pump motor.

Depending on the field of application, various materials have been used for preparation of the membrane. Most of the membranes, presently in use, are made of polymeric material which include polysulphone, cellulose acetate, nylon, polyester, poly-amide, polyvinyl chloride etc. In recent years, inorganic membranes utilising alumina, cordierite, mullite, silicon carbide, silicon nitride, zirconia, silica, titania etc. are gaining ground replacing polymeric membranes in several areas of application. Besides organic and ceramic membranes, porous metallic membranes made of stainless steel, monel metal, nickel, hastalloy, silver, inconel are also commercially available specially for particulate filtration.

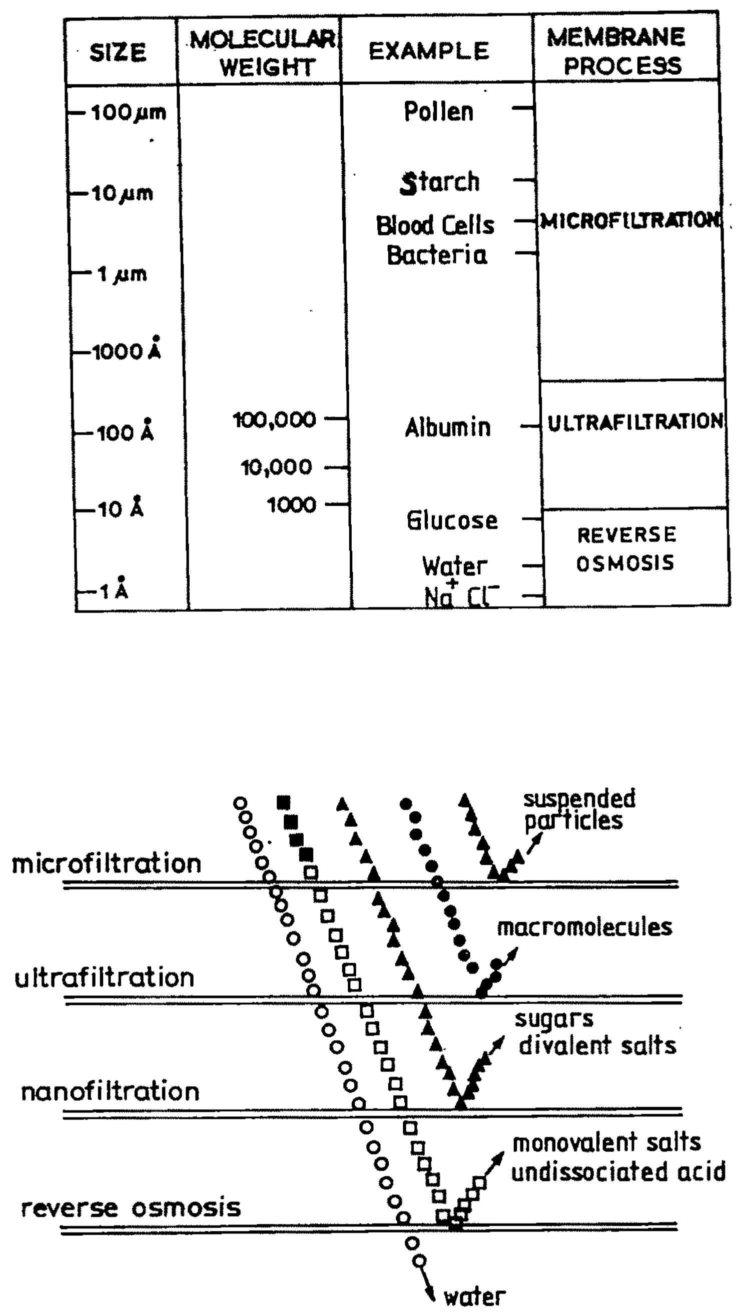

Fig. 1.2 Pictorial representation membrane separation processes

Among the above three classes, ceramic /inorganic membranes are lately receiving more attention because of their several advantages over polymeric membranes. Some of these advantages are described below:

(1) The priamry advantage of ceramic membranes is their thermal stability. The thermal inertness of the membranes readily permits long term operation at elevated temperatures. This advantage is of special interest in applications in which the natural feed temperature is high. High temperature reduces viscosity of the feed material, thereby increasing the membrane flux. A related advantage is the practicality of steam cleaning and sterilising of the membrane devices in food, dairy, beverages and pharmaceutical applications.

(2) Ceramic membranes have shown very long life in many applications, from 3 to 5 years. Depending on replacement cost relative to the competing polymeric membranes, this normally results in reduced operating cost.

(3) An outstanding advantage of ceramic membranes is their ability to withstand prolonged exposure to non aqueous media. This capability makes them suitable for separation of hydrocarbons and various organic solvents used in a variety of chemical industries.

(4) Another advantage of ceramic MF and UF membranes is their chemical stability over a wide pH range. This advantage can be important for applications in which feeds with extreme pH, especially on the alkaline side, are used. It can also pertain to cleaning cycles in which hot caustic or acid is used for cleaning.

(5) Ceramic membranes can resist high pressures upto 30 atmospheres normally used in back flusing technique.

(6) Another advantage is associated with the membrane configuration. In general the configuration of ceramic membrane modules is tubular, or equivalent in multiple- passageway

monolith modules. That is, the flow geometry corresponds to an inside flow tubular flow path. This configuration is less susceptable to membrane fouling and more readily cleaned than many polymeric membrane devices in current use.

Though ceramic membranes have several advantages, as mentioned above, over their polymeric counterpart, still they have some disadvantages as well which may be as follows :

(1) Current ceramic membrane products have one overwhelmeing disadvantage: an uncompetitively high price. Compact, polymeric membrane modules have prices from US $8 to US $20 per square foot. Ceramic membrane have had prices of US $150 to US $200 per square foot, although some modules are available at a price as low as US $ 120 per square foot [1].

(2) Ceramic membranes produced to date have shown fragility due to brittleness associated with ceramic support materials. However, this may become relatively unimportant for large diameter multiple channel, monolithic devices.

So ceramic membranes can displace polymeric membranes only if (i) they can perform separation which can not be achieved with a polymeric product, such as producing very high solid concentrates or at high operating temperatures and (ii) operating conditions permit a substantially higher membrane flux for the ceramic membrane products, thereby making them cost competitive.

In spite of these limitations there is great interest in ceramic membranes in both the membrane manufacturing industry and also the current user industries. For liquid separation, microfiltration and ultrafiltration membrane are mostly used.

Application areas are water cleaning /filtration, clarification and sterilisation of beverages and the concentration of proteins in food and dairy industries [2-5]. A possible new application is the separation of high molecular hydrocarbon at temperatures of a few hundred degree celcius in the petrochemical industries [3].Table 1.1 summarizes some of the specific advantages of inorganic membranes in micro and ultrafiltration applications.

Table 1.1 Advantages of inorganic membranes for specific applications

Application	Advantage
Milk and beverage industries	Good resistance to cleaning in alkali media.
Biotechnology and pharmaceutical industries	Steam sterilisation
Textile, engineering and paper industries	High temperature resistance
Oil industries	High temperature and solvent resistance
Other application	Chemical, mechanical and thermal resistance

Reverse osmosis or hyper filtration membranes are used in the areas like desalting of water and separation of one solvent from another. Table 1.2 gives in detail, the application areas of the ceramic membranes.

As the inorganic membranes can be used in stringent operating conditions (complete pH range, repeated vapour sterilisations at 120^{o}C, organic solvents, temperatures upto (800 - 1000^{o}C) industries have greately benefited from this technology in the following fields: agri- foodstuffs industries, biotechnology, biomedicine, paper industries, engineering, textile and petrochemical industries [3, 6-7].

Table 1.2. Industry - wise applications for ceramic membrane

Industry	Use
Food and beverages	Clarifies and sterilizes fruit juices and vinegar; concentrates and homozenises milk and eggs: separates contituents in whey, removes phenols, tannis, cools, and heat unstable proteins for wine
Bio technology /pharmaceuticals	Concentrates vaccines and enzymes; purifies amino acids Vitamins and organic acids; removes viruses from culture broths.
Gas separation	Removes hydrogen from refinary stream, carbon di-oxide, and hydrogen sulphide from natural gas; nitrogen, enrichment; methane recovery in milling operation
Environmental control	Removes precipitated radionuclides and metal oxide, waste water processing and dewatering of hazardous waste, recycling of machining coolants etc.
Petrochemical	Waste oil hydrogenation process; catalytic dehydrogenation of large molecules at low temperatures and pressures; coal gasification
Metal refinig	Removes impurities and undesirable metal oxides from molten aluminium magnesium and superalloys.
Electronic	Purification of water, acids, solvents, and organic compounds

Fig. 1.3 compares the different membrane separation processes along with their application areas. Among different processes, microfiltration process covers the maximum area.

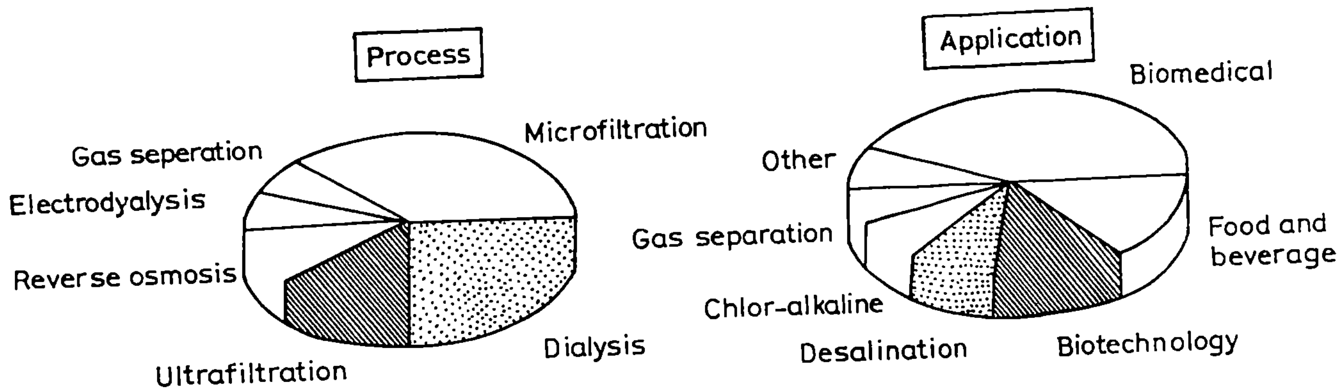

Fig. 1.3 Current market for advanced separation systems in 1990 (ref. 2)

In addition to the above areas of application there are some membrane separation applications which have not yet been commercialised only because of the lack of stability of polymeric membranes. Thus some promising new applications for ceramic MF and UF membranes include the following:

(1) Heavy hydrocarbon separation such as purification of waste lubricating oils, de-asphalting of residual oils, and colloidal ash removal from coal liquids.

(2) High temperature processing of both primary and secondary coolant of pressurized- water nuclear reactors for removal of colloidal contaminants.

(3) High temperature processing of Kraft mill black liquor for lignin removal.

(4) Bio reactor and catalytic reactor applications in which reaction and separation occurs simultaneously.

Among the different types of membranes, most commercial activity to date has been with MF, followed closely by UF. A small amount of commercial activity in pervaporation is in evidence (particularly in Japan), and negligible commercial activity can be found for gas separation membranes. This commercial evolution reflects the ease of development of the respective products. Obviously MF membranes have relatively large pores (0.1 to a few microns) and are easiest to make at a commercial scale. UF membranes, especially with pore sizes in the 10 - 30Å range are appreciably more difficult to fabricate. Membranes for pervaporation and gas separation, with pore sizes smaller than 10Å are very difficult to produce [3]. The Fig. 1.4 shows the possible growth rate of application of different types of membranes.

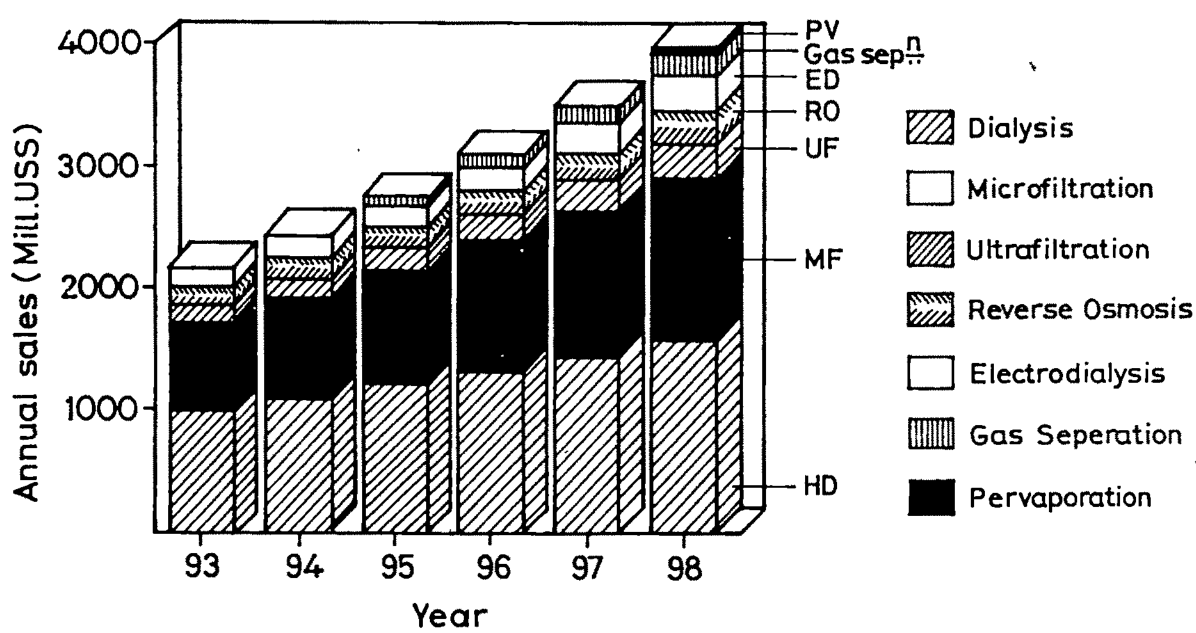

Fig. 1.4 Gradual increase in annual sales of membranes for different processes

Ceramic and other inorganic membranes have found application in many industries since about 1980. Much of the development of this technology took place in Europe especially in France. The French leadership can be traced to pioneering effort at two companies, SFEC and CEA [8,9]. They marketted the CARBOSEP membranes based on the concept of a tubular macroporous support made of carbon coated with a thin microporous layer of zirconia. The CARBOSEP membranes can work in the whole pH range of 0 to 14 and upto a temperature of 300°C under a pressure gradient as large as 15 bar and in all media.

Since then, several other firms have become interested in inorganic membranes. In 1984, a product named MEMBRALOX was proposed by a company CERAVER, a subsidiary firm of CGE. It was composed of a macroporous alumina block, bored through with multiple channels of a few millimeter in diameter, coated with a separating alumina layer [10]. The experience acquired by CERAVER in the realisation of French programme of uranium isotope separation by gaseous diffusion was of great benefit. Also in 1984 the NORTON company of USA produced a tubular ceramic membrane for microfiltration application having a composite alumina body with a trade name CERAFLO with pore diameter of 0.2 to 0.45μm [11].

The Japanese firm TDK ELECTRONICS has also marketted a microfiltration membrane of alumina, with a trade name DYCACERAM [12]. Recently a French firm CERAMFILTRE proposed a membrane prepared from silicon carbide [3].

The Clemson University of America marketted a dynamical or mixed mineral membrane called CARRE [13]. Still more recently the PECHINEY company through its subsidiary Alliages Fritts (sintered alloy) has commercialised the PORAL membrane [14], a composite membrane with a stainless steel substrate and a zirconia separating layer.

A considerable expansion of the field of membrane technique is foreseen; some studies of the sales predict an annual growth rate of the order of 10% & for organic and inorganic membranes in the decade 1989 - 99. For the inorganic membranes alone the annual growth rate should be around 30% over the same period, as shown in Table 1.3.

Ceramic membranes generally possess a multilayred structure and are composite in nature. There is a gradual decrease in pore size and layer thickness starting from the bottom layer to the top layer [16]. The bottom layer is called support with pores 1 to 15μm, middle layer is called intermediate layer having pore size 0.1 to 1 μm. Top layer is called separation layer with pore size 3 to 100nm.

Table 1.3 Summary of the sales of inorganic membranes materials (Million US $) (ref. 15)

Material	1986	1988	1989	1994	1999	89 - 99 (% Ann. inc.)
Ceramics	6	15	18	75	435	34
Carbon	0	2	3	9	50	32
Metal/ other	5	7	8	13	25	12
Glass	0	0	0	1	3	>100
other	1	2	2	4	9	16
Total	12	26	31	102	432	30

Conventionally ceramic membranes are prepared in various ways depending on the membrane material and support structure, pore size, porosity and membrane thickness. Some of the conventional fabrication techniques are (i) Phase separation and leaching particularly for porous glass membranes [17] (ii) Slip casting and dip coating particularly for polycrystalline oxide membranes [18,19].

Considering the fact, thinner the membrane higher is the permeate flux and less is the pressure gradient required, an attempt has been made in this investigation to prepare thin ceramic membranes by tape casting process which is normally used in electronic ceramic industries for making dense substrates and multilayer capacitors. This is possibly the first time ceramic membrane has been fabricated by tape casting method.

One of the primary objectives of this investigation has been to determine the optimum condition for preparation of tape casting slip for the preparation of tapes with desired porosity, pore size and pore size distribution. For this purpose, the effects of starting powder size, its distribution, tape composition and sintering condition have been studied in details.

Successful casting of tape with requisite properties and reproducibility depends upon the degree of dispersion of the powder as well as the overall composition. Tapes used for making dense substrates generally contain 7 to 10% of binder [20 -23], but in this investigation it has been tried to cast the tapes with relatively high binder content to get a fired tape with relatively high porosity.

Thin tape cast membranes have poor mechanical strength. Therefore, another objective of the investigation has been to design and fabricate a flat perforated ceramic support as the holder for this new type of membranes. The holder has been fabricated by lamination of several tape cast layers.

Finally the effectiveness of the prepared membranes has been investigated so far as their usefulness is concerned in obtaining bacteria free water particularly for micro-biological and bio-technological laboratories and also their suitability to reuse after regeneration by different techniques.