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Editorial

The demand from industry for better environmental solution and cleaner technology has put membrane technology in the fore front of separation science and technology. Membrane based separation technologies are currently proven only within a few main areas, namely, water purification and treatment of effluent waste streams, production of high purity gases and specific processes with membrane electrolysis. However its commercialization for other applications, such as, fuel cells, recovery of valuable radionuclides from high level liquid waste is yet to be realized but the trends in this direction look positive. In nuclear industry membrane based separation processes are being studied for recovery of valuable radioisotopes from high level radioactive waste. Though a lot of R&D work has been going on in this direction, membrane based separation processes are yet to be adapted on large scale in nuclear industry.

The present bulletin is an effort towards emphasizing the need for taking membrane based research from laboratory to plant scale. I am grateful to Dr. B.M.Misra for readily agreeing to my request to be the guest editor of this bulletin. I am thankful to all the contributors of the articles in this bulletin for timely submission of their contributions, but for which it would not have been possible to bring it out in time. I sincerely hope that this bulletin will ignite the minds of young scientists looking forward to pursue their career in separation science and contribute in realizing the dream of utilizing the membranes at commercial scale.

B.S.Tomar

FUEL CHEMISTRY DIVISION

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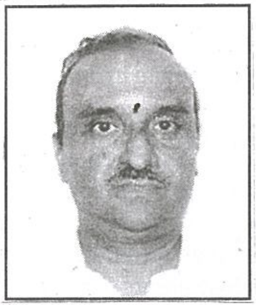
Innovative Semipermeable Membranes for Saline Water Treatment



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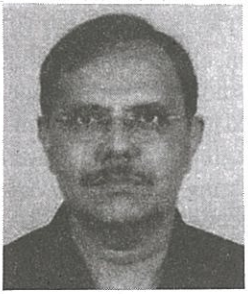

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Introduction

Synthetic polymeric membranes are primarily used as separation barriers in chemical, pharmaceutical and food industries. Permeability and selectivity of membranes are the two fundamental properties which determine the productivity of a given membrane process. Membrane processes are driven mainly by either hydrostatic pressure gradient, concentration difference or electrical potential gradient. Characteristics of some of the commercially significant membrane processes are given in Table 1. Material science of semi-permeable membranes is an

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important area and is a continuously evolving subject of research. Though synthesis of polymeric semi-permeable membranes is widely published, a large amount of literature is patented and protected.

Essential Polymer Characteristics for Membranes

The single feature which distinguishes polymers from other materials and which makes them ideal as membrane candidates is their large size and fibrous nature. The large average size of macromolecules, their size distribution, their architecture, specific nature of their chemical groups, the arrangement of these groups around the polymeric backbone and the state of aggregation of these macromolecules are the fundamental polymer properties which determine the membrane characteristics. Membrane making requires high molecular weight polymer grades from the point of integrity and processing criteria. Glass transition temperature of polymers is another important property governing perm-selectivity of resultant membranes. Rubbery polymers with low glass transition temperatures tend to have low selectivity and high permeability, whereas polymers in glassy state with high glass transition temperatures provide high perm-selectivity and low permeability. Mechanical strength of polymers is another important property of interest. The mechanical strength requirement of polymeric membranes is dictated by the chemical structure of the polymeric segments and the application intended. Polymers with adequate mechanical strength are needed for high pressure applications so that membrane performance is stable with time. Polar or non-polar nature of polymers strongly influences the solubility characteristics of the polymer and its permeability behavior. Adequate solubility of polymers is an essential requirement for membrane synthesis. With respect to reverse osmosis for aqueous applications, hydrophilic/hydrophobic balance is of major importance which is measured in terms of moisture regain at appropriate temperature and humidity.

Cellulose Derivatives

Cellulose or regenerated cellulose is the most important naturally occurring polymer for membrane applications, particularly dialysis. The best source of cellulose for membrane applications is cotton linters which contain the highest concentration of alpha cellulose (high purity and high molecular weight fraction). The high structural regularity and intermolecular hydrogen bonding of its hydroxyl groups make cellulose difficult to dissolve. Principal solvent for the manufacture of cellulose membranes is an aqueous solution of cuprammonium hydroxide.

Cellulose can be modified by reaction between suitable monomers and the active hydrogen of the hydroxyl groups to form cellulose derivatives. The most important derivatives of cellulose for membrane applications are inorganic (nitrate) and organic (acetate) esters. Cellulose nitrate (CN) was the first synthetic polymer utilized to produce filtration membranes. Cellulose acetate (CA) , being less inflammable and cheaper, has overtaken cellulose nitrate. Today CA is considered a versatile membrane polymer due to its low cost, availability in a wide variety of viscosity grades, outstanding tractability and reasonable resistance to oxidation by chlorine. CA was utilized by Loeb and Sourirajan in their classic development of integrally skinned membranes, which heralded the modern membrane era. Cellulose triacetate (CTA) is a polymer of importance for micro-filtration, electrophoresis and reverse osmosis. In reverse osmosis for single stage sea water desalination, it is used in hollow fiber form. The utility of CTA for single stage sea water desalination is due to its increasing perm-selectivity with increasing degree of acetylation. CA/CTA blend polymer provide high water permeability and high perm-selectivity for high saline brackish water desalination Limitations of CA derivatives are borderline glass transition temperatures($68.6^{0}C$) which limits its utility at elevated temperatures and pressures, a tendency to undergo rapid hydrolysis in alkaline media and a lack of resistance to attack by micro organisms.

Polyamides and polyimides

Fully aromatic polyamides (PA) are suitable as membrane polymers with exceptional chemical, thermal and hydrolytic stability and perm-selectivity. Polyamides are poly-condensation reaction products of diamines and diacids or diacid chlorides. The most important structural feature of polyamides is the CONH group, the amide link which has a strong capacity for hydrogen bonding. Optimum balance between processing feasibility and end use properties is achieved by randomizing the molecular structure through the use of meta- and para-substituted monomers . Some recent aromatic polyamides for desalination are prepared from all meta- substituted monomers, approximately 10% of whose aromatic rings are sulfonated. These aromatic polyamides lack chlorine resistance due to electrophilic substitution of aromatic rings by chlorine which disrupt intermolecular hydrogen bonding resulting in increased permeability and reduced selectivity. A number of polyamides, namely polyamide hydrazide, polyetheramide hydrazide and crosslinked polysulfonamide have proved to be useful as polymer membrane candidates capable of giving high perm-selectivity under reverse osmosis test conditions.

Polysulfones

Polysulfones(PS) are the polymeric product of the reaction between the disodium salt of bisphenol-A and dichlorodiphenyl sulfone. Among the properties which qualify PS as an outstanding membrane polymer is its high thermal and oxidative stability, high strength and resistance to extremes of pH. The closely related polyethersulfone (PES) is totally devoid of aliphatic hydrocarbon groups and exhibits even higher thermal stability. The sulfone groups act as a sink for the electrons in the aromatic groups and confer thermo-oxidative resistance. Another desirable property of the aromatic groups is that they may be substituted, thereby providing an excellent means of introducing ion exchange groups and potential cross linking sites. Membranes from unmodified PS and PES are utilized in both flat sheet and hollow fiber forms in ultrafiltration and microfiltration. They are widely utilized as porous supports in thin film composite membranes for RO desalination.

Interfacially Synthesised Polymeric Membranes

Interfacial polycondensation is unusual in that neither monomer purity nor exact stoichiometry of reagents is required and can be adopted for the direct synthesis of the films in-situ over a micro-porous support. This technique is utilized commercially for the preparation of polyurea (NS100), polyamide(PA300) and crosslinked aromatic polyamide(FT30) membranes. In each case a micro-porous polysulfone membrane with surface pores of <0.1 μm size is first wetted with a dilute aqueous solution of the water soluble component like polyethyleneimine (PEI) or meta-phenylenediamine and interfacially reacted with hexane solutions of toluene diisocyanate(TDI), isophthaloyl chloride or trimesoyl chloride. As compared to asymmetric membranes, interfacially synthesized membranes provide high permeability rates without sacrificing selectivity.

Membrane Preparation Techniques

Integrally skinned asymmetric semipermeable membranes are synthesized by phase inversion technique wherein the polymer is brought into a homogenous solution in a solvent in presence of suitable additives. The polymer solution is subsequently spread in a chosen configuration and allowed to gel in a non solvent medium to generate the membrane. The final membrane for use is obtained by suitable post treatment techniques depending on the intended application. The choice of solvent, additive, their concentration, temperature, solvent evaporation period prior to gelation, nature and composition and temperature of the non solvent gelling medium, the casting atmosphere temperature and humidity are of paramount importance in obtaining membranes of desired selectivity and permeability. These membranes are asymmetric in morphology as they have different pore structure on either side of the membrane. The air exposed side has a denser pore structure and is called the skin of the membrane and faces the feed solution. The other side is made of more porous structure and serves as a support to the skin. The skin layer thickness is the actual barrier affecting the permeability. Thin film composite membranes are synthesized by in-situ interfacial polymerization over a previously formed micro-porous membrane support as already mentioned above.

Interfacial Layer

The successful development of first sea water desalting cellulose acetate membranes originated from the concept of preferential sorption of water at membrane solution interface and the theoretical possibility of draining out this preferentially sorbed water through appropriate porous membrane. The starting point of this concept is the well known Gibb's adsorption equation which indicates the at surface forces can give rise to steep concentration gradients at interfaces.

$$\Gamma = -(\delta\gamma/\delta \ln a)/RT$$

Where Γ is the surface excess of solute in mol/m^2, γ is the interfacial tension at the air-solution interface in N/m, a is the activity of the solute in mol.m^{-3}, R is the gas constant and T is the temperature in ^{0}K. For aqueous sodium chloride solutions, there is a negative surface excess of solute resulting in a pure water layer at the air solution interface. If the surface of a porous membrane in contact with the solution is of such chemical nature that it has preferential sorption of water or preferential repulsion of solute, then a multimolecular layer of preferentially sorbed pure water could exist at the membrane solution interface.

A continuous removal of this interfacial water can then be effected by letting it flow under pressure through membranes. This concept also gives rise to an important property, namely, the critical pore diameter for maximum separation and permeability. This is obviously twice the thickness of the interfacial pure water layer 't'. If the pore diameter is bigger, permeability will be higher, but solute separation will be lower, since the concentrated boundary solution will also flow through the pores. If the diameter is smaller, the separation could be maximum but permeability will be reduced. For maximum separation and permeability, it is necessary to maintain the pore size equal to 2 't' only at the interface. The connecting pores in the interior bulk of the membrane away from the film-solution interface, could be and should be bigger. These requirements are essential from a practical point of view because the total resistance to fluid flow will be less. A schematic of the principle is given in Figure 1.

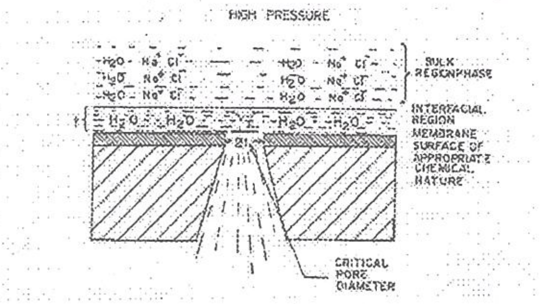


Fig.1 Schematic representation of pure water layer formation at Membrane –aqueous NaCl solution interface and their separation

Structure of Water

The structure of water in the dense skin of desalting membranes is another important parameter to explain its permselective nature. The bound water in the skin layer of the membrane is shown to be 'frozen' or 'ice like' which excludes salt just like ice excludes salt. Utilizing statistical mechanics approach Strathmann has estimated the water cluster number ranging from one to eight for polymers of varying polarities. Surface of reverse osmosis membranes are assumed to contain capillary pores of varying sizes. When a hydrophilic reverse osmosis membrane is in contact with an aqueous solution of an electrolyte , an equilibrium layer of bound water forms both on the membrane surface and the walls of the capillaries. The hydrated ions because of their size are not transmitted through most of the capillaries. On application of pressure liquid flows through the capillaries disrupting the initial equilibrium and decreasing the thickness of the bound water layer on the membrane surface. Simultaneously the bound water layer equilibrium is reestablished by the interaction of membranes with the hydrated envelopes of ions which are partially dehydrated so as to be able to pass through the membrane capillaries. Consequently the extent of reverse osmosis separation depends on the degree of dehydration of ions. This strength is different for different ions. The strength of hydration envelope increases with decrease in the crystallographic radii of ions and with increase in their charge. Separation increases with decrease in crystallographic radii and with increase in charge of ions.

Electrostatic Repulsion

Electrostatic forces govern the disposition of ions at the interface and the structure and size of membrane pore on surface govern the mobility of the interfacial fluid. The electrostatic potential for ionic repulsion in the vicinity of uncharged materials of low dielectric constant is given by the Onsagar-Samaras equation.

$$\Phi \text{ potential} = \frac{N z_i^2 \varepsilon^2 (D-D')}{16\Pi\, Dd\, (D-D')}$$

where N is the Avagadro number, z_i is the valency of the ion, ε is the electronic charge, d is the distance between the polymer surface and the center of the solute molecule. D' is the dielectric constant of the polymer membrane material and D is the dielectric constant of water. The dielectric constant of water is 78 at 25°C and that of cellulose acetate material is between 3 and 8. Consequently with electrolytic solutes in aqueous solutions water is preferentially sorbed at the membrane solution interface giving rise to positive solute separation in RO. Gluekauf pointed out that at the interior of a neutral pore, the strength of electrostatic repulsion could be even higher than at plane surface. His analysis predicts that RO separation of an electrolyte solute increase with decrease in pore radius on membrane surface, ionic radius, solute concentration and dielectric constant of the material and also increase in ionic charge. All RO experimental data involving inorganic electrolyte solutes are qualitatively consistent with the prediction of Gluekauf. They also estimated that due to electrostatic repulsion, ions of NaCl could not enter pores(assuming the void space on the membrane surface are made up of cylindrical pores) of sizes less than 10A⁰ diameter in cellulose acetate membranes.

Reverse Osmosis Process for Desalination

RO is a moderate to high pressure (15-80 bar) driven process for separating dissolved solutes from aqueous solutions by means of a semi-permeable membrane. The pressure to be applied needs to be in excess of the osmotic pressure of the saline water feed. This process is carried out by flowing a feed saline water solution along a membrane surface under pressure. Retained solutes (such as particulate matter and dissolved salts) leave with the flowing process stream and do not accumulate on the membrane surface. The permeate through the membrane is devoid of most of the dissolved solutes. The amount of salt and other impurities is often referred to as TDS, or total dissolved solids. The higher the TDS, the more feed pressure required. Seawater RO has a conversion rate of 35 percent to 40 percent, which means 35 percent to 40 percent of the feed water is permeated and the remainder is concentrated to be returned to the water source(s). The conversion rate of brackish RO could be more than 90 percent. RO, using cross-flow membrane separation, was the first to be widely commercialized. An advantage of cross-flow filtration is that the impurities concentrated on the membrane surface are constantly swept away by the concentrate stream, thus continually cleaning the membrane surface. This prolongs its life, reduces fouling of the membrane surface and reduces maintenance costs. Another advantage of the RO process is that it removes most organic compounds and up to 99.5 percent of all ions.

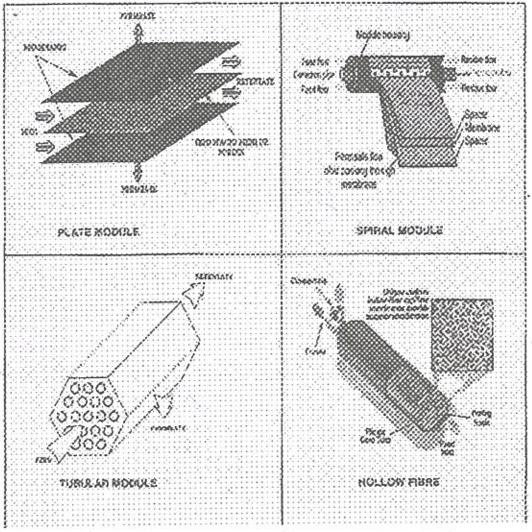


Fig.2 Different Configurations of Reverse Osmosis Modules

RO membranes are used in various configurations, namely, sheets, tubes and hollow fiber. Figure 2 gives the different configurations. Sheet membranes are rolled in spiral configurations leaving separate leak proof channels for feed and

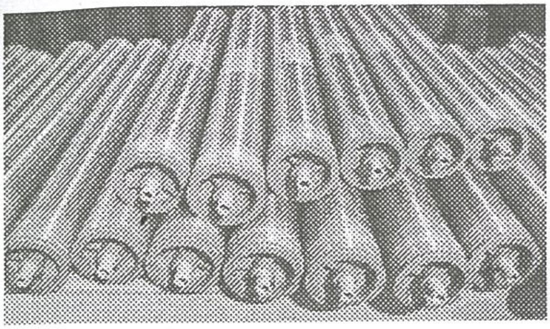


Fig.3 Commercially available Spiral Wound Membrane Elements.

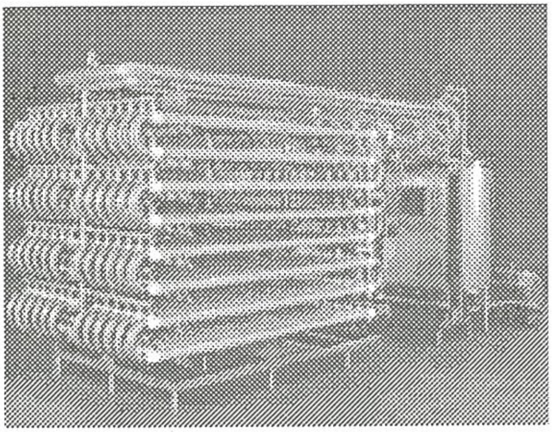


Fig4 Typical Tubular Membrane Assembly.

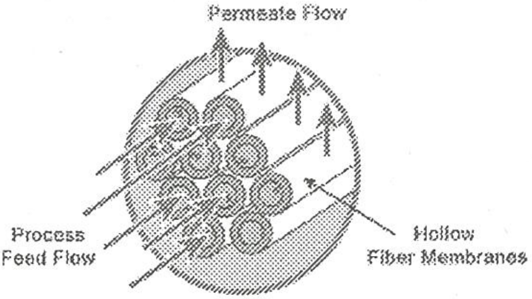


Fig 5 Flow patterns in a Typical hollow fiber membrane assembly.

permeate flow. These spiral wound elements are commercially available for various applications namely, for brackish water desalination or sea water desalination and come in 4"(100 mm) dia or 8" (200mm)dia and 40"(1000mm) length or 60"(1500mm) length. These commercially available elements (Figure 3) are designed to withstand high pressure , up to 80 bar for high recovery applications. Spiral wound elements are generally the more economical to operate. Spiral systems are: (a)compact high membrane packing density results in more efficient utilization of floor space and (b) energy efficient lower power consumption compared to other membrane configurations.

Tubular membranes operate in tangential, or cross-flow, design where process fluid is pumped along the membrane surface in a sweeping type action. Figure 4 gives a typical tubular membrane assembly in a plant The membrane is cast on the inside surface of a porous tube. The feed solution is pumped through the center of the tube at velocities as high as 20 ft/sec. These cross-flow velocities minimize the formation of a concentration polarization layer on the membrane surface, promoting high and stable flux and easy cleaning, especially when the objective is to achieve high suspended solids. Permeate is driven through the membrane to be directed out of the system or back into the process depending on the application. There are many advantages in tubular membrane configurations. Besides their rugged construction, they have a distinct advantage of being able to process high suspended solids, and concentrate product successfully and repeatedly to relatively high end point concentration levels without plugging. Tubular membrane systems do not require significant pre-filtration.

Hollow fiber membranes (Fig.5) offer the unique benefits of high membrane packing densities, sanitary designs and, due to their structural integrity and construction, can withstand permeate back pressure thus allowing flexibility in system design and operation The hollow fiber geometry allows a high membrane surface area to be contained in a compact module. This means large volumes can be filtered, while utilizing minimal space, with low power consumption.

Nanofiltration (NF)

Nanofiltration is a moderately low pressure (typically 7 to 15 bar) process in which monovalent ions will pass freely through the membrane but highly charged, multivalent salts and low molecular weight organics will be rejected to a much greater degree. Typical NF applications include water softening, desalination of dyestuffs, acid and caustic recovery and color removal. Surface pores have not been observed in NF membranes under any microscope, However, water can still pass through the membrane and multivalent salts and low molecular weight organics are rejected. It is difficult to predict the performance of NF membranes, especially if more than three solutes are present in the solution, since membrane rejection is influenced by the size, structure and charge of the components in solution. As a result, piloting is highly recommended for NF applications, even if a detailed feed water analysis is available.

NF is wrongly categorized as a "loose RO" membrane. The differences are subtle, yet distinct. A significant feature is its ability to reject uncharged, dissolved materials and positively charged ions according to the size and shape of the molecule in question. This effect is desirable for a number of applications where moderate salt removal is acceptable since operating pressures and power consumption are significantly lowered. So, in exchange for less than complete salt removal, costs are reduced. NF pretreatment reduces the RO membrane fouling (plugging) by the removal of turbidity and bacteria; prevents plant scaling (both RO and multistage flash distillation) by removal of scale forming hardness and sulfate ions; and lowers required pressure to operate an RO plant by reducing total dissolved solids (TDS) of seawater feed by more than 25 percent. Permeate recovery of NF/RO is approximately 50 to 80 percent, which is favorable when compared to the 35 to 40 percent produced by the standard sea water RO process. Further, as mentioned before, NF pretreatment requires less pumping pressure by reducing the TDS of seawater feed.

Ultrafiltration (UF)

UF is a low pressure (3 -5 bar) process for separating larger size solutes from aqueous solutions by means of a semi-permeable membrane and retains oils, particulate matter, bacteria and suspended solids large macromolecules and proteins and passes most surfactants, water, acid and alkaline compounds· Pore sizes range from 0.005 0.1μ . The permeate is clear (non-turbid) solution void of suspended solids.

Microfiltration

MF is a low pressure (0.3 to-3 bar) process for separating larger size solutes from aqueous solutions. This process is carried out by having a process solution flow along a membrane surface under pressure. Retained solutes (such as particulate matter) leave with the flowing process stream and do not accumulate on the membrane surface. ·The MF membranes pass some suspended solids and all dissolved material· Pore sizes range from 0.1 μ to 3 μ. Applications of MF process include wastewater treatment, caustic cleaner recovery and clarification of dark juices. For example, in the clarification of wine and dark juices (such as cranberry), MF is employed to separate the suspended solids from the juice to produce a low turbidity juice while allowing the passage of color and flavor.

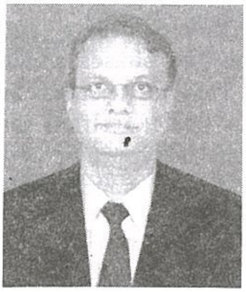
Concluding Remarks

Membrane processes are finding increasing application in a variety of chemical and pharmaceutical industries, because of a single step molecular scale separation of a wide spectrum of contaminants. The low pressure requirement, easy adoptability in industries, the ambient temperature operation and the availability of highly productive membranes make them ideally suited as a technologically viable alternative over conventional separation techniques. The search for better membranes and technological innovations to enhance economy and efficiency is continuing

Table 1 : Characteristics of Commercially Significant Membrane Processes

Process	Average Pore size	Separation Mechanism	Driving force	Technology status
Reverse Osmosis (RO)	5 10 A^0	Preferential sorption capillary flow	Net hydrostatic pressurs of osmotic pressure	Commercial
Nanofiltration (NF)	10-30 A^0	Preferential sorption capillary flow	Net hydrostatic pressurs of osmotic pressure	Commercial
Ultrafiltration (UF)	30-100 A^0	Sieve mainly	Net hydrostatic pressure	Commercial
Microfiltration(MF)	Above 100 A^0	Sieve mainly	Net hydrostatic pressure	Commercial
Electrodialysis(ED)	Nonporous	Electrically driven	Applied EMF	Commercial
Diffusion dialysis(DD)	Nonporous	Diffusion	Concentration gradient	Commercial
Liquid Membranes(LM)	NA	Diffusion	Concentration gradient	Pilot scale trials
Bipolar Electrolysis	Nonporous	Electrically driven	Applied EMF	Pilot scale trials

Ceramic Membranes



__Dr. K.S. Seshadri__ joined BARC after obtaining his M.Sc (Chemistry) degree in 1977 from Madurai University. He got his Ph.D. on the project "Synthesis, characterization and application of ceramic membranes for radioactive waste treatment" from Anna University. Presently he is involved in the R&D activities of Centralised Waste Management Facility of Kalpakkam. His present project is on the management of spent ion exchange resin. He has more than 20 publications and presentations.

Introduction

Ceramic membranes are ideal materials for many applications in the chemical and pharmaceutical industries or in water and waste water processing. They are ecologically friendly and more favored. Filtration with ceramics is a high selective process without phase transformation. No additives are necessary and process temperature is not limited. Running costs are limited by closed production cycles and continuous processes. Ceramic membranes offer:

- Chemical, mechanical and thermal stability
- Ability of steam sterilization and back flushing
- High abrasion resistance
- High fluxes
- High durability
- Bacterial resistance
- Possibility of regeneration
- Dry storage and cleaning

Disadvantages are their high weight and considerable production costs of ceramic components. However the latter are compensated by high service life.

Historical development of ceramic membranes:

The development of industrial ceramic ultrafiltration (UF) and microfiltration (MF) membranes resulted from the combination of three factors:

1. The know-how accumulated by the companies that built the nuclear gaseous diffusion plants.

2. The existence of ultrafiltraion as an industrial process using polymeric membranes.

3.The limitations of polymeric membranes in terms of temperature, pressure and durability.

The first attempt to use ceramic supports dates back to the 1960s when dynamic membranes made of a mixture of zirconium hydroxide and polyarcylic acid deposited on a porous carbon or ceramic support were developed by the Oak Ridge National Laboratory in the U.S. (Kraus and Johnson 1966).

This concept later evolved into the ***Ucarsep***^{R} membrane made of a layer of un sintered ceramic oxide (including ZrO_2) deposited on a porous carbon or ceramic support, which was patented by Union Carbide in 1973.

Ceraver country was the first company to industrially produce multichannel membranes. Since 1984, these membranes, which have 19 channels per element with a 4 mm channel diameter are sold under the trademark ***Membralox.***

In 1986, CGE sold the ceramic part of Ceraver,

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including the ceramic membranes division to Alcoa Separations Technology, Inc.

A few other players in the nuclear membranes activity also developed inorganic membranes for the filtration of liquids. This was the case with Norton-USA who with the know how of Eurocerал developed MF membranes made of an a-Al_2O_3 tubular support with an γ- Al_2O_3 layer. The inner tube diameter was 3 mm and the outer diameter was 5 mm.

In 1988-1989, Norton also produced the mulitchannel membrane elements. These membranes produced by Norton are now sold by Millipore under the trademark **Ceraflo.**

The asymmetric alumina membranes obtained by the anodic oxidation of an aluminum sheet were first developed for uranium enrichment in the 1950s in France (Charpin, Plurien and Mammejac 1958) and in Sweden (Martensson et al. 1958). Such membranes are now marketed under the trademark of **Anopore** by Anotec, a British subsidiary of Alcan.

In the second half of the 1980s, an increasing number of companies entered the field of ceramic membranes, the most significant ones being ceramic companies such as NGK of Japan which also developed a mutichannel membrane element (19 channels, 3 mm diameter). Nippon Cement and Toro also from Japan and very recently Corning also

Classification of ceramic membranes:

A membrane can be described as a semi permeable barrier between two phases which prevents intimate contact. This barrier must be permselective which means that it restricts the movement of molecules in it in a very specific way. The barrier can be solid, liquid or gas. Permselectivity can be obtained by many mechanisms.

1. Size exclusion or molecular sieving
2. Difference in diffusion coefficients (bulk as well as surface)
3. Difference in electrical charge
4. Difference in solubility
5. Difference in adsorption and /or reactivity on (internal) surfaces

The flux of liquids or gases through the membranes is in most cases driven by a pressure gradient and sometimes by an electric field gradient. Membranes can be used for:

1. Separation of mixtures (liquids, gases or liquid-solid mixtures)
2. Manipulation of chemical reactions:

	Main characteristics	Comments
Dynamic	Non permanent	Ion exchange in hydroxide layers on a support
Porous metal or nonmetallic	Symmetric, asymmetric supported, non supported	Permselective, diffusion affected by the pore characteristics
Inorganic	Pore shape, morphology and sizeChemical nature of pore surface	
Dense	Metal foil	Solution diffusion of atomic or ionic species

shifting the equilibrium situation or manipulation of the conversion or selectivity of catalytic reaction.

Inorganic membranes can be categorized as shown in Table 1.

Pore diameters larger than 50 nm are called macropores, between 2 and 50nm mesopores, below a diameter of 2 nm is called microporous. The obtainable pore sizes are schematically represented in Figure 1 together with the most important fields of application.

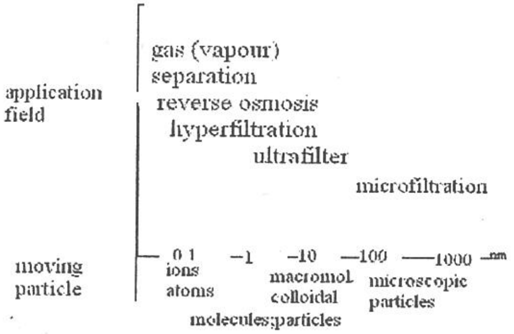

Figure1. Pore size range of ceramic membranes and related application fields

Synthesis of ceramic membranes:

Ceramic Asymmetric Membranes

The asymmetric membrane system consists of a porous support, a few millimeters in thickness, with pores in the range 1-10 μm, a porous intermediate layer of 10-100 μm thickness with pores of 50-500 μm, and a top layer (the proper separation layer, e.g. for ultrafiltration) with a thickness of 1 μm (or smaller) -10μm with pores of 2.50 nm.

The main process for making ceramic membranes is to first prepare a dispersion of the fine particles (called slip) and then to deposit the particles contained in the slip on a porous support by a slip casting method. The capillary pressure drop created on letting the slip into contact with the macro porous support forces the dispersion medium of the slip to flow into the pores of the particles. When relatively large particles are used to make the support or intermediate layer (with pore size >1 μm) the particles can be precipitated from supersaturated solutions. These need to be calcined for permanently fixing with the support.

Glass Membranes

Glass membranes with an isotropic spongy structure of interconnected pores can be prepared by thermally demixing a homogeneous Na_2O-B_2O_3-SiO_2 glass phase in two phases. Some porous metal membranes have been made in a similar way with a strong acid or other types of leachant (Hsieh 1988).

Anodic Membranes

Pores with linear form are produced by the so-called anodic oxidation process (Smith 1974). Here one side of a thin high-purity aluminum foil is anodically oxidized in an acid electrolyte. A regular pattern of pores is formed. The pore size is determined by the voltage used and by the type of acid.

The stability can be improved by treatment in hot water or in a base. Such a treatment can also be used to decrease the pore size on one side of the membrane, and as a consequence an asymmetric membrane can be produced. The disadvantage of the method is that only unsupported membranes can be produced in the form of membrane foils. To get sufficient mechanical stability, they must be supported in some way for most applications.

Track-Etch Membranes

Pores with a very regular, linear shape can be produced by the track-etch method (Quninn et al. 1972). Here a thin layer of a material is bombarded with highly energetic particles from a radioactive source or accelator. The track left behind in the material is much more sensitive to an etchant in the direction of the track axis than perpendicular to it. So etching the material results in straight pores of uniform shape and size with pore diameters ranging between 6 nm and 1200nm. To avoid overlap of pores, only 2.5% of the surface can be occupied by the pores. This process has been applied on polymers and on some inorganic systems like mica.

Pyrolysis

Membranes with extremely small pores (< 2.5 nm diameter) can be made by pyrolysis of polymeric precursors. Molecular sieve carbon or silica membranes with pore diameters of 1nm have been made by controlled pyrolysis of certain thermo set polymers (e.g. Koresh, Jacob and Softer 1983) or silicone rubbers (Lee and Khang 1986), respectively. There is, however, very little information in the published literature. It has been claimed that zeolitic membranes can be prepared by reaction of alumina membranes with silica and alkali followed by hydrolysis (Uhlhorn, Keizer and Burggraaf 1989).

Dense Membranes

They may consist of thin plates of metals (Pd and its alloys, Ag and some alloys) or oxides (stabilized zirconia or bismuth oxides, cerates). These membranes are permeable to atomic (for metals) or ionic (for oxides) forms of hydrogen or oxygen and have been studied, especially, in conjunction with chemical reactions like (oxidative) dehydrogenation, partial oxidation etc., in membrane reactors. Their main drawback is the low permeability. This might be improved by making very thin layers (micrometer to nanometer range), e.g. by deposition in a pore system.

Packing of Particles from Suspensions

The thin top layer with (very) small proes is applied on top of a support system which consists of one or two much thicker layers with (much) larger pores. The main support consists of a packing of rather coarse grained material (micron range) which is produced in a classical way by cold isostatic pressing of powder, by co-extrusion of a paste of ceramic powder with additions of binders and plasticizers or by slip-casting. After burning away the organic material the so-called "green" compact is sintered. In order to obtain defect-free membranes.

Sol-Gel Process

The sol-gel process can be divided into two main routes, the colloidal suspension route and the polymeric gel route. In both cases a precursor is hydrolyzed while simultaneously a condensation or polymerization reaction occurs. The essential parameter to control is the hydrolysis rate with respect to the poly condensation rate. The precursor is either an inorganic salt or a metal organic compound. The chemistry of the initial stages has been described by Livage (1986).

In the colloidal route, a faster hydrolysis rate is obtained by using a precursor with a fast hydrolysis rate and by reacting the precursor with excess water. A precipitate of gelatinous hydroxide or hydrated oxide particles is formed which is peptized in subsequent step to a stable colloidal suspension. The elementary particle size ranges, depending on the system and processing conditions, from 3-15 nm and these particles form loosely bound agglomerates with sizes ranging from 5-1000 nm. The size of the agglomerates can be decreased. e.g. by ultra sonification of the suspension and by manipulation of the electrical charge on the particles. By increasing the concentration of the suspension and or by manipulation of the surface (zeta) potential of the sol particles the colloidal suspension is transformed to a gel structure consisting of interlinked chains of particles or agglomerates .

In the polymeric gel route, the hydrolysis rate is kept low by adding successively small amounts of water and by choosing a precursor which hydrolyzes relatively slowly. The gel will form and shrink even within the liquid. It is not necessary to remove this liquid to obtain a gel as in the colloidal route. This means that concentrations of solid material in polymeric gels are usually smaller than in particle gels.

The Slip-Casting Of Ceramic Membrnes

A common method to silp-cast ceramic membares is to start with a colloidal suspension or polymeric solution. This is called a slip. The porous support system is dipped in the slip and the dispersion medium (in most cases water or alcohol-water mixtures) in forced into the pores of the support by a pressure drop (ΔP_c) created by capillary action of the micoroporous support. At the interface the solid particles are retained and concentrated at the entrance of pores to form a gel layer as in the case of sol-gel processes.

Finaly, binders or plastiizers can play an important role in the prevention of cracks in the layer. As shown by Van Praag et al. 1990, titania supported membranes can be formed with plastizers on normal supports. Frequently used binders/plasticizers include polyvinylacohols, cellulosic compounds and polyglycols in an aqueous medium and polyvinylbutyral in an alcoholic medium. It is important that the organic material can be completely pyrolyzed at relatively low temperature without leaving carbon or metal residues. After drying, the xerogel is first calcined to form an oxide structure. Further heat treatment strongly affects the final pore size of the membrane Temperature and time also strongly influence the phase compositons

It is obvious that the pore diameter can be regulated by heat treatment to values as small as 3-6 nm (minimum) and up to 50-200 nm depending on the material.

Characteristics of Inorganic Membranes

The separation efficiency of inorganic membranes depends to a large extent, on the microstructural features of the membrane /support composites such as pore size and its distribution, pore shape, porosity, tortuosity pore charge density etc.

Microstructural Characteristics

Microscopic Morphology

Some commercial inorganic membranes such as porous glass and metal membranes have a symmetric or homogeneous microstructure (However, the majority of the commercially important inorganic membranes are asymmetric and composite in nature). They usually consist of a thin film responsible for separating components, and a support or substrate with single or multiple layer having larger pores for imparting the required mechanical strength to the membrane composite.

Thickness

The thickness of the separative membrane layer for asymmetric membrane structures represents a trade-off between the physical integrity requirement, on the one hand, and the high flux requirement, on the other. Current commercial products show a membrane thickness of as thin as approximately 5 microns but generally in the 10 to 20 micron range. The bulk support and any intermediate support layers vary in thickness, but the bulk support needs to be thick enough (about 1-2mm) to provide high mechanical strength. The intermediate layers range from 10 to 50 microns in thickness.

Pore Size

Pore size plays a key role in determining permeability and permselectivity (or retention property) of a membrane. The structural stability or porous inorganic membranes under high pressures makes them amenable to conventional pore size analysis such as mercury porosimetry and nitrogen adsorption/desorption.

The commercial mercury porosimeters can usually provide pore diameter distribution data in the range of 3.5nm to 7.5 microns. It is a useful and commonly used method for characterizing porous particles or bodies

For membranes with pore diameters smaller than 3.5nm, the nitrogen adsorption/desorption method based on the widely used BET theory can be employed. The measurement technique, however, is good only for pore diameters ranging from 1.5 nm to 100nm (=0.1 micron).

Another possible solution to the problem of analyzing multiple-layered membrane composites is a newly developed method using NMR spin-lattice relaxation measurements (Glaves 1989)., Another nondestructive method for ascertaining information on membrane pore size distributions has been developed and well tested at Oak Ridge Gaseous Diffusion Plant (Fain 1990). The method consists of measuring the flow of a mixture of an inert gas (such as nitrogen) and a condensable gas (such as carbon tetrachloride) through membrane pores of various sizes.

Permeabilities and retention properties

The retention characteristics can be generally and generically obtained by using some model molecules. The most commonly used model molecules are polyethylene glycol (PEG), polymers which are linear and flexible in nature, and dextrans which are slightly branched. These model molecules are widely used primarily due to their relatively low cost. They are, however, far from being perfectly spherical and, as such, the molecular weight cutoff curves using these model molecules are not ideally sharp.

Maximum pore size and structural defects

A commonly used simple method for determining cracks or pinholes in microporous membranes is the so-called bubble point test. It has been used by many organic membrane manufactures and users alike and is also being adopted by some inorganic membrane manufactures. A frequently used liquid medium is water. However, alcohols or hydrocarbons have also been used due to their lower surface tension (e.g. surface tension of some fluorocarbon liquids is only 16 dyne/cm compared to 72 dyne/cm for water) which results in a lower pressure difference required to displace the liquid.

Characteristic of pore network

The size of the crystallites forming the network of membrane pores and the porous nature of the network affect the permeation and separation properties of porous inorganic membranes.

Form the mercury porosimetry data, porosity can be calculated. A higher porosity means a more open pore structure, thus generally providing a higher permeability of the membrane. Porous inorganic membranes typically show a porosity of 20 to 60% in the reparative layer. The porous support layers may have higher porosities.

The size of crystallites that make up inorganic membranes with narrowly distributed pores in the nanometer range can be estimated by using transmission electron microscopy (TEM). X-ray diffraction line- broadening measurements, when implemented in a computerized X-ray diffraction system, can be used to estimate the crystallite size.

The internal surface area of a porous inorganic membrane is often significantly affected by the heat treatment temperature. The surface area of a transition-phase alumina membrane decreases with increasing calcination temperature. Consequently, the mean pore diameter of the resultant membrane increases with the calcination temperature.

A commonly used empirical approach to describing the degree of randomness of the pore structure in a membrane is the factor "tortuosity" which is determined from the permeability, internal surface area, pore volume fraction, pore shape and thickness of the membrane and the permeate viscosity.

Materials properties

Chemical resistance

For situations which call for long contact between corrosive chemicals such as strong acids or bases and the inorganic membranes, the issue of potential chemical attack needs to be addressed. Also, it is generally known that non-oxide ceramic materials will not tolerate long-term exposure to oxidizing environments, particularly at high temperatures.

Porous glass membranes show excellent resistance to acid attack, but exhibit some degree of dissolution in the presence of strong caustic solutions, particularly at elevated temperatures. They are also known to undergo some structural changes upon long exposure to water due to partial dissolution of silica. Different phase of a given metal oxide such as alumina can also exhibit markedly different chemical relativities in wet systems. For example, as a general rule, as the density of an alumina (and hydrous alumina) phase increases, its chemical resistance increases. The hexagonal alumina crystals show very good resistance to chemical attack including strong acids or bases. In contrast, the cubic crystalline transition alumina with a pore diameter of a few nanometers does not possess good resistance to highly acidic or basic media.

Various membrane materials are to be compared for corrosion resistance in hydrofluoric acid. Membrane samples are ultrasonically cleaned for 5 minutes and dried at 200°C for hours followed by immersion in 35% HCl solution, making sure that no air bubbles are trapped in pores. The acid exposure at the test temperature (e.g. 25°C) continues for a given period e.g. one week. The tested samples are ultrasonically washed with demineralized water for 5 minutes and dried at 200°C for 2 hours. The weights of the cleaned membrane samples before and after the acid exposure are compared to assess the relative corrosion resistance of various membrane materials.

Surface Properties

It is generally recognized that the surface charges of a membrane, which are largely dependent on the membrane material and operating conditions, can significantly influence the separation performance of the membrane in terms of both flux and permselectivity. The electrostatic component of the interaction forces between the molecules in solution and the surface layer of the membrane depends to a great extent on the charge density of the membrane surface and its pores (Nystrom, Lindsrom and Matthiasson 1989). The surface charge density is characterized by the zeta potential of the membrane.

Membrane element and module configurations

The structural elements of commercial inorganic membranes exist in three major geometries: disk, tube or tube bundle, and multichannel or honeycomb monolith. The disks are primarily used in laboratories where small-scale separation or purification needs arise and the membrane filtration is performed in the flow through mode. The majority of industrial applications require large filtration areas (20 to over 200m^2) and, therefore, the tube /tube bundle and the multichannel monolithic forms, particularly the latter, predominate. They are almost exclusively operated in the cross-flow mode.

Applications of ceramic membranes:

Initially ceramic membranes were used in waste water technology. Meanwhile successful possible applications cover all industries:

- Chemical industry:
- Product separation and cleaning
- Concentration of polymer suspensions and metal hydroxide solutions
- Separation of catalysts
- Recovery of dyes and pigments
- Desalination of products
- Cleaning, recycling of organic solvents
- Metal industry/ surface engineering
- Recycling and disposal of degreasing and rinsing baths
- treatment of oil/water emulsions
- Recovery of heavy metals
- Cleaning of waste water
- Treatment of waste water from glass and glass fibre production
- Textiles/pulp and paper industry
- Concentration, fractationation isolation and sterilization for antibiotics, enzymes proteins and acids and vitamins
- Separation concentration and dewatering of bio mass and algae
- Disposal of fat emulsions
- Separation of yeast
- Desalination
- Food and beverages
- Clarification of juice and beer
- Concentration of juice
- Sterilization of milk and whey
- Separation or fractionation of millk and whey ingredients
- Demineralization of whey
- Dewatering of products
- Purification of drinking water
- Recycling and environment
- COD/BOD reduction
- Oil/water separation
- Recovery of pharmaceuticals and pesticides
- Retention of micro organisms
- Retention of heavy metals and radioactive substances

Recycling of water from swimming pools

Table 2 below shows some typical high temperature application of inorganic membranes in the synthesis of chemicals in industry.

Membrane Reactor System	Reaction/catalyst	Results	Reference/ Remarks
Porous glass tube (in double pipe configuration) wall thickness 2.7 mm, inner diameter 14.4 mm, length 391 mm, mean pore diameter 40 Å. Feed enters the reactor at tube side, permeate at shell side.	Dehydrogenation of cyclo hexane Pt/Al_2O_3 catalytic pellets (0.5 wt% Pt) packed on tube side	T ~ 180^0C, P_{feed} ~ 1bar P_{perm}~ 1bar. Conversion of C_6 H 24%. The equilibrium conversion of C_6 H at 180?C is 10%.	Itoh elal (1988). Experiments at high temperatures also led to similar results.
Porous supported γ-Al_2O_3 tube (in module configuration) membrane thickness 4-10 μm, mean pore diameter 0.01 μm Feed at shell side, permeate at tube side	Dehydrogenation of ethyl benzene to styreneLi 0.5 Fe 2.4 Cr 0.1O4 with 12 wt % K_2O wt % V_2O_5 catalytic pellets packed on reactor shell side	T ~ 625^0C, P_{feed} ~ 4 bar P_{perm}~1 bar. Conversion of ethyl benzene 65.2%, selectivity to styrene 94%. In the absence of membrane the conversion was 50.7%.	Bitter (1986)
Micro porous glass tube (in double pipe configuration), wall thickness 0.8 mm, outer diameter 10 mm, mean pore diameter 300 nm,. Feed enters the reactor at tube side, permeate at shell side	Water gas shift reaction. Thin dense film (thickness 20 μm) of Pd catalyst coating the external glass tube surface.	T~400^oC, P_{feed}~ 1 bar. Conversion of CO 100%. The equilibrium conversion was~ 60 %.	Kikuchi etal (1989) under the best operating conditions, the rate of hydrogen permeation through the Pd film was evaluated to be of the same order as the rate ofproduction of hydrogen due to the reaction.

Conclusions:

The development of ceramic membranes was initially oriented towards uranium enrichment but it has proved its usability in many fields. The recent years have seen the start of a much broader exploration of the manifold potentialities of ceramic membranes both in terms of materials and applications. Thus, a multifaceted new field of technology is emerging.

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Recovery of Actinides and Valuables from Nuclear Wastes Using Liquid Membrane Separation Methods: An Overview

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Membrane separation processes have become one of the emerging technologies which have shown rapid growth during the past few decades. In recent years, membrane processes have been found to be quite effective in areas such as treatment of industrial effluents, water reclamation, gas separation etc. with the ready availability of membranes with different properties and configurations [1]. Though pressure driven membrane separation processes are employed for various applications mentioned above, they have limited use when applied for selective separations. In such cases, the role of liquid membranes (LM) or grafted polymeric membranes (GPM) with specific functional groups assumes significance.

In spite of many applications of membranes in water treatment, food processing and medical industries, their use in nuclear industry is still at an infancy stage [2]. Some pressure driven membrane systems such as microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO) are employed for the treatment of liquid radioactive wastes (LRW) at various facilities around USA and Canada and are discussed in another article by Pabby et al. in this bulletin [3]. However, these techniques can preconcentrate particulate matter, organic substances as well as dissolved solids along with the desired radioactive contaminants. For selective separations the nuclear industry still banks heavily on techniques such as solvent extraction and ion exchange.

Solvent extraction plays a pivotal role in majority of the separations involved in the nuclear fuel cycle both at the front as well as the back end. However, there are many drawbacks of the solvent extraction methods and with increasing concern for the environment, alternative separation methods will be employed for large scale separations in the nuclear industry as well. Two of the major drawbacks of the solvent extraction methods viz. third phase formation and phase disengagement can be over come with the LM based separation methods as they involve non-dispersive mass transfer. LM systems also have distinct advantages over ion-exchange. Ion exchange beds are unsuitable for solutions containing large concentrations of dissolved solids as well as

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suspended matters whereas liquid membrane based separation methods can be quite useful for pre-concentration. Though LMs have a major disadvantage of stability, newer techniques such as polymer inclusion membrane (PIM) and Hollow Fibre Supported Liquid Membrane (HFSLM) operated with strip dispersion or in the non-dispersive solvent extraction (NDSX) mode have proved to be beneficial.

Hollow fibre based separations have a distinct advantage of fast and efficient mass transfer due to large surface to volume ratio [1]. Several applications of hollow fibre modules are envisaged in nuclear industry for the pre-concentration of lean solution of radioactive material such as low and intermediate level wastes. There are a few reports on the application of HFSLM technique for high level waste processing. Researchers at the plutonium facility at Los Alamos National Laboratory have studied the separation of actinides from waste solutions using water soluble metal binding polymers (phosphonic acid derivative of polyethyleneimine) and hollow fibre membranes [4].

Though plant scale application of LM technology to the nuclear fuel cycle will still take some more time, many lab scale studies show highly encouraging results. This article deals with the separation / recovery of actinides and valuable fission products such as Cs-137 and Sr-90 from the radioactive waste streams and their lab scale test results. The transport behaviour of lanthanides is also discussed due to their chemical similarity with the trivalent actinides thereby often being used as their surrogates.

Types of Liquid Membranes:

Liquid membrane usually consists of a water immiscible (organic) layer separating a source aqueous phase consisting of a mixture of metal ions (feed) and receiving aqueous phase where the metal ion of interest gets concentrated (receiver) preferentially. Broadly speaking, there are three different types of liquid membranes. Bulk liquid membrane (BLM) is a stirred organic phase of lower density than the aqueous phase positioned under it or vice versa. In emulsion liquid membrane (ELM), the receiver aqueous phase containing oil droplets are dispersed into the feed aqueous phase. The volume of the receiving phase inside the oil droplets is at least ten times smaller than that of the source phase. The thickness of the membrane (organic film) is very small, while the surface area is enormous resulting in very fast separations. And finally, supported liquid membrane (SLM) where the carrier solution is entrapped in the pores of a solid polymeric film / tube. The SLMs are categorized into two types viz. with flat sheet (FSSLM) or with hollow fibre (HFSLM). Here a polymeric filter, with its pores filled with the organic phase, act as a membrane. Fig. 1 shows the different types of LMs.

The principle involved in supported liquid membrane transport is as follows: two homogeneous, completely miscible liquids, which may be refered to as feed or source phase (F or s.p.) and receiver phase (R or r.p.) solution are spatially separated by a third liquid (M) which is practically insoluble in F and R and is immobilized in a porous hydrophobic polymeric support. Due to the favourable thermodynamic conditions created at the F/M interface some components are selectively extracted from the F and transported into the membrane liquid. Simultaneously, at the M/R interface, conditions are such that the reverse transport is favoured. Thus the metal extractant chemistry in case of SLM is identical to that found in the solvent extraction system but the overall process is governed by kinetic rather than equilibrium parameters. Various factors that could affect the transport of a metal ion through

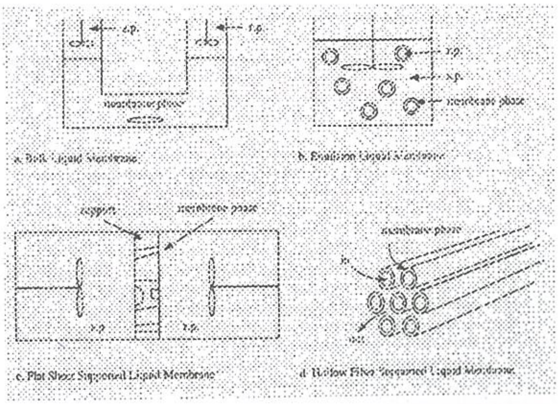


Fig. 1: Schematic representation of some liquid membrane systems

the LM are: (a) the (transport) resistance encountered by the metal ion in the F and R phases, (b) the physico-chemical properties of the carrier and diluent and (c) the nature of membrane support like its pore size, porosity, tortuosity, hydrophilicity, surface tension and surface area to volume ratio encountered in the transport process. This is an economically cheap separation technique because of the relatively small inventory of extractant, low energy consumption, low capital and operating costs and the possibility of achieving high separation factors.

Recovery of uranium:

Uranium, the most widely used fuel element in nuclear reactors is pre-concentrated / purified using various solvent extraction and ion exchange methods. Though recovery of uranium from acidic feeds are usually accomplished by solvent extraction processes such as AMEX, DAPEX and PUREX, liquid membrane based separation methods are an attractive alternative, especially from lean solutions. The role envisaged for the LM separation methods is predominantly pre-concentration which can be followed by purification to the nuclear grade using solvent extraction / precipitation methods. TBP (tri-n-butyl phosphate) is being used at various stages of nuclear fuel cycle such as for refining at the front end and recovery from the spent nuclear fuel at the back end. Liquid membranes containing TBP were evaluated for U recovery from nitric acid solutions by LM techniques such as BLM, ELM and SLM [5]. Though lab scale studies have been encouraging, large scale applications are still eluding due to major disadvantages such as slow transport rates due to high viscosity of TBP and significant acid transport.

TBP has few other disadvantages such as not being completely incinerable and degradation products which affect metal ion extraction / transport behaviour. Amides, considered to have answers to these problems, are being evaluated for their extraction / transport behaviour in many research laboratories. Di-*n*-hexyl octanamide (DHOA) used for the effective transport of uranyl ion from 4 M nitric acid to a strip solution containing either 1.0M Na_2CO_3 or 0.01M nitric acid suggest possibility of recovery from not only from lean solutions but also feeds containing up to 100 g/L U. Hollow fibre based non-dispersive extraction (HFNDX) showed promise as less than 20 minutes were required to transport >90% U from a feed containing 10 g/L U in 4 M HNO_3 (Fig. 2) [6]. Under identical condition, non-disperive extraction (NDX) of Th was <10% suggesting possible separation of U from macro concentration of Th. A sterically modified amide viz. di-2-ethylhexyl *iso*-butyramide (D2EHIBA) in *n*-dodecane was also used as the carrier for the selective transport of trace U(VI) in presence of large excess of Th(IV) [7]. The decontamination factor obtained in this method is attributed to lower nitric acid transport rates as compared to TBP / n-dodecane system which has much higher permeability coefficient as compared to D2EHIBA / n-dodecane system. This work is particularly interesting as it offers an alternative membrane based separation method to the conventional TBP extraction based separation methods.

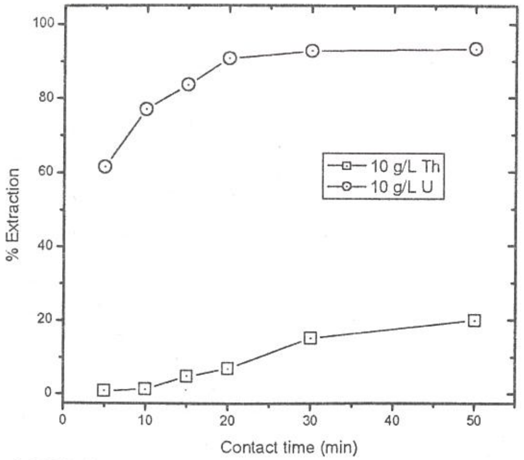


Fig. 2: HFNDX data for U and Th extraction using 1.1 M DHOA. Feed : 4 M HNO_3*, Strip : 0.01 M* NO_3

Tri-alkyl phosphine oxides such as TOPO (tri-n-octyl phosphine oxide) are versatile extractants of uranyl ion from acidic solutions. Numerous reports are available in the literature on the use of TOPO as a carrier for U transport studies. Using TOPO and HDEHP mixture, emulsion liquid membrane technique (ELM) was applied for the recovery of uranium from Wet Process Phosphoric Acid (WPPA) [8]. The simultaneous extraction and stripping operation resulted in a kinetically controlled uranium separation, removing some of the limitations of the thermodynamically dominated solvent extraction system. Flow sheets have been developed for a large scale operation of U recovery using the LM approach [9].

Amines were used as carriers in LM separation of U from acidic solutions. Babcock et al. [10], have suggested that the coupled transport of U from a sulphate medium using a tertiary amine is equally efficient as the solvent extraction systems employed for the same purpose and at least 2.5 times cheaper than the conventional solvent extraction system. Similar to solvent extraction, the amines when used as the carrier transported anionic complexes of uranyl ions from nitric acid feed solutions to an alkaline aqueous phase. On the other hand, the transport of uranyl ion from HCl medium using 30% Aliquat 336 in $CHCl_3$ as the carrier [11] suggested significant amount of acid transport (about 15%) which affected the metal ion transport though >90% transport of U was observed in about 3 hours. However, relatively non-transport of Th suggests possibility of a clean separation of trace amount of U from macro concentrations of Th (Fig. 3) which may find application in AHWR fuel reprocessing. Diluent has a major role (perhaps affecting ligand aggregation behaviour) to play in the transport of uranium using amines as carriers. Higher flux values for uranium at lower carrier concentration was explained based on the aggregation behaviour of the carrier molecules in membrane phase [12].

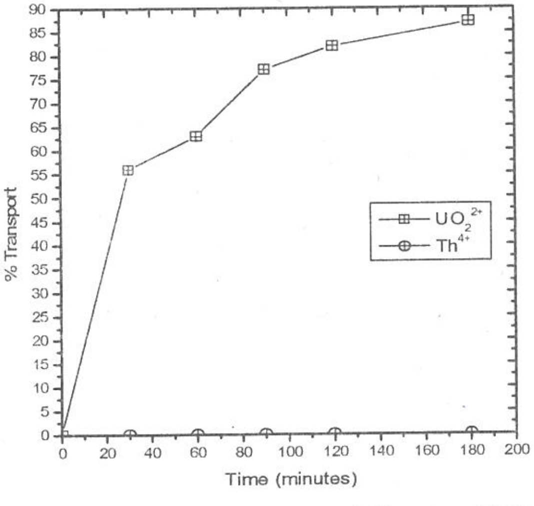


Fig. 3: Transport data of U and Th using 30% Aliquat 336 in chloroform. Feed: 6 M HCl; Strip: water

In a direct application of the LM technology, an HFSLM study involving a hollow fibre module containing a total membrane area of 9.8 cm^2 and dialkyl phosphinic acid (Cyanex 272) as the carrier, was used for the decontamination of the severely contaminated Hanford site ground water [13]. U was concentrated in the strip solution to about 10^8 times though significant amount of Fe(III) also got co-transported.

Recovery of Pu:

Compared to the application of LM methods for U recovery, those for Pu are less common. Most of the publications are from BARC some of which are cited here. Use of TBP as the carrier for the transport of Pu(IV) has been investigated by both FSSLM as well as HFSLM methods. The transport mechanism involved the extraction of species similar to those observed during the solvent extraction studies. And similar to U transport behaviour, viscosity as well as acid transport tends to affect the metal transport. Studies on the transport of Pu(IV) in the presence of fission products from medium active acidic waste employing 30% TBP as a carrier through HFSLM showed that recovery could be enhanced by using fresh strippant each time [14]. Using TBP as the carrier, it was possible to quantitatively separate and recover Pu from nuclear waste solutions using an HFSLM system. In presence of various fission products the selective permeation of Pu through the HFSLM was observed to be more than 90% into a stripping phase consisting of 0.1 M $NH_2OH.HCl$ in 0.3 M HNO_3. The membrane radiation stability was found to be good even after exposure to 1 MRad dose.

Carrier-facilitated Pu(IV) pertraction through an FSSLM was standardized for its decontamination from oxalate wastes employing a commercially available Cyanex-923 (TOPO analog) in dodecane as the receptor [15]. More than 95% of plutonium could be easily recovered from Pu oxalate wastes solution during Pu reconversion operations.

As an alternative to TBP, amides were also evaluated for Pu transport behaviour. Several newly synthesised monoamides such as di-butyloctanamide (DBOA), methylbutyldecanamide (MBDA), methyl butyl octanamide (MBOA), di-butyl decanamide (DBDA), di-n-octyl ethylhexyl amide (DOEHA), and di-hexyl octanamide (DHOA) were also tested as carriers across SLMs for selective transport of Pu(IV) [16]. Of them, MBDA and DBOA proved to be quite suitable as extractants from HNO_3 media providing >95% and >82% transport of Pu(IV) when operated for 7 hours. Several other tertiary amines alongwith TOA have been used as carriers in SLM studies [17]. The diffusion-limited and amine-facilitated Pu (IV) cation permeation in nitric acid media across a SLM was investigated to quantify the membrane carrier type effects on its transport using basic extractants viz. Primene JM-T (JMT) as primary, Amberlite LA-2 (Amb LA-2) as secondary, trilaurylamine (TLA) and triiso-octyl amine (TIOA) as tertiary and Adogen-464 and Aliquat-336 as quaternary amines. Recovery of Pu steadily increased from primary to quaternary amines as it follows the order quaternary > tertiary > secondary > primary, similar to that generally observed in liquid-liquid distribution experiments. More than 95% pertraction of Pu (IV) was easily accomplished using tertiary or quaternary amine as carrier employing a feed solution containing about 5 mg/L Pu in 4 M nitric acid solution while the receiving phase was 0.1 M $NH_2OH.HCl$ (in 0.3 M HNO_3). On the other hand, plutonium permeation was found to plummet to about 49% on employing secondary amine, Amb LA-2, as the carrier [18].

Transport of Pu(IV) from 3M HNO_3 solutions across Aliquat-336/ Solvesso-100 by HFSLM is also reported. Using a bundle of hollow fibres made-up with 20 lumens, of 67 cm^2 surface area, 9 cm length and operated at a flow rate of 10^{-8} m^3 /s more than 80% Pu from oxalate bearing wastes generated during reconversion process could be transported through 10% Aliquat-336/Solvesso-100 into hydroxylamine hydrochloride strippant in about three runs [19].

Recovery of trivalent actinides and lanthanides:

Current perception of radioactive waste management after operations involving the aqueous processing of the spent nuclear fuel materials involves minor actinide partitioning using reagents such as CMPO, Diamide or TODGA (Fig. 4). A large number of publications have appeared using these reagents as carriers in the SLM studies. Danesi has made pioneering efforts in this area and most of the subsequent reports cite his work extensively. At Radiochemistry Division, BARC work has been carried out on the transport behaviour of trivalent actinides and lanthanides using carriers such as DMDBTDMA, TODGA and Cyanex-301.

SLMs consisting of an organic solution of n-octyl(phenyl)-N,N diisobutylcarbamoylmethylphosphine oxide (CMPO) and TBP in decalin were capable of selective separation and concentration of actinide and lanthanide ions from aqueous nitrate feed solutions and from synthetic nuclear wastes where the strip solution is a mixture of formic acid (FA) and hydroxylammonium formate (HAF) [20]. TBP is added to CMPO to improve its solubility in aliphatic diluents. Though low concentration of nitric acid was initially used as the strippant solution, a gradual decrease in the transport rates due to the nitric acid transport led to the use of FA + HAF mixture as the strippant. The effectiveness of this strip solution was gradually reduced by the simultaneous transfer of HNO_3 in the strip solution. A possible way to overcome this drawback was to make use of a second SLM consisting of a primary amine which was able to extract only HNO_3 from the strip solution. The use of second liquid membrane in the synthetic nuclear waste/CMPO-TBP membrane/HCOOH-HAF strip solution/primary amine membrane/NaOH solution allowed the quantitative removal of actinide and lanthanide ions from the feed solution. A mixture of citric acid, formic acid, and hydrazine hydrate was also used as the receiving phase for partitioning of actinides from high level waste of PUREX origin [21]. The studies indicated good transport of actinides like neptunium, americium, and plutonium across the membrane from nitric acid medium. A high concentration of uranium in the feed retards the transport of americium, suggesting the need for prior removal of uranium from the waste. The separation of actinides from uranium-lean simulated samples as well as from actual high level waste was found to be feasible using the above technique. Though TBP

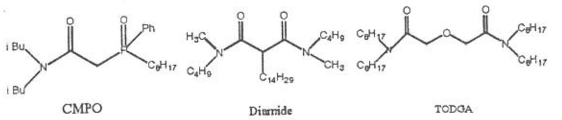


Fig. 4: Structures of reagents used for the extraction of trivalent actinides from acidic wastes

has been used along with CMPO and n-dodecane as the carrier solution, it also facilitates the transport of HNO_3 to the strip side.

Americium removal from nuclear waste streams has been carried out at the Rocky Flats Plant (RFP) using SLM containing DHDECMP (dihehexyl-N,N-diethyl carbamoylmethyl phosphonate) supported on Accurel polypropylene hollowfibres [22]. The waste from the Pu-purification cycle contained HNO_3 concentration in the excess of 7 M which was neutralized partially to yield >7 M nitrate and ~ 0.1M hydrogen ion concentration. >95% Transport was observed into a stripping solution containing 0.25 M oxalic acid. The permeability coefficients were maximum up to 1×10^{-3} cm/sec. Octyl(phenyl)-N,N-diisobutylcarbamoyl methyl phosphine oxide (CMPO) in diethyl benzene was used as a carrier for the investigation on the feasibility of treating low level radioactive waste water using a stirred permeation cell. The transport rates were positively influenced by the addition of sodium citrate to the strip solution. For a simulated radioactive waste solution containing ~ 550 ppm of Ce(III), at a treatment rate of 1 m^3 per day (for >99.9% Ce removal) a membrane of 3.3 m^2 surface area was recommended. Contaminated reactor pool water was reported to have been treated by supported liquid membrane method, though the pertractions rates were very low [23].

Kathios et al. [24], have investigated the use of HFSLM modules for process scale metal separations such as radioactive waste stream clean up and environmental remediation under simulated conditions (Nd was used as a surrogate of Am) using CMPO in di-*iso*-propyl benzene as the carrier. The major challenge in such case is to develop radiation resistant polymers.

SLM studies on the transport of Am^{3+} from nitric acid medium using dimethyl dibutyl tetradecy malonamide (DMDBTDMA) in dodecane as the carrier into 0.01M nitric acid has suggested slow transport rates as a consequence of significant transport of acid into the strip side [25]. It was observed that a mixture of 0.1M DTPA, 0.4M hydrazine and 0.4M formic acid led to highest transport rate (> 60% in 8 hours) when used as the stripping solution. Studies on the transport of Am^{3+} from nitric acid medium into a receiving solution of distilled water using a supported liquid membrane (SLM) made from N,N,N',N'-tetraoctyl-3-oxapentane diamide (TODGA) in *n*-dodecane as the carrier inside microporous PTFE membranes was quite encouraging [26]. Membrane stability was good enough to suggest scaling up of this method for large scale separations.

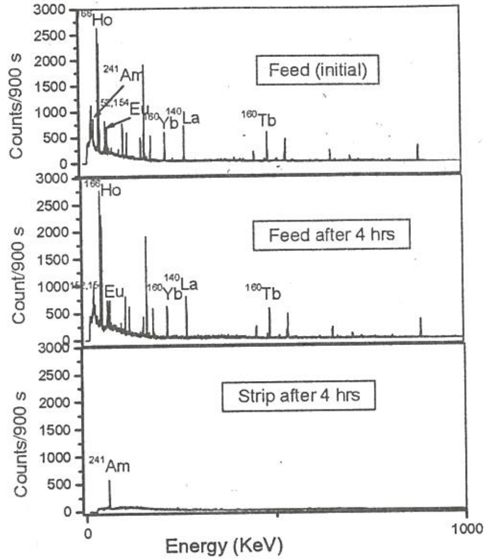


Fig. 5: Gamma spectra of the feed and strip phases after selective transport of Am-241

Lanthanide – actinide separation:

Separation of lanthanides and actinides is a pre-requisite for the development of safer and economically viable methodologies of high level waste (HLW) management. Though literature reports on liquid membrane separation of An(III) and Ln(III) are relatively scarce, some of them are discussed here. SLM studies using PP membranes containing 0.1 M bis- (2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex-301) in *n*-dodecane as the carrier, pH 3.4 solution (sulphanilic acid buffer) as the feed and 0.1 M EDTA as the receiver indicated quantitative transport (>99% in 20 h) of Am^{3+} while that of Eu^{3+} was negligible [27]. A synthetic solution containing Am-241 and several lanthanide radiotracers has revealed encouraging results (Fig. 5). Attempts to scale up using HFSLM technique using a feed containing 2 g/L rare earths were quite encouraging as clean separation was achieved in about 1 h of operation. However, the major concern is the stability of the reagent which turned greenish upon continuous use.

Lanthanide actinide separation was also attempted by HFSLM method using diphenyldithiophosphinic acid derivatives. Geist et al., have employed a synergistic mixture of bis(chlorophenyl)-dithiophosphinic acid and TOPO in a hollow fibre module for the lanthanide actinide separation [28]. About 99.99% Am(III) could be extracted by the contactor from 0.5M nitric acid with about 33% of lanthanides such as Y, La, Ce, Pr, Nd, Sm, Eu and Gd being co-extracted.

Recovery of valuables fission products from radioactive wastes:

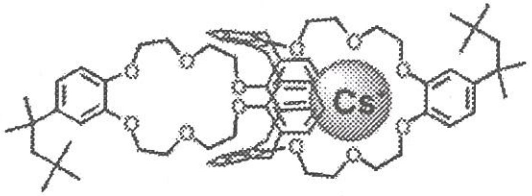
The radioactivity in the HLW is primarily from the fission products ^{137}Cs and ^{90}Sr. These radionuclides are produced by the fission of uranium or plutonium in a relatively high yield and they pose a serious radiation hazard to health and environment. Therefore, a great interest was devoted over the last decade to develop separation technologies for removal and safe disposal of ^{137}Cs and ^{90}Sr from the nuclear waste solutions. Removal of ^{137}Cs from nuclear waste facilitates not only the safe and less expensive disposal of HLW in deep geological repositories as vitrified mass, it also has potential use as an alternative to Co-60 in irradiators. Similarly, ^{90}Sr finds use as a heat source in RTGs. LM based separation methods for these radionuclides are not too many and some of them are discussed here.

Di-t-butyl dicyclohexano 18 crown 6 (DTBCH18C6) in 1-octanol was used as the carrier for the selective permeation of Sr through PTFE membranes from an aqueous nitrate solutions, though feed solutions comprising of 2M $Al(NO_3)_3$ + 4M HNO_3 yielded much improved results. The presence of dissolved solids in HLW influenced the transport rates though the selectivity was not affected significantly [29]. A reversal in the selectivity for Sr to Cs was observed when the cyclohexano group was changed to benzo group. Using di-t-butyl-dibenzo 18 crown 6 in nitrobenzene as the carrier very good transport of ^{137}Cs was observed while ^{90}Sr was obstructed. When the diluent composition was changed from pure nitrobenzene to a mixture of 40% toluene and 60% nitrobenzene, the permeability coefficient increased about 2.5 times.

Though crown ethers were best suited for selective Sr transport, selective transport of Cs was reported with calix-crown ligands. BOB Calix, one of the most selective ligand for Cs extraction, is shown in Fig. 6. Calix-4-arenes mono/bis-crown-6 bound to heteropolysiloxane matrix was used for the selective transport of radionuclides such as ^{137}Cs from a waste containing ^{241}Am [30]. While using calix-crown ligands, the role of diluents play an important role as the solubility of the reagent and viscosity of the diluent decide the transport rates.

Future Perspectives:

Selective pre-concentration using liquid membranes may find use in the nuclear industry sooner than later. This is based on the fact that exotic reagents such as calix-crowns, crown ether, etc. having prohibitive cost can be employed for separation by LM technique at a much lower inventory. The low ligand inventory will not only reduce the cost of operation, but also can help in minimizing the secondary waste volumes. The major concern in prolonged use is the stability of the LM and also the radiation stability of the reagent / polymer. These can be alleviated by the use of grafted membranes and radiation resistant polymers. Faster mass transport can be achieved by using HFSLM / HFNDX techniques.



Calix[4]arene-bis(t-octylbenzo-crown-6)
"BOB Calix"
(As complexed with Cs$^+$ ion)

Fig. 6: The Cs-selective calix-crown

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Membrane Based Separations in Chemical and Nuclear Technology

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Introduction

Research and developments in membrane separation technologies are rapidly expanding all over the world and new membrane separation technologies are overcoming the commercialisation barrier **(1)**. The applications of membranes are getting paramount importance in the field of chemical, nuclear, biotechnology and pharmaceutical industry. In this review, the following membrane processes will be discussed to highlight the important applications in the field of chemical wastes treatment, nuclear wastes decontamination and process developmental work related to reprocessing operation.

-Pressure driven processes

-Non-dispersive membrane technology

-Important process developmental work related to reprocessing operation

Pressure driven processes

1. Pressure driven processes for chemical effluent treatment

In recent decades various membrane separation processes have been developed and utilised in the field of potable water purification and more recently in the treatment of various process and waste streams. Some of the membrane processes are capable of removing both dissolved and particulate contaminants. The best known and most utilized processes in the field of water and waste water treatment are those utilising pressure gradient as the driving force. These processes include reverse osmosis, nanofiltration, ultrafiltration and microfiltration.

In the earlier decades industrial effluents were discharged into the river streams so that the constituent species got diluted and was considered

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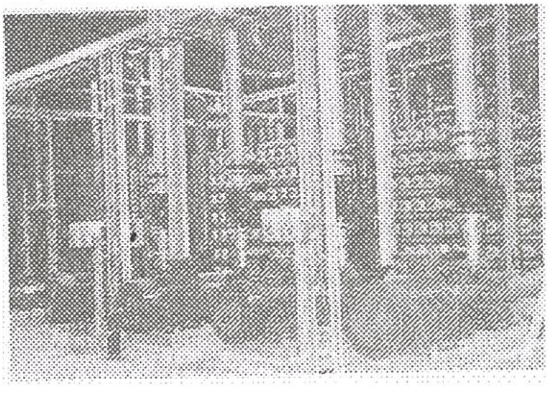


Fig. 1 Fixed membrane reverse osmosis system with a throughput of 240 m³/h

to be safe. However, with growing industrialization, the water availability has decreased and the pollutant levels have reached alarming proportions. Since water was available at affordable costs and quantity, treatment methods aimed at isolating the specific pollutants by physical or chemical means and the resultant aqueous stream was discharged into the environment. However with increasing demand for water and its costs, treatment methodologies aim at not only making pollutants free but also in recovering other valuable products including relatively pure water. In this context membrane processes have their key role to play with its proven ability to preferentially separate water from solution. The concentrated stream then becomes amenable for further processing to recover valuable by-products.

Typically industrial effluents consist of silt, colour, odour, BOD, COD and inorganic species. The quantity of the individual constituents would depend on the type of industry. A typical RO effluent treatment plant was setup about ten year back at Madras Fertilizers Ltd., Chennai for a capacity about 15 million liters per day (15 MLD).

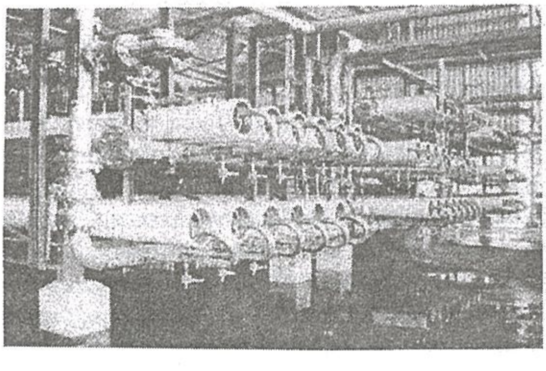


Fig. 2 Fixed membrane ultrafiltration /reverse osmosis system with a throughput of 670 m³/h

Similar plants are in operation at Chennai Petroleum Corporation Ltd., and Rashtriya Chemical Fertilizers, Mumbai. At CCPL the conventional pretreatment section is replaced with ultrafiltration system. Figure 1 shows a membrane system containing reverse osmosis elements only. This is an industrial sized unit, with throughput of 240 m³/h, treating contaminated ground water in a nickel refinery. (2). Figure 2 shows a membrane system containing ultrafiltration and reverse osmosis membrane systems. This is a large installation with a throughput of 670 m³/h, treating effluent from a municipal sewage treatment plant. The treated water is reused in a petroleum refinery (2).

Pressure driven processes for nuclear waste treatment

Membrane based processing of nuclear plant radioactive wastes, and radioactive liquids in general, is rapidly gaining acceptance within the nuclear industry. New membranes and anti-fouling techniques are now available making this technology viable for liquid radioactive waste processing. Recent experience with these improved systems has been quite favorable, and with proper application, the systems are dependable and possess significant processing capability. The performance of these systems compares very favorably to conventional processing technologies.

While early membrane systems experienced considerable difficulties with respect to hardware reliability and sustained performance but with installation of advanced systems, nuclear plant operators have proved that membrane based processing of liquid radioactive waste can be cost effective with superior performance when compared to use of conventional processing technologies. In specific installations, the conversion to membrane based processing produced significantly improved clean water with less secondary waste generation and lower operator radiation exposure.

An attempt has been made in Nuclear Recycle Group to apply membrane process in reprocessing plant for treating various low active streams. The following techniques are discussed in brief:

(a) Removal of activity from fuel pond water using ultrafiltration unit(UF)

The primary function of ultrafiltration (UF) systems are to remove colloids and other particulate foulants from feed streams. Presently, ion-exchange columns are used to remove activity from the fuel pond water. This process is having its inherent draw backs and also generate substantial amount of secondary waste during the regeneration of ion-exchange bed. Hence, ultrafiltration technique was thought to be one of the best option to demonstrate for treating fuel pond water. Considering this, a pilot plant study was conducted for treatment of fuel pond water in reprocessing plant. Table 1 presents typical composition of fuel pond and delay tank water. Table 2 shows details of the spiral wound module used for UF and RO studies. The set-up of UF membrane pilot plant is shown in Fig. 3. Pilot plant scale results showed that 12000 liters of fuel pond water was successfully treated and DF of 4 and 5 was obtained with respect to alpha and beta respectively. The results of pilot plant operation are shown in Table-3. The final product obtained from UF has turbidity in the range of 0.1 NTU (feed turbidity :0.3 NTU). The membrane flux declined by 15% due to possible membrane fouling. The UF module was bcakflushed with pH 2 solultion and original flux value of the permeate was restored. Long term performance evaluation study was conducted by monitoring the quality of permeate (DF value) and radiation dose on the module. No hot spot generation was observed during pilot run of UF with FHA water.

Table-1 Composition of fuel pond and delay tank solutions

Composition of fuel pond water		**Composition of delay tank water**	
pH	6.8 to 7.8	pH	6 to 8
TDS	28 ppm	TDS	1700 ppm
Turbidity	0.3 NTU	Gross alpha	2.8 10^{-5} mCi/L
Gross alpha	4.6 10^{-6} mCi/L	Gross beta/gamma activity	3.5 10^{-4} mCi/L
Gross beta/gamma activity	3.2 10^{-4} mCi/L		

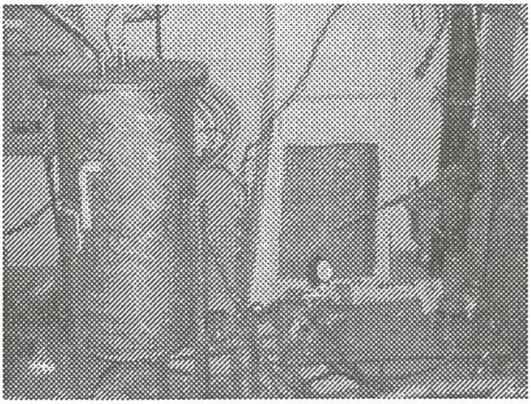


Fig. 3 UF membrane set-up utilized in fuel handing area

Table 2 Details of UF and RO module

Details of membrane module	UF	RO
Dia of UF module	6.25 cm	15 cm
Length of module	30 cm	75 cm
Membrane area	0.5 m^2	3 m^2
Centrifugal pump	180 lph	430 lph
Membrane material	Polysulfone	Polyamide TFC (Thin film composite)
Membrane pore size	100 Å	5-10 Å
Operating pressure	1 bar	15 bar

(b) Removal of activity from delay tank solutions using RO unit

Reverse osmosis (RO) technology will help in achieving ALARA concept, which will be beneficial for the environment. In recent years, RO systems have been used to replace or augment existing evaporation and/or ion exchange technology, due to lower operating costs. The final discharge of low level active waste (containing evaporator condensate, ammonium diuranate filtrate, hand washings etc. from the reprocessing plant) is carried out from delay tank. In present study, the removal

Table 3. Typical analytical results of ultrafiltration pilot plant studies conducted in FHA area

S.N.	Feed activity mCi/L		DF		Permeate NTU	TDS (ppm)[c]	
	α	β/γ	α	β/γ		Feed	Permeate
Sample at 500 litres	2.8×10^{-6}	3.5×10^{-4}	5	4	0.05	28	<10 (45 ppm)[a]
Sample at 2000 litres	3.8×10^{-6}	4.5×10^{-4}	4	3	0.1	22	<10 (38 ppm)
Sample at 4000 litre	1.4×10^{-6}	5.8×10^{-4}	4	4	0.1	22	<10 (42 ppm)
Sample at 8000 litres	2.4×10^{-6}	3.9×10^{-4}	4	4	0.1	35	<10 (54 ppm)[b]
Sample at 12000 litres	5.2×10^{-6}	3.4×10^{-4}	4	4	0.1	35	<10 (53 ppm)[b]

a, The alpha and beta/gamma activity of concentrate was found to be 2.2×10^{-5} mCi/L and 5.5×10^{-3} mCi/L; ,b, The alpha and beta/gamma activity of concentrate was found to be 3.9×10^{-5} mCi/L and 3.5×10^{-3} mCi/L; c, TDS values shown in brackets belong to concentrate

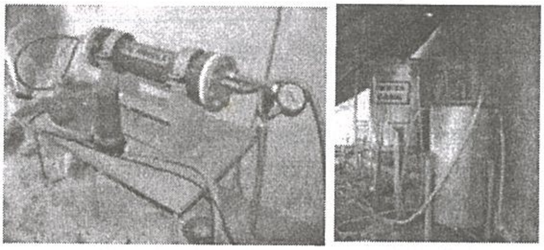


Fig. 4 RO set-up installed at delay tank site in PREFRE plant , Tarapur

of alpha activity, beta activity, nitrate and total dissolved salt (TDS) are investigated from delay tank solution utilizing RO pilot plant.

The membrane module was supplied by Desalination Division, BARC, Mumbai, having specification as given in Table-2. RO set-up installed at delay tank site is shown in Fig. 4. The Delay Tank water composition is given in Table-1. This module was operated at 15 bar pressure which was adjusted by a throttle valve placed on the reject line. The experiments were performed both in once through and recirculation mode. The α and β activity was monitored periodically by sampling the feed, permeate and reject solutions. Samples were analyzed for α and β activities and TDS and nitrate were estimated by standard analytical methods.

The typical results of the RO studies are presented in Table 4. The decontamination factor (DF) values for alpha and beta are ranging 6-10 and 6-15 respectively. TDS and nitrate were also rejected by RO significantly. After passing 25,000 litres, the results of permeate solution shows that the performance of the pilot plant was quite promising. Further, the same RO set-up was used for delay tank solution containing slightly high alpha and beta activity. The results indicated (Table 4) that DF values obtained for alpha were 12-15 which are slightly higher than those values presented for lower activities. This is because the feed input alpha activity is higher. In recirculation mode, good permeate quality was maintained whereas alpha and beta activity of concentrate reached up to 10^{-3} mCi/L and 10^{-4} mCi/L respectively and TDS reached more than 15,000 ppm. These concentrate could be easily

Table 4 Typical analytical results of RO pilot plant studies conducted for delay Tank solution both in once-through mode

S.N.	Feed activity mCi/L		DF		Nitrate_(ppm)_		TDS (ppm)	
	α	β/γ	α	β/γ	Feed	Perm.	Feed	Permeate
Sample at 400 litres	$1.8\ 10^{-6}$	$2.6\ 10^{-4}$	10	15	1330	70	2700	150
Sample at 2800 litre	$2.5\ 10^{-5}$	$2.8\ 10^{-4}$	8	8	1700	100	3500	300
Sample at 4000 litres	$2.7\ 10^{-5}$	$3.4\ 10^{-4}$	7	10	---	---	----	---
Sample at 8000 litres	$1.6\ 10^{-5}$	$2.2\ 10^{-4}$	7	8	2200	150	2900	400
Sample at 15000 litres	$2.9\ 10^{-5}$	$2.4\ 10^{-4}$	9	8	---	---	-----	-----
Sample at 22000 litres[a]	$8.0\ 10^{-5}$	$8.4\ 10^{-4}$	17	12	1259	278	1875	335
Sample at 25000 litres[a]	$7.0\ 10^{-5}$	$6.8\ 10^{-4}$	13	11	---	----	1705	365

a, The delay tank solution contains high alpha and beta activity and value given in the same row in brackets indicate reject TDS.

treated by waste management falility, Tarapur by standard conventional techniques.

(c) World scenario of membrane technology in nuclear industry

During the last 5-10 years membrane technology has been gradually introduced into nuclear power plants for treatment of low radioactive wastes (LRWs). The main reason for this has been the desire to achieve one or more of the following, (a)reduction of radioactivity discharge to the environment, (b) reduction of solid waste from existing effluent treatment facilities, (c) recycling of boric acid

Many nuclear power plants in the United States of America, for example, have traditionally treated low level liquid effluent by direct evaporation of the liquid waste, by conventional filtration and ion exchange, or by combination of these. The common limitation of these processes is that they generate significant quantities of radioactive solid waste to be disposed of. Furthermore, the treated liquid effluent is not pure enough for environmental discharge or recycling.

The major limitation of evaporation is the considerable operating cost with high energy consumption. The limitation of conventional filtration and ion exchange resin is that colloidal particles, some radio-nuclides pass straight through to the product (treated water). Colloidal particles containing $^{58/60}$Co, ^{54}Mg, ^{55}Fe, and ^{125}Sb are typical examples of these. Ultrafiltration is capable of removing these particles completely and has been adopted at a number of sites to complement the existing conventional filtration /ion exchange systems. At other sites, ultrafiltration has been implemented in combination with reverse osmosis, and ion exchange has been discontinued or is utilized as polishing step.

In most of these cases, the reverse osmosis units actually utilize nanofiltration membranes to

Table 5 Examples of industrial use of membrane technology[a] (1)

Membrane process	Facility	Wastes processed
RO	AECL Chalk River (Canada)	reactor coolant clean-up with boric acid recovery
RO with conventional pretreatment	Nine Mile Point NPP (USA)	BWR floor drains and various other wastes
	Pilgrim NPP (USA)	BWR floor drains and various other wastes
RO with UF pretreatment	Wolf Creek NPP (USA)	PWR floor drains, reactor outage waste, spent resin sluice water, and other waste
	Comanche Peak NPP (USA)	Floor drains, resin sluice water, boron recycle water
	Dresden NPP (USA)	inventory of TRU contaminated batch of liquid waste
	Bruce NPP (Canada)	aqueous wastes from steam generator chemical cleaning
RO with MF pretreatment	AECL Chalk River (Canada)	nuclear research wastes
UF	Diablo Canyon NPP (USA)	spent media transfer liquid
	River Bend NPP (USA)	BWR floor drains
	Salem NPP (USA)	PWR floor drains, equipment drains, and other various sources
	Seabrook NPP (USA)	PWR floor drains and spent resin tank drain-down
	Callaway NPP (USA)	floor drains, equipment drains, reactor coolant
	Mound Laboratory (USA)	wastes from fuel reprocessing activities
	Sellafield Nuclear Center (UK)	alpha-containing tail wastes
	Projected facility for treatment of laundry (detergent) wastes	laundry (detergent) wastes
MF	AECL Chalk River (Canada)	contaminated ground water
	Rocky Flats (USA)	contaminated ground water

a, Performance of listed plants can be referred in Ref. 1 for more details

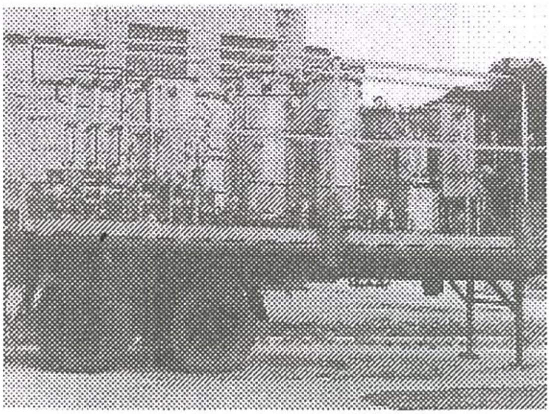


Fig 5. The ECO-2 mobile system for LRW processing, containing ultrafiltration and electrodialysis equipment

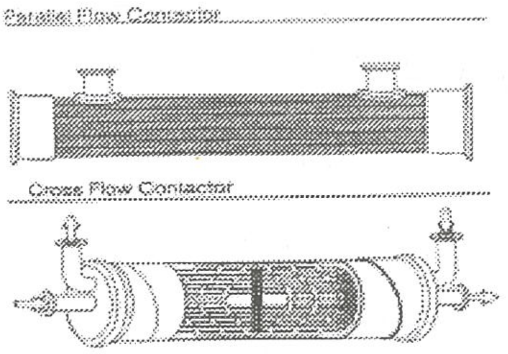
allow passage of boric acid to the permeate side while rejecting any residual dissolved radioactivity. This allows the permeate to either to be discharged to the environment or recycled. This represents the most extensive use of reverse osmosis (or nanofiltration) in nuclear plants.

As each application of membrane technology in a nuclear plant or elsewhere is unique due to specific local conditions, different processing objectives and various other factors, the membrane systems used vary from application to application. Examples of this are given in Table 5.

Fig. 5 shows mobile system 'ECO-2', used to treat small batches of liquid waste at various sites in Russian Federation. Various mobile plants in the ECO series have a similar process configuration, consisting of spirally would ultrafiltration, ion exchange softening, electrodialysis and adsorption. This particular mobile plant, ECO-2 (Fig. 5), was put into use in 1993. More than 450 m^3 of LRWs, originating as surface runoff from a solid radioactive disposal site, were treated. In 1997, about 400 m^3 of low level liquid wastes were processed by this mobile plant at the RADON facility in Volgograd (3).

Non-Dispersive membrane technology

The hollow fiber contactor (HFC) is a device, which provides diffusive mass transfer between two contacting phases without dispersion in one another. Fig. 6a shows the commercial hollow fiber membrane contactor (Lique-Cel, CELGARD). Thus non-dispersive solvent extraction (NDSX) is simply a liquid-liquid extraction in a HFC in which aqueous and organic solutions flow through the capillary and shell side respectively in recirculation mode. Both the phases having dispersion-free contact with each other in the pore mouth of the fibers, which minimizes the possibilities of forming emulsion/third phase or crud formation with extractant. The flow rates are so adjusted that the aqueous pressure in tube side was higher (0.2-0.5 bar) than organic pressure at shell side therefore no mixing of the two phases take place



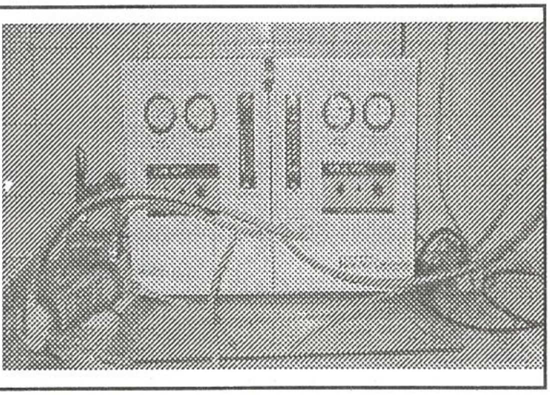


Fig.6a Commercial hollow fiber membrane contactor (Liqui-Cel, Hoechst)
Fig. 6b NDSX set-up used for gold recovery (set-up contains two gear pumps, two flow meters, two pressure gauges and one Liqui-Cel hollow fiber contactor)

Table-6 Surface area of different contactors utilized for liquid-liquid extraction

Contactor	Surface area per unit volume (m^2/m^3)
Free dispersion columns	3 - 30
Packed / trayed columns	30 300
Mechanically agitated columns	150 500
Membranes	1500 - 6000

Source: Ref. 4

and the interface is maintained at the pore mouth of the fibers. It offers a number of important advantages over conventional dispersed phase contactors (pulse columns, mixer settlers etc.) such as non-dispersion of phases in contact, independently variable flow rates without flooding limitations, lack of phase separation requirements, lack of phase density difference limitations, very high surface area to volume ratios which may be upto 10^4 m^2/m^3 and direct scale-up due to a modular design. A comparison of surface area per unit volume of different contactors utilized for liquid-liquid extraction is shown in Table-6[4].

(a) Non-dispersive solvent extraction (NDSX) in hydrometallurgical applications

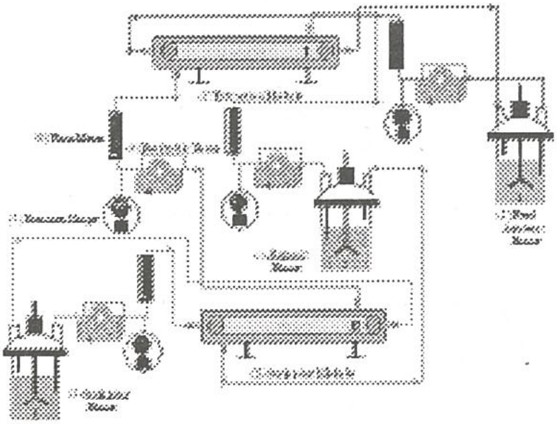


Fig. 7 A Schematic view of the integrated membrane based process for Au(I) recovery from cyanide media using two hollow fiber contactors

In the recent laboratory studies, Pabby et. al. have achieved NDSX of gold cyanide from aqueous alkaline media with LIX 79 (N,N'-bis-(2-ethylhhexyl)guanidine, RH) and stripping of gold from organic complex simultaneously using two microporous hydrophobic polypropylene HFCs each for extraction and stripping in the integrated membrane process [5-7]. The whole process was patented [8]. Fig. 6b shows the NDSX set-up used for gold recovery. A Schematic view of the membrane based solvent extraction and stripping process of Au(I) using two hollow fiber contactor in recirculation mode is shown in Fig. 7

(b) Pseudo-emulsion based hollow fiber strip dispersion (PEHFSD)

In PEHFSD, the feed solution containing the target species is circulated through the tube side of a microporous hydrophobic polypropylene hollow fibber membrane contactor and a dispersion prepared by continuous stirring the organic phase and the aqueous stripping phase forming a water-in-oil pseudo-emulsion, is passed continuously through the shell side in counter current mode, using a single hollow fibber membrane contactor. As a case study, the extraction of gold cyanide using PEHFSD was carried out using LIX79 /heptane system. PEHFSD set-up (Fig. 6b) was same (the equipment used is same as NDSX) used for gold recovery and chromium extraction. Experimental results expressed as the Au(I) concentration in the feed, strip and organic phase against time obtained in HF module are given in Figures 8a and 8b. Au(I) was transported almost completely from the feed to the organic phase within 100 mins., whereas transfer from organic phase to the stripping solution took place in two and half hours (150 minutes). In this study, feed was

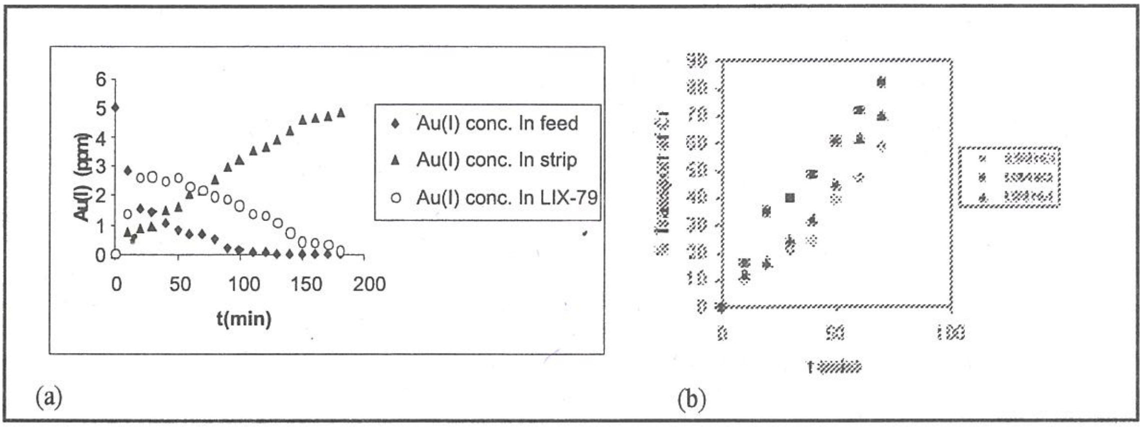


Figure 8(a). Concentration of $Au(CN)_2^-$ in the feed , strip and organic phase as a function of time in recycle mode.

Fig. 8(b). % Transport of Cr(VI) with variation of HCl conc. in feed in recycle mode.

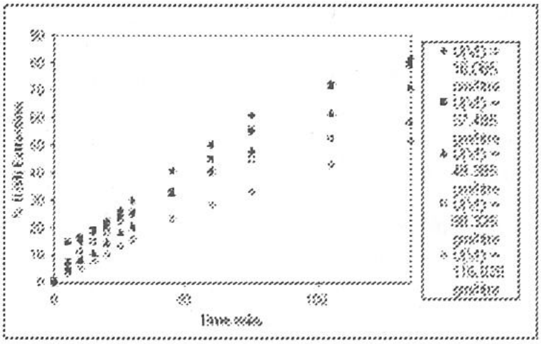


Fig.9 Effect of U(VI) concentration on extraction using NDSX technique

continuously replaced with fresh solution but same stripping solution was recirculated (without replacing with fresh). Similarly, this technique was also applied for chromium extraction from 1M HCl solution using 0.35 M CYANEX 921 /solvesso-100 and 20 g/L hydrazine sulphate as stripping solution.

(c)NDSX and PEHFSD in separation/removal/ concentration of actinides

Based on the performance in hydrometallurgy, a comprehensive programme was made for utilizing the technique of NDSX with hydrophobic microporous hollow fiber contactor, for the recovery of actinides from process effluents. As a representative case, application of NDSX for macro concentration of uranium was investigated. After obtaining preliminary results on NDSX of metals, the present study involves the investigations on NDSX behavior of macro quantities of uranium [U(VI)] which are carried out under different physical, chemical and hydrodynamic conditions. Tri n-butyl phosphate/n-dodecane was used as an extractant. The effect of extractant concentration on extraction of U(VI), different concentration of TBP in n-dodecane (v/v) showed that percentage extraction of U(VI) was also increased when the TBP concentration in diluent is increased from 5-50% but for economical plant scale operation 30% TBP was selected as optimum concentration to evaluate further parameters. The total recovery was achieved more than 98% in three consecutive runs with fresh extractant without adjusting the feed acidity (9). Effect of U(VI) concentration (ranging 16-116 g /L) on extraction showed that 81% extraction was achieved in case of 16 g dm^{-3} uranium concentration after 135 minutes (Fig. 9). Further, extraction of uranium was found to decrease to 51% when U(VI) concentration was increased to 116 g dm^{-3}. This decrease was compensated either by increasing the surface area of the module or running the experiment for longer time. Stripping of U(VI) from loaded organic phase was achieved with 0.05 M HNO_3 as strippant (10a). Feasibility of separation of uranium in presence of oxalate ions from typical reprocessing waste solutions across HFC using 30% TBP/n-dodecane as extractant solution and 0.05 M HNO_3 solution as strippant is clearly established as an alternate to other conventional methods. Similarly, NDSX of Pu(IV) from acidic nitrate media with tri-n-butylphosphate (TBP) as an extractant using HFC also investigated in detail (10b). It was possible to extract and concentrate Pu(IV) from aqueous phase by employing this technique. For back extracting the Pu, uranous nitrate and hydroxylamine hydrochloride solution as strippants were examined, which flowed through the tube side (flow rate: 6.11 $cm^3 s^{-1}$) and the loaded organic was passed through the shell side with the flow rate of 1.66 $cm^3 s^{-1}$.

Transport study of U(VI) and Pu(IV) was performed under similar experimental conditions for both hollow fiber supported liquid membrane (HFSLM) and pseudo emulsion based hollow fiber strip dispersion (PEHFSD). The stability of was improved by utilizing the PEHFSD technique. Thus PEHFSD mode with 20% TBP in nph as extractant could be successfully utilized for separation and concentration of U(VI). Similarly, PEHFSD studies with Pu(IV) and Am(III) from nitric acid media is also carried out and found to be promising.

Important Process Development work related to reprocessing operation

(A) Electrodialysis for low level waste decontamination and concentration

The Low level liquid waste (condensate, regenerant and detergent) generated in reprocessing plant is first subjected to electrodialysis for concentration of radioactive cations into very small volume and thus converting major portion of the waste into a dischargeable environment friendly waste (510^{-5} mCi/L gross beta activity). For this purpose , an electro-membrane cell containing ion exchange membrane in central compartment was designed and fabricated in the PREFRE laboratory. This cell was used to reduce further the volume of concentrated stream generated during electrodialysis A laboratory model electrolyser unit (Fig 10) having 41 pairs of cation and anion exchange membrane of effective size 200 x 80 mm, arranged alternatively and vertically, was used for the study. The membranes were obtained from M/s Thermax Ltd., Chemical Division Pune. These membranes are of the interpolymer type and are composed of high density polyethylene, polystyrene and divinyl benzene while the inorganic groups are sulfonic acid for cation exchange and quaternary ammonium group for anion exchange membranes (11).

About five litres each of regenerant and detergent liquid waste was recirculated through the ED cell at the rate of 16 L/h. Samples after each pass were collected and analysed for fission product activities.

The major contributor to effluent's radioactivity were Cs-137, Cs-134 and Ru- 106. Most of the radioactivity from the low level radioactive effluents could be removed by electrodialysis operation. Decontamination factor (DF) achieved was more for cesium as compared to that for ruthenium due to non-ionic nature of the latter (12). The degree of decontamination increased with

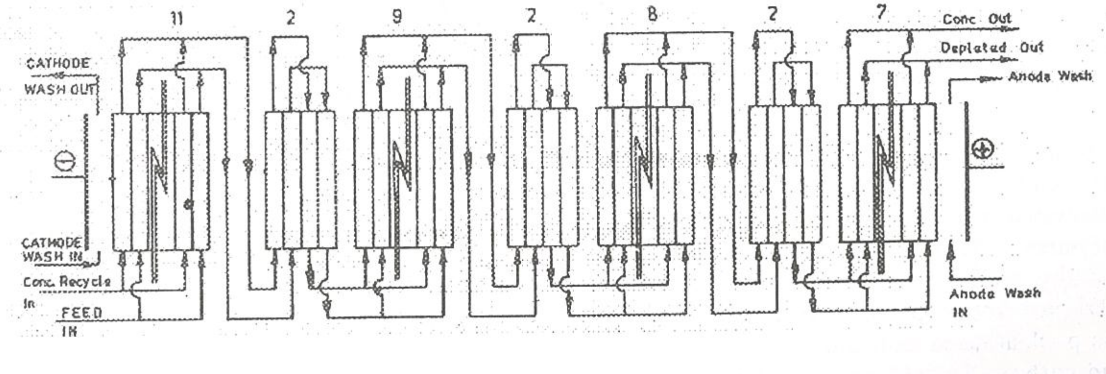


Fig 10 Flow diagram of electrodialysis cell

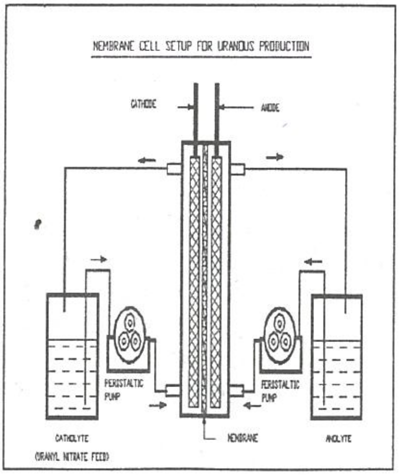


Fig.11. Schematic Diagram of Electrolyser

number of electrodialysis stages performed. Salt content and radionuclide concentration did not cause any significant influence on decontamination factors of these nuclides (6). Concentrate streams generated during electrodialysis operation contained Cs-137 from 0.005 to 0.05 mCi/L and the volume reduction factor achieved in the electrodialysis operation was about 10.

(b) Application of membrane electrolysis in fuel reprocessing operation

Uranous nitrate [$U(NO_3)_4$] solution is used for quantitative reduction of plutonium from loaded tributyl phospate (TBP) phase (13). The membrane cell technology was investigated for the production of 100% uranous nitrate solution (14), which is to be used in the partition cycle of the PUREX process in the fuel reprocessing plant. The membranes used hitherto suffered from mechanical instability. A study was carried out in PREFRE plant to achieve 100% uranous by using membrane electrolytic cell. In this study a thin polymer film that was reinforced with a fabric made of Teflon was used as a membrane. This has been used as a separator between anolyte and catholyte chambers which is made from perflourinated polymers, offering high thermal and chemical stability. Nafion perflourinated membranes are fabricated from copolymers of tetrafouroethylene and perflourinated monomers, containing sulfonic and carboxylic acid groups. One side of the membrane contains sulfonic acid group while the other side contains carboxylic acid group. This membrane is originally designed for use in caustic soda production membrane cells. The perflourinated membranes have the extraordinary chemical and thermal stability of Teflon resins, but, while Teflon is one of the most hydrophobic substances known, perflourinated membranes are one of the most hydrophilic. They absorb water rapidly at room temperature, in amounts dependent upon the number of sulfonic and carboxylic groups. This study paper deals with the application of the cell to produce 100% of $U(NO_3)_4$ solution using different pairs of electrodes. The schematic of the cell is illustrated in Fig.11. The membrane was used for over three years in nitric acid and hydrazine medium without any apparent damage. It offered high chemical resistance and mechanical strength. In each batch operation, the percentage conversion of uranous nitrate was 100%. The membrane has established a life of 128 amp-hr/cm^2 without any change in electrochemical performance. About 10% dilution of product was observed due to electro-osmosis. The 100% uranous nitrate solution generated was utilized for the actual plant process. Further study on the membrane process is being continued.

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Membrane Based Chemical Sensors

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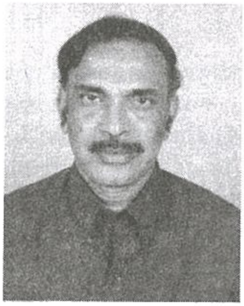

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Introduction

Sensors are defined as "a compact and portable device that detects or measures a physical property and records, indicates or otherwise responds to it" [1]. Depending on the mechanism of sensing or on the method of response generation, sensors are classified as physical and chemical sensors. The chemical sensors can be defined as "a miniature device that responds to a particular analyte in a selective way through a chemical recognition and can be used for the qualitative or quantitative determination of the analyte" [2]. The *IUPAC* has

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defined chemical sensor as "a device that transforms chemical information into an analytically useful signal". The objective of chemical sensor research is the aspiration to obtain analytical information as efficiently as the sensors available in nature. The aim of analytical chemistry is to provide valid information through simple and automatic yet cost effective systems wherein chemical sensors play a key role. Chemical sensors should meet certain demands of analytical chemistry:

- Real-time measurements (field and on-line applications)
- Simplification of analytical process, unattended operation (automatic)
- Nearly reagent less method (minimum and simple chemistry for sample preparation)
- Measurements in location where sampling is difficult (on-line, *in situ*, in vivo or remotely)
- Miniaturized devices
- Cost effective analytical tool (preconcentration and measurement)

It is difficult to have a chemical sensor, which meets all the above requirements. However, efforts are generally focused to design a chemical sensor that satisfies most of the requirements. Presently, most of the research in analytical chemistry is focussed on this area, and it requires interdisciplinary efforts involving a combination of material science, supramolecular chemistry, optoelectronics, microelectronics and signal-processing techniques. Ideally a chemical sensor should be sufficiently selective, sensitive, stable and robust, and have a short response time. The samples for chemical sensors can be in solid, liquid or gaseous form.

Design of chemical sensor

In general, chemical sensors have two basic functional units: (i) receptor, and (ii) transducer. The scheme of a basic design of a chemical sensor is depicted in Fig. 1.

The receptor is the region where selective recognition of an analyte takes place by means of a chemical reaction. Depending on the type of recognition they are categorised as chemical receptors and biological receptors. In chemical receptors, the chemical recognition process is based on a typical equilibrium reaction (acid-base, complexation, redox) that can be used for ionic or molecular recognition. Supramolecular receptors (crown ethers, calixarenes) and molecular imprinted polymers having shape and size-selective centres are also classified under this category. In biological receptors, the analyte recognition is mainly a result of a biochemical reaction.

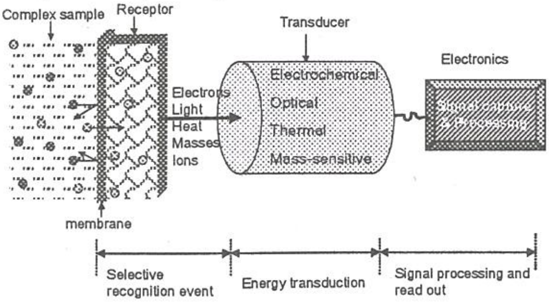

Fig. 1: Schematic representation of a chemical sensor

The transducer is a Latin word which means- "to lead across". Thus, this unit leads across, or converts, chemical information of the analyte into a measurable signal, which is further processed and recorded. The main transduction techniques that are generally used in the context of chemical sensors are given below:

Electrochemical transducers:

This class of transducers transforms an electrochemical interaction between an analyte and the electrode, under zero-current conditions or stimulated electrically, into an electrical signal. Depending on the measured quantity, they can be classified as: (a) Potentiometric, (b) Voltametric, (c) Conductometric, and (d) Capacitance transducers. The potentiometric transducers are based on the measurement of the potential (emf) of a cell at zero current. In voltametric transducers, the substance to be analysed is oxidized by applying an increasing potential or reduced by applying a decreasing potential on the cell until the peak current is measured. When the appropriate oxidation or reduction potentials are known, they can be applied directly to measure the current. This is termed as amperometric sensor. Conductometric transducers are based on observing changes in the electrical conductivity of solutions or changes in conductivity following electron transfer between adsorbed analyte and a semiconductor surface. Capacitance transducers are based on the change in relative dielectric constant of a polymer-coated capacitor due to the absorption of an analyte.

Optical transducers:

The optical transducer converts an optical signal generated from a sensor into an electrical signal. Depending on the optical property utilised, they can be classified as (a) absorbance, (b) luminescence, (c) reflectance, (d) light scattering and (e) refractive index based transducers. The absorption of electromagnetic radiation by the analyte itself or by a compound related to the analyte is measured in absorbance transducers. In the case of non-transparent transducers, reflected light intensity due to the analyte is measured. Luminescence transducers are based on variations in the intensity of the light emitted (fluorescence, phosphorescence) by the analyte itself or after its reaction with a suitable reagent. Alternatively, the intensity of the light emitted in a chemical/ biochemical reaction involving the analyte can be measured (chemiluminescence/ bioluminescence). An indirect determination based on selective quenching of the luminescence can also be used as the analytical signal. Light scattering from particles of a definite diameter in the sample can be the basis of the sensing principles. Elastic scattering modes, as well as inelastic modes, or Raman scattering can be included in this category. Refractive index variations stemming from a change in the sample composition can also be the basis of transduction mechanism. The surface plasmon resonance effect may be included in this group.

Mass transducers:

The mass transducer recognises the change in the mass as a result of chemical interaction. They are classified as (a) piezoelectric, (b) surface acoustics wave and (c) microcantiliver based transducers. Piezoelectric transducers are based on the measurement of the frequency change of a quartz oscillator plate upon the adsorption of a certain mass of the analyte into it. Surface acoustic wave devices based on variations in the velocity of propagation of a generated surface acoustics wave due to the accumulation of the analyte on the piezoelectric substrate. In microcantilever-based transducers, the surface of a cantilever is coated with a layer that selectively sorbs specific chemical or biochemical species, thereby giving rise to a change in the natural resonant frequency of the cantilever as a consequence of the mass change. In addition, when only one side of the cantilever is coated, or there is differential adsorption on opposite sides, it will respond by bending due to the adsorption-induced stress. The motion of the cantilever can be detected with quite high sensitivity by means of various techniques, such as optical beam deflection, changes in piezoresistivity, piezoelectricity, capacitance, and tunnelling current.

Thermal transducers:

The thermal transducer monitors the heat effect as a result of the chemical interaction. Depending on the property utilised they are classified as (a) catalytic and (b) thermal conductivity transducers. Catalytic thermal transducers are based on the measurement of a combustion reaction or an enzymatic reaction using a thermistor. Thermal conductivity utilizes variations in the transfer of heat from a hot body (detector) to the surrounding gas as a function of the thermal conductivity of the gas.

Radionuclide transducers:

These transducers are similar to optical transducers, but utilize the scintillation produced by interaction of the radiations (α and β) emitted by the radionuclides in the sensing material.

The chemical sensors are named generally based on the signal transduction technique. In most of the chemical sensors, the membrane is a key component in the design.

Role of membrane in chemical sensors

A problem of paramount importance in chemical sensor is selectivity, particularly at low analyte concentrations in the presence of interfering substances. Therefore, the membrane is the heart of any chemical sensor. As shown in Fig.1, the membrane acts as a barrier between the bulk solution containing an analyte in a complex mixture and the transducer. Thus, primary function of the membrane is to restrict the accessibility of interfering species to the sensing material. This property of the membrane is extensively utilized in electrochemical sensors like ion-selective electrodes. In some chemical sensor design, a membrane serves as a selective preconcentration layer for the analyte and, therefore, offers a possibility of simultaneous preconcentration and detection of the target analyte. In optical chemical sensors, the membrane is also involved in the chemical transduction. In this class of chemical sensors, the membrane contains the receptor and indicator in its matrix. In general, polymeric membranes such as ion-exchange membranes or carrier based ion-selective membranes are used in the chemical sensors. Since the chemical and physical properties of polymers are often tailor-made by the chemist for a particular application, they have gained importance in the construction of membranes based sensor devices.

Preparation of Membranes

The membranes used in the chemical sensors are similar to those used in the separation science. In optical sensors, the indicator chemistry is also incorporated in the matrix of membrane. In electrochemical sensor, it is desirable that the membrane is capable of conducting electrons. The commercially available ion-exchange membranes like Nafion-117 are used in the construction of chemical sensors though this class of membranes are not highly selective. In optical chemical sensors, the ion-exchange membranes are used for immobilization of indicator by means of electrostatic binding. Since it is difficult to get tailor-made membranes for specific chemical sensors, membranes have to be synthesized depending upon the requirements. There are two routes for preparation of membranes. These are covalent immobilization and physical immobilization of required components in the polymer matrix. The membranes prepared by covalent immobilization are called grafted membranes. The membranes prepared by physical immobilization of receptor and indicators are classified into two groups: (i) polymer inclusion membranes, and (ii) sol-gel membranes.

Grafted Membranes

This class of membranes are prepared by grafting required monomers on polymer chains, generally poly (propylene), by using free radical mechanism. There are many possible methods of grafting i.e. radiation induced grafting, plasma grafting, UV-grafting, thermal grafting etc. The radiation and plasma grafting do not require initiator as the free radicals are directly produced on the polymer chains. Radiation induced grafting of monomer can be carried out uniformly in the bulk matrix. Plasma-induced grafting is good for the surface grafting. UV-grafting requires a photo-initiator but it is does not affect the mechanical properties of the substrate. The grafted membranes are subjected to chemical treatment to produce required functional groups. We have developed a pore-filled method for grafting the required monomers in the pores of membrane [3]. The pore-filled membranes are prepared by incorporating the polyelectrolyte gel within the pores of a robust micro-porous host membrane. The micro-porous host membrane provides containment and mechanical strength to the ionic gel and mitigates the impact of osmotic forces. The appropriate chemistry of the ionic gel, the guest component, leads to good separation characteristics the resulting membrane. There are two possible routes for preparing the pore-filled membranes. These are: (i) *in situ* polymerization of a suitable monomer with a cross-linker within the pores of a host micro-porous membrane, and (ii) *in situ* cross linking of preformed polymer with a suitable cross-linker within pores of a micro porous membrane. The extent of pore filling in both the routes is dependent on the solubility of the monomer or preformed polymer in the solvent used for the incorporation step. Typically the high solubility of monomers as compared to polymers means that membranes with a high degree of gel incorporation can be prepared by the *in situ* polymerization method. However, high incorporations using the *in situ* polymerization route typically require substantial amount of a cross-linking agent, divinyl benzene (DVB). This, in turn, leads to a significant decrease

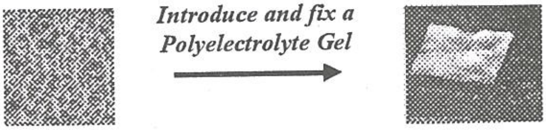

Fig. 2 AFM of a porous substrate before and after covalent or chemical immobilization.

in the ion-exchange capacity of the resulting pore-filled ion-exchange membranes. The AFM image of water-swollen grafted membrane is shown in Fig 2.

These grafted membranes are highly stable and kinetically faster because of the presence of water channels. The selectivity of these membranes can further be enhanced by molecular imprinting approach. Imprinted polymer has a high degree of selectivity due to geometrical shape recognition. Molecular imprinting can be accomplished in two ways: the self-assembly approach and the pre-organization approach. The first approach involves host guest complexes produced from weak intermolecular interactions, such as ionic or hydrophobic interactions and hydrogen bonding between analyte and the functional monomers. The self-assembled complexes are spontaneously formed in the liquid phase and are sterically fixed by polymerization. After extraction of the analyte, vacant recognition sites specific for the imprint are established. Monomers used for self-assembly are methacrylic acid, vinyl pyridine and dimethylamino methacrylate, etc.

The pre-organization approach involves formation of reversible covalent arrangements of the monomers with the print molecule ions before polymerization. Thus, the print spcies have to be chemically derivatized with the monomers before actual imprinting is performed. After cleaving the covalent bonds and removal of the print molecules, recognition sites complementary to the analyte are obtained again. The schematic representation of imprinting in a polymer membrane is shown in Fig.3.

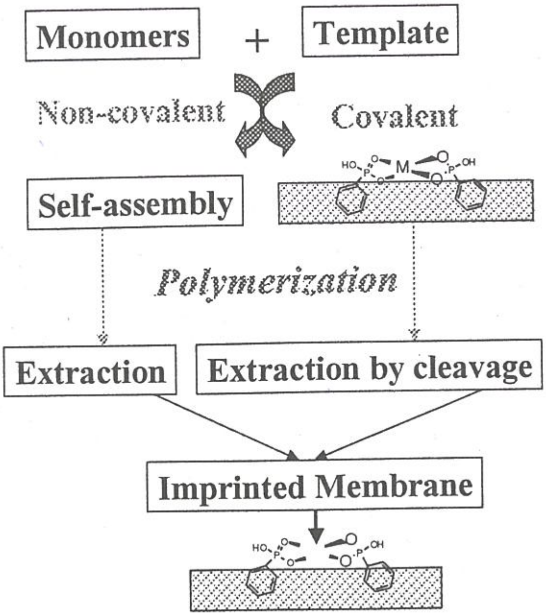

Fig. 3 Schematic representation of imprinting in membranes

The covalent immobilization of indicator/probe molecules along with receptors involve very complicated synthetic chemistry. Therefore, the grafted membranes are mostly used as electrochemical or mass sensor where membranes are not involved in the chemical transduction. In optical chemical sensors, physical immobilization of a receptor and an indicator is more popular than chemical immobilization.

Sol-gel membranes

The sol-gel process allows the preparation of membrane where indicator chemistry can be incorporated [4]. These types of membranes are prepared by sol-gel method using organically modified siloxanes as the basic structure material. The sol-gel process involves the preparation of inorganic matrices via three steps. Components of the sol-gel cocktail are the sol-gel precursor, water, a catalyst, the indicator chemistry and a solvent such as ethanol. Mixing these components causes hydrolysis of the ester, silanol-ester condensation, and silanol-silanol condensation of the precursors. The first step involved here is hydrolysis resulting in the formation of "sol" followed by polycondensation resulting in formation of "gel", which on drying gives a membrane for use as sensor material.

"Ageing" is the process that takes place after mixing precursor, water, solvent and catalyst to form a sol. Ageing or pre-polymerization of the sol causes aggregation due to hydrolysis and condensation reactions, and consequently an increase in viscosity. During this step, the sol is allowed to stand either at room temperature or at a higher temperature for a period of time during which hydrolysis and condensation reactions cause aggregation and crosslinking. In the case of a coated sol, the mixture is allowed to "age" before coating.

Sol-gel membrane is ion-permeable due to residual hydroxy groups (OH) and its porosity, and can be used for entrapping (caging) indicator dyes and receptor in the material. Often, water soluble indicator dyes need not be chemically modified for immobilization as they are retained in the pores of the sol-gel glass due to their size and do not wash out. The covalent binding of the indicators can also be carried out using appropriate organically modified siloxanes.

Polymer inclusion membranes

Solvent polymeric membranes or polymer inclusion membranes (PIM), first introduced by Sugiura et.al [5], are recently being used on wider scale in chemical sensors. These membranes are easy to prepare and have reasonably good optical and electrical properties. These membranes are prepared by physical immobilization of receptor and indicator in the plasticized polymer matrix. The stability of this class of membranes is dependent on their hydrophobicity. The composition of these membranes are flexible, therefore, the membrane can be tailor-made without involving exotic synthetic chemistry. The solvent used in these membranes plays the dual role of: (1) plasticizing, that is making the membrane flexible (plastic), and (2) solubalizing and holding the extractant and indicator into the membrane matrix. Two of the commonly used polymer matrices are poly (vinyl chloride) (PVC), and cellulose triacetate (CTA). These polymers can be plasticized with a variety of plasticizers. Some of these are: 2-nitrophenyl octyl ether (NPOE), dioctylphthalate (DOP), bis (2-ethylhexyl) terephthalate (DOTP), dioctylsebacate (DOS), and tri-(2-ethylhexyl) phosphate (T2EHP). The network of overlapping chains of CTA polymer provides mechanical support to the PIM. CTA and PVC are inert and highly hydrophobic polymers. The strong interactions between the polymer chains and plasticizer make PIM stable in the aqueous medium and prevent the extractant from leaching out. Hence, the chemical cross-linking of the polymer chains are not necessary for PIM. PVC based membranes have been used in potentiometric sensors as Ion Selective Electrodes (I.S.E.) and Field Effect Transistors (F.E.T.) CTA is a better polymer for optical chemical sensor because of two reasons: (i) CTA can hold plasticizer amounting to twice of its own weight without affecting the mechanical properties, and (ii) have good optical properties. High amount of plasticizer in PIM increases liquid fraction, which forms the ion-diffusional transport channel. PVC based membranes are known to take up water from aqueous phase and become opaque. The CTA based membranes do not absorb any water. However, CTA is not very stable in high concentration of acid. The PIM made of CTA should be used in aqueous medium having acidic pH range. The new polymers like polysulfones are being tested as an alternative material to CTA and PVC [6].

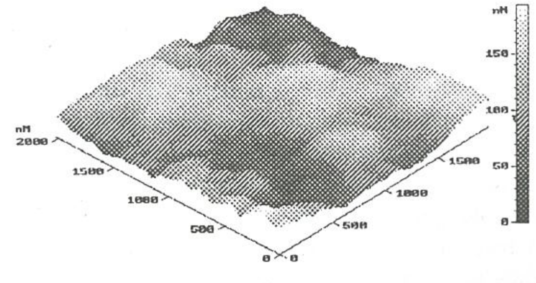

Fig 4. AFM image of a polymer inclusion membrane, wherein the extractant is physically immobilised in plasticized CTA matrix.

The polymer chains in plasticizer form the gel like network in PIM, which is expected to increase the viscosity and prevent the carrier (extractant) from leaching out [7,8]. Atomic force micrograph given in Fig. 4 shows clearly that these membranes have gel like structure. In order to increase the transport selectivity and enhance the flux, receptor molecules that selectively form complexes with solute molecules are dissolved in the membrane and serve as carriers for transport.

Examples of membrane based chemical sensors

In this article, it may not be possible to describe all varieties of chemical sensors. Therefore, the scope of this article is limited to optodes (a class of optical chemical sensor), radionuclide sensors, and quartz crystal microbalance based mass sensors. These chemical sensors are still at research level but have immense potential in the field applications.

Optical sensors (Optodes)

The word "optode" is derived from Greek, meaning "the optical way" of generating signal in the sensing layer. These chemical sensors generate an optical response to the chemical reaction that result from the interaction of the analyte with the receptor. Most of the optode designs involve simultaneous preconcentration and determination of the target analyte, and are therefore amenable for continuous monitoring of toxic species in aqueous environment [9]. The reagents immobilized in the sensor are responsible for the extraction of the analyte into the sensing material and generating an optical signal proportional to the change in the concentration of the analyte. The immobilization can be performed directly on the surface of optical fibres (intrinsic sensors), or on a suitable substrate, which serves as the interface between the sample and the fibre-optic system (extrinsic sensors) [10]. The extrinsic sensors are easy to design as compared to intrinsic sensors. The two widely used configurations of extrinsic sensors are: (i) pool optodes, and (ii) membrane optodes. In pool optodes, the target analyte permeates through a membrane into a detection cell containing aqueous solution of a suitable reagent capable of generating an optical signal. Ion-selective membrane optodes have been extensively employed in numerous sensing schemes for trace analysis of metal ions [11].

Colour changing optodes:

The membrane optodes have been prepared using new indicator dyes; ionophores, chromoionophores and fluoroionophores using highly diversified methods of immobilization [12]. Bulk optodes for different ions like Zn^{2+}, Pb^{2+}, Ca^{2+}, Na^+, and NH_4^+ were developed based on immobilization of an ion selective ionophores and a proton selective chromoionophore in a plasticized poly (vinyl chloride) matrix by the former group of Prof Simon [13-17]. The effect of different immobilization methods and matrix materials on the analytical performance of a Cu (II) sensitive membrane optodes has been investigated by Oehme et. al [18]. The immobilization methods used in this study were: (i) physical entrapment, (ii) electrostatic immobilization, and (iii) covalent immobilization. The physical immobilization of the indicator dye Zincon in the hydrogel and plasticized poly (vinyl chloride) (PVC) was found to provide membrane optodes with the highest sensitivity for Cu (II). Different types of chromophores have been immobilized in plasticized PVC matrix to develop membrane optodes for Cu (II), K and Gd [19-21]. Suzuki et. al. designed a colour changeable membrane optode for Li, by using two kinds of lipophilic dyes, KD-C4 and KD-M11, whose colours and pKa values are different [22]. In this membrane optode, the hues of red $\rightarrow$ orange $\rightarrow$ yellow $\rightarrow$ green $\rightarrow$ blue can be obtained for lithium ion concentration in the range of 10^{-6} to 1 mol/L.

A colour changeable film sensor (optode) for Cr (VI) determination has been developed in our laboratory [23] by immobilizing 1,5-diphenylcarbazide (DPC) as the indicator in a plasticized cellulose triacetate (CTA) matrix. Poly (vinyl chloride) (PVC) is generally used for preparation of membrane sensors (optodes and electrodes) due to its relatively low cost, good mechanical properties and amenability to plasticization. However, PVC based membranes are known to take up water from aqueous phase and become opaque [24]. The CTA based membranes do not absorb any water and have good optical properties [25]. Therefore CTA was used as the matrix-forming polymer instead of PVC. The stability of Cr (VI)-DPC complex in the membrane was examined using an anion exchanger (Aliquat-336) and a cation exchanger (dinonylnapthalene sulphonic acid) as the additives in the membrane optode matrix. The membrane optode with Aliquat-336 was found to have requisite properties to function as an optical sensor. Fig. 5 shows the change of colour and its intensity of the above optode as a function of the amount of chromium Cr (VI) taken up by the membrane. The membrane changes colour from transparent to purple and the intensity of purple colour depends on the amount of Cr (VI). The membrane becomes yellow in colour when higher amount (100 µg) of Cr (VI) was present in the equilibrating solution.

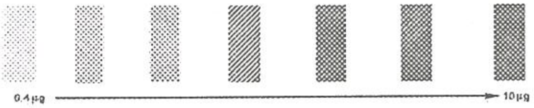

Fig. 5. Change of colour of the optode with increasing concentration of Cr (VI). Membrane samples (1x3 cm²) were equilibrated for 1 h. (under stirring condition), with 25 mL of solution (pH = 3) containing Cr (VI) over a range of 0.1-10µg.

This optode has been optimised for obtaining quantitative extraction of Cr (VI) in the membrane optode, its optimum optical response and maximum working range. This membrane optode has been tested for Cr(VI) determination in spiked tap water and seawater samples. Using this optode, Cr(VI) even at levels of 13.6 ppb (in 25 mL of seawater) could be quantitatively detected. The optodes developed in the present work were found to be stable, cost effective, easy to prepare and efficient for direct preconcentration and determination of Cr(VI) in a variety of aqueous samples using spectrophotometry. However, this membrane optode is for one time use only as the reaction of Cr(VI) with DPC is irreversible.

Using the same concept, the colour changeable optode for uranium and thorium have been reported using Alizarin Red S [26] and 4-(p-nitrophenylazo)-pyroctachol (NAP) [27], respectively. However, these dyes are not very specific, therefore, applications of these optodes require careful evaluation of possible interferences in actual applications.

Scintillating radionuclide sensor:

Migration of radionuclides to soil, surface water and groundwater near nuclear sites is a possibility and it is essential to monitor them continuously from environmental, health and waste management points of view. Of these radionuclides, the actinides are one group of major concern due to their long half-lives and high radiological toxicities Actinide separation and preconcentration can be carried out by a variety of methods such as ion-exchange, liquid-liquid extraction and extraction chromatography. However, these methods involve multiple steps like loading, elution and liquid scintillation counting and cannot be used for developing chemical sensor for field applications.

Recently, the preparation of a polymer film has been reported which changes colour on exposure to γ / UV-radiations [28]. The mechanism of this film is based on the generation of H^+ ions on coming in contact with the radiations, which further react with the chromophore "Fluoran" to form the colour. This kind of system would be highly useful for quick visualization of radiation field. For α/β-emitting radionuclides, the scintillation process appears to be the most suitable optical response mechanism for radionuclide sensors as this can provide detection of radioisotopes in presence of a large excess of their stable isotopes. Organic scintillators are generally used for α- and β- particle detection because of their fast response time. The α- and β- radiations have high linear energy transfer (LET) in the matrix and short ranges which, in turn, lead to the possibility of their detection only in close proximity to a detector or scintillation transduction material. Hence, an ideal radionuclide sensor based on the α- / β-scintillation response mechanism should have the following features: (i) high levels of selective preconcentration of radionuclides, (ii) α- / β- emitting radionuclides must spatially localize in close proximity to a scintillating material, (iii) it must have radiation selectivity, (iv) sensing material must retain the radionuclides to accumulate signal and (v) sensor should be reusable for multiple measurements.

In order to develop a chemical sensor for field application, the chelating scintillation fibers have been developed for the measurements of ^{137}Cs [29].

The chelating scintillation fibers were developed by coating them with Cs$^+$ ion selective dual-mechanism bifunctional polymer (DMBP). DMBP is composed of phenol-formaldehyde oligomers grafted onto a polystyrene-based resin bearing diphosphonate ligands. A scintillating polymer inclusion membrane (S-PIM) for preconcentration and determination of α- emitting actinides in the aqueous medium [30] has been developed. The schematic representation of the scintillating radionulcide sensor is given in Fig. 6. These S-PIMs were prepared by physical immobilization of an extractant bis(2-ethylhexyl)phosphoric acid (HDEHP), a primary scintillator 2,5-diphenyloxazole (PPO) and a wavelength shifter 1,4-bis(2-methylstyryl)benzene (MSB) in the dioctyl phthalate (DOP) plasticized cellulose triacetae (CTA) matrix.

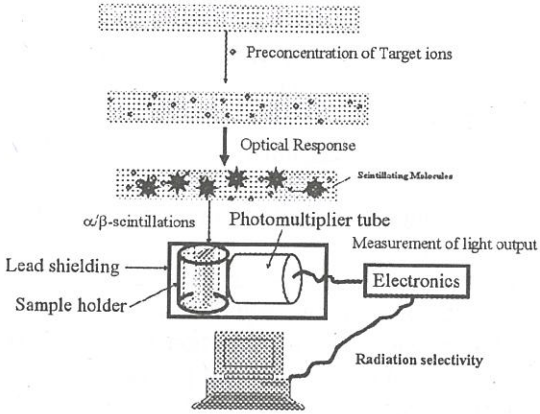

Fig 6. Schematic representation of a scintillating radionuclide sensor

The S-PIM developed in this work has been characterized in terms of its extraction efficiency towards actinides (chemical selectivity), scintillation counting efficiency and α / β discrimination based on scintillation pulse height analysis (see Fig.7). The β- emitting lanthanides (^{147}Pm and ^{154}Eu) have been studied in order to quantify the possible interference of lanthanides. The S-PIM could preconcentrate and determine 46 Bq (present in 100 mL) of a representative α- emitting radionuclide (^{241}Am) in the tap water and seawater samples.

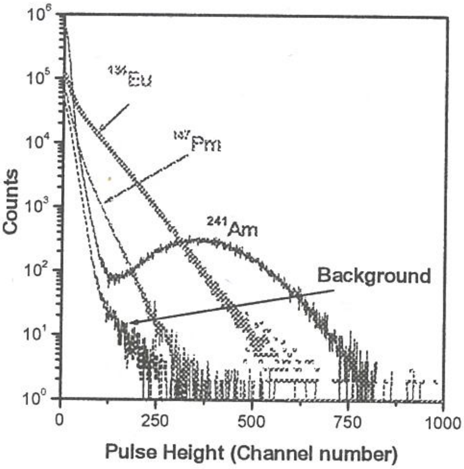

Fig.7 a- scintillation pulse height spectra of blank S-PIM and S-PIM loaded with ^{241}Am, ^{147}Pm and ^{152}Eu. S-PIM samples (1x3 cm^2) were equilibrated for 12 h (non-stirring condition), with 15 mL of solution containing the appropriate radionulcide at pH = 2.5.

Mass sensors

Pierre and Jacques Curie discovered piezoelectricity in 1880 by showing that a quartz crystal the surface becomes charged, when weight is placed on it and the magnitude of this charge was proportional to the weight. This piezoelectric effect is a property exhibited by anisotropic crystals. These material lack centres of symmetry and when a force deforms the lattice, surface charge is produced. Conversely, if an oscillating field (bias) is applied to such materials, they vibrate as a result of changing mechanical deformations. Each crystal has its own resonant frequency at which it vibrates most easily, converting electrical energy into mechanical energy. Any change in the characteristic of the material as a result of interaction with the analyte will alter the vibrational frequency of the oscillator, which can be measured.

The basic concept of a shear mode resonator is given in Fig. 8. The relation ship between resonant frequency of an oscillating piezoelectric crystal (f_o in MHz) and the mass deposited on the crystal surface ("Δin g) is given by

$$\Delta f = \frac{-2.3\text{x}10^{6} f_0^{\,2} \Delta m}{\text{A}}$$

Where Δf is change in frequency in Hz and A is piezoelectrically active area in cm^2 (typically < 1 cm^2). The negative sign indicated that increase in the mass results in decrease in the frequency.

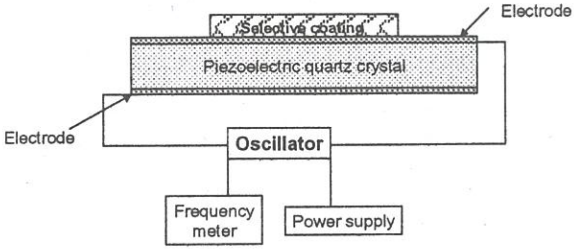

Fig. 8 A schematic representation of experimental set up of a piezoelectric sensor.

The major drawback of the quartz crystal microbalance (QCM) is the lack of selectivity to the source of the mass changes. Polymers play an important role again as the selective extracting medium. A thin coating of the selective polymer is immobilized onto the surface of the piezoelectric crystal. Sensors for inorganic and organic compounds have been reported that are operative either in liquid or gaseous phase [31-33]. This class of sensors have been well established in gas and vapour phase work, and in solution despite the lower resolution caused by the viscous damping of the oscillation by the liquid. The polymer based QCM sensors for Cu^{2+} [34], Ni^{2+} [35], and K^+ [36] have been developed, wherein the receptor molecules specific to these ions have been immobilised in a polymer matrix.

Conclusions

Membrane based sensors play an important role in various fields of science and technology. Sensors can be developed for monitoring of various elements and ions in solutions, even trace levels. In industries, these sensors can be used for online monitoring of levels of various ions and elements in solution flowing in loops. These sensors can be used to have a check on the amount of elements being disposed in waste streams. These sensors can play an important role in various industries, especially in continuous monitoring, process control and quality control at different stages. These sensors can also be used in field applications to monitor the levels of various elements/ions in various environmental samples

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Track-etch Membranes: Production and Applications - an Indigenous Effort

***Dr R.H. Iyer** received his M.Sc degree in Chemistry from Kerala University and his PhD Degree in Nuclear Chemistry in 1966 from Purdue University, USA for his work on Ternary Fission of ^{238}U. On completion of the one year training course, he joined the Radiochemistry Division, BARC in 1959. Dr Iyer is internationally known for his basic and applied research contributions in the areas of nuclear fission, applications of solid state nuclear track detectors (SSNTDs) in science and technology, chemistry of actinides and lanthanides, and Radioanalytical chemistry. He steered the Radiochemistry programme during 1992-1996 as Head, Radiochemistry Division. Subsequent to his superannuation from BARC in 1996, Dr Iyer was appointed as Emeritus Scientist by the Council of Scientific and Industrial Research (CSIR), wherein he developed micro-porous track-etch membranes(TEM) using the BARC-TIFR Pelletron accelerator.*

Dr Iyer was Visiting Scientist, San Diego State University, San Diego, California, USA (1974- 75). He is on the Editorial Board of the International Journal "Radiation Measurements". Dr Iyer has guided 11 Ph.D. students so far. He has published about 300 research papers and reports with 90 articles in International Journals. Presently, Dr Iyer is Dean, College of Pharmacy at Dombivili (E) – an ISO 9001-2000 certified and AICTE approved institution affiliated to University of Mumbai

Introduction

While serving primarily as excellent facilities for research in atomic and nuclear physics the world over, heavy ion accelerators have in the last couple of decades opened up completely new perspectives for applied research in the area of large scale production of nano- and micro-porous polymeric membranes, also known as Track-etch membranes (TEMs) with precisely controlled characteristics. Large scale production of these porous membranes with well defined and uniform pore size and pore density, uniform thickness, high tensile strength, nearly unit tortuosity (ratio of the length of the pore to the thickness of the membrane) and inertness to toxic environments is justified for meeting the growing demand for a number of scientific, industrial, medical and many other technological applications.

In this article an overview of the indigenous efforts initiated as part of a CSIR-BARC project for the preparation / production , quality control, and certification of Track-etch membranes (TEMs) using the BARC-TIFR Pelletron accelerator will be provided. A brief outline of some of the new and emerging applications involving large scale uses of TEMs and the related development efforts in various R&D centres is also given.

Accelerator-produced micro porous polymeric membranes generally known as Track-etch membranes (TEMs) are finding extensive applications in many areas of science and technology and in particular medical sciences. Track-etch membranes offer distinct advantages over conventional membranes due to their precisely determined structure. Their pore size, shape and pore

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density can be varied in a controllable manner so that micro porous membranes of well-defined and user-specific transport and retention characteristics can be produced (1, 2)

The motivation for this R&D effort comes from two well-recognised facts:

(a) The growing demand in recent times for accelerator-produced micro porous membranes with well defined and uniform pore size and pore density, for a number of new and emerging scientific and industrial applications (3) (other than the traditional ones, namely, ultra and micro filtration), with possible large scale uses of TEMs such as separation sciences, super clean environment, conducting polymers and sensors, gaseous diffusion, medical sciences, nano- technology devices etc justifying indigenous production of TEMs .

(b) The basic expertise and facilities to develop this emerging technology indigenously is available with us. It would, not only be possible but also desirable for us to scale up production of these membranes to several thousands of square meters per year to be able to put them to actual use/ applications on a commercial scale.

Scientific Background

The most widely used membrane materials are made commercially by solvent cast methods, by exposing polymer films to consecutive steps of cold stretching, hot stretching and heat setting and by various other methods (4). These chemical membranes have some disadvantages such as low tensile strength, non-uniform pore density and pore diameter, and large tortuosity but their porosity is high around 60-85 %. Their poor mechanical properties are usually countered by their relatively large membrane thickness, typically 150 mm or so.

Heavy ion beams produced by accelerators are characterised by extremely high linear energy transfer (LET). All kinds of modifications of polymers (which are essentially dielectric solids) are brought about by the creation of the so called "latent tracks" or "as implanted tracks" from the primary deposition of high energy (~MeV) inside a tiny target volume and within an extremely short time The energetic heavy ions with ranges slightly above the thickness of the foils pass right through the polymer foils (usually 10 to 25 μm thick) making them porous. Since the original pore size created by the heavy ions is of the order of 5-10 nm, (50-100 A^0), simple chemical etching is required to enlarge the pore size to micrometer range. In the case of most polymeric materials such as polycarbonates (PC), polyethylene terephthalate (PET), chemical etching is done using alkali solutions e.g. 6N NaOH at 60 ^{0}C for a known duration.

During chemical etching the damage zone is transformed into a hollow channel. The variation of pore size with etching time is linear. This allows us to make user-specific TEMs. The pore diameter can vary from about 5-10 n.m to several micrometers. The pore density can vary from as low as 1 to as large as 10^{10} cm^{-2}. No other type of membrane provides such a possibility (5).

Some of the other useful properties of TEMs are:

⇒ Absence of hygroscopicity (< 0.5% swelling in water)

⇒ Biological inactivity

⇒ Higher strength compared to other types of membranes and flexibility

⇒ Practically no leachable components into the filtrate

⇒ Possibility of regeneration by means of membrane cleaning with a tangential or pulsed reverse flow

⇒ Resistance to most acids, organic solvents and dilute alkalis

⇒ A smooth and transparent surface, which permits studying the retained / collected material by optical and electron microscopy

⇒ Small weight and low ash content which is important in gravimetric analyses.

⇒ Absolute absence of radioactivity in the polymeric membrane material

⇒ Absolute retention of particles with sizes larger than the pore diameter

Because of these unique features, the demand for TEMs is increasing in recent times for a number of scientific and technological applications such as:

- micro filtration
- ultra filtration
- super clean environment
- medical science and pharmaceutical industries
- hospital treatment of burns/wounds
- respiration protection
- gaseous diffusion/separation
- analytical sciences
- separation sciences
- nano technology

Review of status of R & D in the subject

International Status

Reproducible production of tailored TEMs based on irradiation of polymeric films is now a mature technology. Heavy ion accelerators are employed for irradiation of materials on an industrial scale in many countries e.g.; USA, France, Germany, Belgium, Japan, Russia. To meet the growing demands of these membranes for various applications, many countries notably in JINR, Russia have established dedicated facilities for production of TEMs of the order of 500,000 m^2 per year with the following specifications and projected demands (5, 6)

Specifications

Pore size/ pore diameter 0.02 10 μm

Membrane thickness 5 50 μm

Width up to 320 mm

Pore density 10^5 to 10^9 per cm^2

Projected demands

Super clean elements production 200,000 m^2 /year

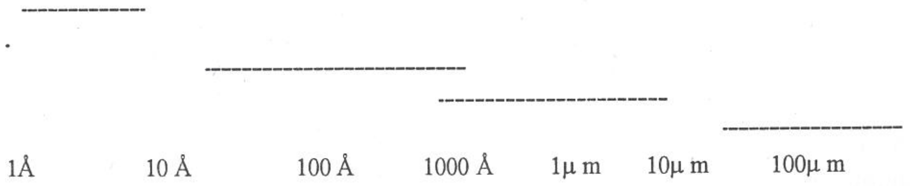
Medical purposes 200,000 m^2 /year

Ecological investigation, respiration protection, analytical sciences, etc. 100,000 m^2/year (This was endorsed during discussions with the Russian delegation of Dr. AN Sissakian, Dr MG Itkis and Dr NA Russakovich from the Joint Institute of Nuclear Research (JINR) when they visited BARC from 11th to 15th December 2000.)

These pore characteristics make them eminently suitable for a wide variety of applications such as ultra filtration (< 0.1μm) and micro filtration (0.1 1.5 μm) membranes for complete removal of viruses, bacteria, dust and colloidal particles from fluid media. This is apparent from the relative sizes of ions and molecules and the optimum ranges of pores sizes for different applications as illustrated below.

Relative sizes of some ions and molecules

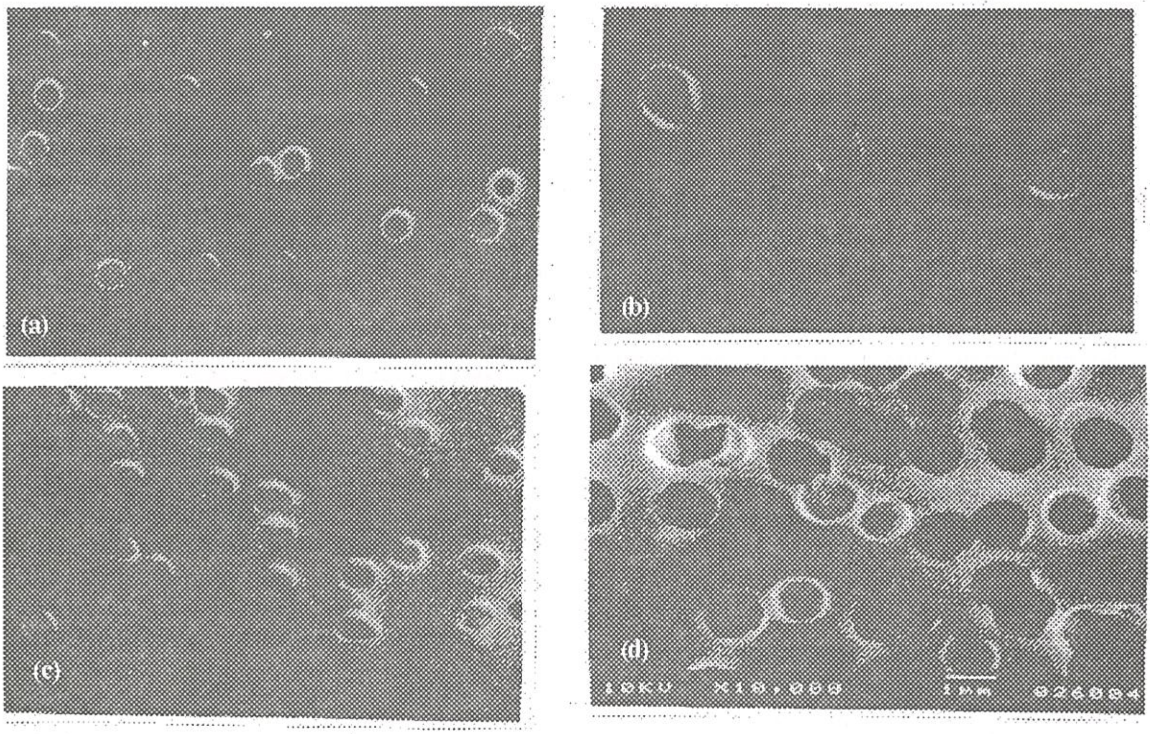
H_2O	2 Å
Na^+	3.7 Å
Sucrose	10 Å
Hemoglobin	70 Å
Influenza virus	1000 Å
Staphylococcus Bacteria	10,000 Å (1 m m)
Starch	10 m m



National Status

Sensing the steadily growing applications of these membranes in many areas of research and industrial applications, we have, as part of a CSIR-BARC project, for the first time in the country standardised the methodology for the preparation of track-etch membranes 10 μm thick, with uniform pore density ranging from 10^5 to 10^7 pores per cm^2 and any user-specific pore diameters ranging from about 5-10 nanometers to about 1-2 μm and areas in the range of about 100-400 cm^2 using Rutherford scattered beams of 100-130 MeV ^{35}Cl, ^{58}Ni, ^{107}Ag and ^{127}I from the BARC-TIFR Pelletron accelerator. An SEM photograph Track-etch membranes prepared by us is shown in Figure-1.

An important aspect of the R&D work was the effort / attention focused on the growing need to examine and/or develop practical technologies that not only can remediate waste streams but also recover valuable components from waste solutions/ effluents - *a topic of vital global concern dealing with the preservation of a clean environment.* Here again realizing the vast potential of Liquid Membrane (LM) processes, particularly Supported Liquid Membrane based processes (SLM) which are the simplest and fast emerging separation process capable of selectively and efficiently recovering one solute from a host of other ions we demonstrated the use of indigenous TEMs in laboratory scale SLM separations giving matching performance with some



Scanning Electron Microscope (SEM) Photographs of Makrofol Track-etch Membranes (TEMs) prepared by bombarding 10μm Makrofol foils with elastically scattered heavy ion beams at the BARC-TIFR Pelletron Facility showing well defined pores. All the foils were etched in 6N NaOH at 60° C for 60 min. (a) ~ 120 MeV ^{35}Cl, (b) ~ 130 MeV ^{58}Ni, (c) ~ 132 MeV ^{107}Ag and (d) 130 MeV ^{127}I. The average pore diameters (μm) decrease with increasing mass of the heavy ion viz 1.81 ± 0.1, 1.63 ± 0.3, 1.39 ± 0.2, and 1.25 ± 0.1 respectively for a,b,c and d.

of the commercially available membranes.(1,2) A significant and visible result emerging from this R&D scheme which abundantly proves the above features of SLM process is the development of a simple SLM-based generator system for the regular supply of pure, carrier-free ^{90}Y, a pure beta emitter useful in beta-ray therapeutic applications, from complex, hazardous and highly radioactive waste solutions. This should provide a fillip to develop similar separation/recovery programs in waste management.

Some common commercial applications of TEMs

Heavy ion irradiated porous polymer foils are said to be used already commercially as seals to protect the interior of sensitive volumes e.g.; small electric motors against penetration of dust and water vapor from the ambient, while maintaining pressure equilibrium and gas exchange with the ambient **(3)**

Process filtration, laboratory filtration and cell culture are three major applications of TEMs as filters. In process filtration, TEMs are used as cartridges. Purification of deionised water in microelectronics; filtration of beverages; separation and concentration of various suspensions are typical examples. Several track membrane-based products are available commercially as reported in the literature **(7)**. e.g.

i. Commercial portable TEM filters for tap water, cartridge filters with 1 - 2.5 m^2 of 0.2 μm TEM for clean drinking water ~ 500 litres/hr,

ii. TEMs are also used commercially for purification of gas media to provide ultra clean air and to bring down the dust levels from class 100 to class 1 with long service life of the TEM reaching 2 years.

iii. Whatman Nucleopore Cryp Test cartridge for removal of water borne protozoan cysts (8).

iv. Another important and possible strategic application of the TEMs reported in the literature is for gas separation using Knudson diffusion process which occurs when the pore size is much smaller than the mean free path l of the gas molecule. Under standard conditions, the mean free path of CO_2 is 58.6 nm and that of CO is 39 nm. Using TEMs of 0.1μm diameter and 10^8 10^9 pores/ cm^2, CO_2/CO separation factor of 1.1 is reported for a single stage. Using 'n' stages the separation factor's' can be increased to 's^n'. Values of separation factors for some typical gas mixtures are as follows:

O_2/N_2	0.94
CO_2/CH_4	0.6
H_2/CH_4	2.83
He/CH_4	2.00
H_2/N_2	3.74
H_2/C_3H_8	4.69
$^{235}UF_6/^{238}UF_6$	1.0036

Some new emerging areas of applications

TEMs hold great promise for a variety of new emerging areas of applications. An overview on existing applications and those which are now under development and suggestions for futuristic/realistic applications that have not yet been tackled may be found in a very recent book (3). A very brief discussion on some selected applications in the areas of (a) medical science and (b) nano- technology devices is included here as illustrative examples.

(a) Medical science

Treatment of burns and wounds

One of the most beneficial applications of TEMs is their possible use in the treatment of burns and wounds. The most likely reason for loss of life resulting from high percent body burn injuries is due to bacterial infection of the affected area which can be prevented by keeping the patient in a bacteria-free ICU ward. However, in many burn wards in hospitals this facility is very limited. According to a recent newspaper report, India loses about 2.4 lakh persons and about 150 million man days due to burn injuries and the cost of treatment of burns is estimated to be about Rs 400 million per year **(9)**. In this regard the setting up of Asia's first and the world's second largest burns institute in Airoli; New Bombay by the Indian Burns Research Society is an important development. This 140 bedded unit with intensive care units and other modern R& D laboratory; diagnostic facilities etc. is an important medical facility in the country.

In wounds and burns treatment, mono and multilayer dressings are used, made from textile materials as well as from formy and spongy materials. Dressings should closely adhere to the surface of the wound, should not irritate the skin and should be sterile and non-allergic. They should also limit evaporation of water from the wound surface, restrain bleeding, be an efficient barrier against bacteria and micro organism, and should be easy in putting and removing.

Most of these special requirements can be met by using large area thin and transparent TEMs with well defined and uniform pores

Dressings with Track-etch membranes with pore diameters below 0.5 μm have been used and clinical investigations were performed concerning their serviceableness for burns and wounds in the Specialistic Centre for Burns Therapy in Nowice Slasskie, Poland. **(10)** The clinical trials provided the following results:

a. Skin allergy to dressings with TEMs were negative

b. Dressings with TEMs gave good results in healing of small wounds and burns

c. Dressings with TEMs allow breathing while acting as a protective barrier against bacteria and microorganisms and preventing infection.

d. Replacement of the dressings is less painful

e. Dressings with TEMs allow introduction of antibiotic solutions under the foil.

f. Transparency of the TEMs enables the attending doctors and nurses to observe the progress of healing without removing the same.

Considering the enormity of the loss of life and man days caused by burns in India and considering, these positive societal benefits accruing from the possible large scale use of thin transparent TEMs of well defined and uniform pores, we have a strong case for indigenous manufacture of accelerator-based TEMs.

In this context, it may be noted that the technology for producing polyvinyl alcohol (PVA)-polysaccharides-based radiation processed **hydrogel dressing** for burn and wound healing is already developed by BARC **(11)**. Once the technology for indigenous manufacture of TEMs is also developed, it is certain that both hydrogel dressings and TEMs will complement each other and enhance the efficacy of hospital treatment of burns and wound and one can visualise the possibility of India taking the lead in this area of medical science.

Antibody chips for MAIA

Multi analyte immuno assay (MAIA), a concept put forth by Ekins over a decade ago, and promises to be cutting edge technology in clinical chemistry **(12).** It will offer the advantage of estimating many analytes in one assay compared to present assays where each assay can estimate only one analyte. MAIA, based on antibody chips (similar to DNA chips) will use miniscule amounts of reagents and patient sample. By enabling simultaneously a battery of tests related to a given disease or associated diseases, it can save valuable time for patient management. In short, antibody chip MAIA can revolutionalise immuno assay technology just as DNA chip is revolutionising gene analysis. At the core of MAIA is the antibody chip a small inert glass or plastic matrix on which a number of antibodies, each specific to a different analyte is immobilised at spatially different sites. In collaboration with the Bio-medical Group of BARC, TEMs were successfully tested as novel substrates for antibody chips in MAIA **(3, 13).**

Conducting polymer-based molecular (micro tubular) bio-sensors

Boisensors come under the general category of chemical sensors-These are devices consisting of an ion specific membrane, an internal aqueous electrolyte solution and a reference electrode. Ion specific membranes can be easily made by immobilising a specific chemical reagent or "carrier" in the pores of a micro porous membrane such as TEM. The ion or molecule to be detected or whose concentration is to be measured in the sample forms a complex with the carrier or reacts with the carrier in the pores of the membrane and diffuses across the membrane The micro porous membrane acts as a support for holding the carrier in the pores as in Supported Liquid Membranes (SLMs). This process is generally referred to as "carrier-mediated" or "carrier-facilitated" transport and is very similar to the diffusion controlled and selective transport of metal ions from complex mixtures under SLM configuration **(1)**. The concentration of the specific ion which has preferentially diffused across the membrane or the reaction products is measured by a detection system usually a current measuring device. The key here is to identify highly specific reactions that convert the species to be analysed into a species readily detected by an existing ion- selective electrode. Because of their extreme specificity, immobilised micro porous membranes form an integral part of the system **(14)**.

The electronic conductivity of polymers such as polyaniline, polypyrrole etc changes over several orders of magnitude in response to changes in pH and redox potential. This property coupled with the fact that one can immobilise some enzymes in the polymers by electrochemical means has been used to fabricate micro tubular bio sensors and sensor arrays using polycarbonate TEMs. Electrochemical potential control to direct enzyme immobilisation to specific sites in the membrane support, results in a micro tubule array that can function as an "electronic tongue" to analyse glucose, urea and triglycerides in a mixture in a single measurement. **(15)**.

(b) Nano technology-devises

A major field of potential future applications of TEMs covers sensors. On the one hand, they can probe physical, chemical and biological parameters such as temperature, pressure, liquid flow through, humidity, magnetic field strength, etc and on the other hand determine the concentration of components or trace elements in gases or liquids or in biological activities **(3)**. the sensor market is rapidly growing all over the world. Though lot of work is being done in our country on the development of electrochemical sensors, there is no indigenous manufacture and India imports 20-25 different sensors for toxic gas and poisonous gas sensing at a huge amount of foreign exchange. At present the car industry is a major user of sensors followed by processing industry, house hold and office equipment production, construction, machine building and aerospace industry.

There are a number of possible approaches to realise TEM-based sensors. One can either use the microporous foils as porous windows of other sensing devices or one can incorporate the sensor material into the micro porous foil itself. The first approach has already found some technological applications while the second one is partly in the development stage.

TEMs can serve as templates for making various micro and nano structures and magnetic, conducting and superconducting nano wires possessing special properties have been prepared (3). Using small pore TEMs as matrices (e.g.; gold nano tubules) electrically switchable ion selective membranes and senors as well as nano tubules with pH switchable transport properties can be produced. (16, 17).

Track-membrane based sensors by incorporating the sensor material into the micro porous foil by capillary action are very routinely done. Chemical reactions can be made to take place in situ in the pores e.g.; formation of photosensitive AgBr by letting $AgNO_3$ and NaBr solutions to penetrate from both sides of a TEM to react inside the pore which acts as a micro reactor is possible. Galvanic deposition of conducting matter within the pores of TEMs is a well-established technique for making conducting micro/nano devices as tubules. In this way the sensor size could be reduced to mm range with an accompanying impressive reduction in power consumption and other operating requirements. The development of a TEM-based first prototype of Clarc sensor, which is an electrochemical sensor, permits micro analytic measurements of oxygen measurements in biochemical materials at a much-reduced cost **(3)**. Another possibility is gas phase deposition by letting a suitable gas to penetrate and decay towards solid residues within the pores of TEMs by pyroltic reactions. This requires high reaction temperatures and can be done using TEMs of polyimides such as

Kapton, which can withstand temperatures of the order of several hundred degrees Celsius (3).

Controlled release technology

Controlled-release technology dealing with the rate at which substances, usually biologically active substances are released to their environment is another emerging area of micro filtration membranes. Controlled release technology allows us to stretch out the time e.g. once -a day or once -a week or even once -a -year over which the concentration of a substance, say a drug remains above the effective threshold. In virtually all cases, there is better utilisation of the active agent because the overdose-underdose problem common to ordinary application methods is avoided. In the case of expensive agents such as pheromones, efficient utilisation is an economic necessity. In principle, controlled -release devises consist of a reservoir of pure liquid agent; say a drug separated by a membrane which acts as the rate controlling barrier. Some reservoir-type zero -order drug delivery systems are available in the market e.g.

* Device for delivery of pilocarpine to the lower cul-de-sac of the eye for the treatment of glaucoma

* Device for delivery of a steroid to the uterus for birth control

* A simple device for the transdermal delivery of scopolamine, for control of motion sickness. It consists mainly of a drug reservoir, a rate controlling membrane and an adhesive layer which binds the device to the skin and provides a path way for the drug to reach the skin. The rate limiting membrane is micro porous polypropylene impregnated with mineral oil.

A similar transdermal device using TEMs is being developed in Defence Laboratory, Jodhpur and is being tested at the SN Medical College, Jodhpur for the controlled delivery of methotrexalate for the treatment of psoriasis (18)

Concluding remarks

The points outlined in the preceding paragraphs make it abundantly clear that heavy ion-produced nano- and micro-porous track-etch membranes with their unique features have numerous scientific, technological , medical and other industrial applications (19). The basic expertise and facilities to develop this emerging technology indigenously is available with us. It would, not only be possible but also desirable for us to scale up production of these membranes to several thousands of square meters per year to be able to put them to actual use/applications on a commercial scale. This can be accomplished by augmenting the existing facilities at the BARC TIFR Pelletron accelerator with a few additional equipment/ facilities for scanning the heavy ion beam across a continuously moving polymeric membrane material. Pore densities of the order of 10^8-10^9/ cm ^{2}is also possible with the direct beam. In order to make some visible impact in a reasonable time frame, the involvement of personnel as multidisciplinary Task groups should be set up for:

(a) Speeding speed up the engineering inputs required to make the beam scanner and associated facility fully operational

(b) Quality surveillance, including SEM, bubble point measurement, membrane burst strength, gas permeability, pore size distribution

(c) Fabrication jobs

(d) Physico chemical treatment of irradiated foils and

(e) Co-ordination with industry (ultra and micro filtration modules/cartridges for water purification, ultra clean air), sensitising R&D units in the country to initiate fresh R&D for using TEMs on a large scale and for new applications (gas diffusion/ separation, medical sciences etc).

This national endeavor, besides helping import substitution will result in locating and forging partnership with industry for transfer of technology and sensitise the best of R&D institutions for identifying innovative applications in diverse scientific and technological areas and will provide a new impetus to the growth of scientific and industrial development of the country.

A base has been created to promote awareness in the country about the vast applications of TEMs in many areas of science and technology as listed in this report. Many countries have embarked on large scale production of TEMs with dedicated heavy ion accelerators (e.g. Accelerating Technological Complex (ATC) in Dubna, Russia) for industrial scale production of TEMs of the order of 500,000 m^2 per year.[7] An important beginning has been made during the course of this R&D scheme to set up a beam scanner and associated facilities for large-scale production/ manufacture good quality TEMs in the country. With a direct beam available in this case for irradiation, production of thicker membranes (20-25 μm), which are naturally more robust and easier to handle than the thinner ones (10 μm) in engineering scale modules, is possible. The encouraging results obtained in the present research (and keeping the Russian example in the background) should definitely act as an impetus to speed up the engineering inputs required to make the beam scanner facility fully operational and sensitize other R&D units in the country to initiate fresh R&D to explore the possibility of using TEMs on a large scale and for new applications. Apart from giving a boost to the SLM-based separations being carried out at present, the indigenous production of TEMs will lead to many other scientific and technological applications of immense economic value and potential benefits to society. It will serve as a National facility.

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