PREPARATION OF LOW-COST MICROFILTRATION MEMBRANES FROM FLY ASH

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Submitted By:

Gurpreet Singh

Reg. No. : 601111008

Under the Guidance of

Dr. Vijaya Kumar Bulasara
Assistant Professor

Department of Chemical Engineering

Thapar University, Patiala

Patiala – 147004, Punjab, India

July 2013

CERTIFICATE

This is certified that the thesis entitled **"Preparation of Low-Cost Microfiltration Membranes from Fly Ash"** is an authentic record of my own work carried out as requirements for the award of the degree of M.Tech. (Chemical Engineering) at Thapar University, Patiala, under the guidance of **Dr. Vijaya Kumar Bulasara** (Assistant Professor, ChED) during January to June 2013.

Date: 11/07/13

Gurpreet Singh

Gurpreet Singh
Roll No. 601111008

It is certified that the above statement made by the student is correct to the best of my knowledge and belief.

Dr. Vijaya Kumar Bulasara (Thesis Supervisor)
Assistant Professor
Department of Chemical Engineering
Thapar University, Patiala

Counter signed by:

24.07.13

Dr. Rajeev Mehta
Head of the Department
Department of Chemical Engineering

Dr. S. K. Mohapatra
Dean of Academic Affairs
Thapar University, Patiala

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Gurpreet Singh

ABSTRACT

Commercial ceramic membranes have undergone a rapid growth during the last two decades. The interest in ceramic membrane has increased concurrently with new processes and new applications. Membrane processes are being used more and more in many fields such as water treatment. The use of membrane technology to replace a separation or purification step in an industrial process may reduce the overall consumption of energy. The development of membrane processes to treat wastewater is generally limited because the price of the membranes is too high, which is particularly true for the inorganic membranes. One of the challenges for future development of the inorganic membranes will be to produce low-cost membranes from natural materials such as clay, fly ash and apatite which are in abundance and which need lower firing temperature than metal oxide materials and have high flux performance to treat large volumes of liquid effluent.

Porous ceramic membranes have great potential for opening new types of applications to which polymeric membranes cannot be applied. Inorganic microfiltration and ultra-filtration membranes have been used in a wide variety of processing. The preparation of porous ceramic membranes, which need to have uniform pore sizes, to be as thin as possible without defects, seems to represent a different strategy from conventional preparation of ceramic bulk bodies. This new research field of ceramic processing will contribute much to the development of membrane science and technology.

The aim and purpose of this work is fabrication and characterization of low cost ceramic membranes using low cost materials. Membranes were prepared using fly ash as major constituent after trying various compositions. Membranes were casted in circular disk of thickness 5mm and diameter 55mm. The membranes were sintered at four different temperature to study the effect of temperature on membrane performance .The membranes characterization was done using techniques like XRD ,SEM and TGA. Membranes porosity was determined using pycnometric method and to check chemical stability of membranes they were subjected to acid and base treatment for 7 days.

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List of Symbols/Abbreviations

ε	Porosity of membrane
V_t	Total volume of membrane (cm^3)
V_p	Volume of pores (cm^3)
t	Average thickness of membrane (cm)
d	Average diameter of membrane (cm)
J	Liquid flux through membrane ($m^3m^{-2}sec^{-1}$)
Q	Volumetric flow rate (m^3/sec)
TGA	Thermo-gravimetric analysis
SEM	Scanning electron microscope
XRD	X- ray diffraction

Chapter 1

INTRODUCTION

1.1 Membrane Definition

The word membrane originates from the Latin word membrana which means a skin. Membrane keeps things separated in the living world and passes materials selectively (Nath, 2008) . Although it is difficult to give an exact definition of a membrane, a general definition could be: a membrane is a thin barrier, placed between two phases, or media, which allow one or more constituents to selectively pass from one medium to the other in the presence of an appropriate driving force while retaining the rest. The term‘ selective’ being inherent to a membrane or a membrane process. Contrary with the conventional mass transfer operation, the two phases between which transfer of one or more species occurs are not in direct contact in membrane separation . Further, the transports of molecules through the pores of membrane belongs to fluid dynamics. Thus, membrane processes are the combination of two unit operations *i.e.*, mass transfer and momentum transfer. Figure 1.1 below shows membrane based separation process.

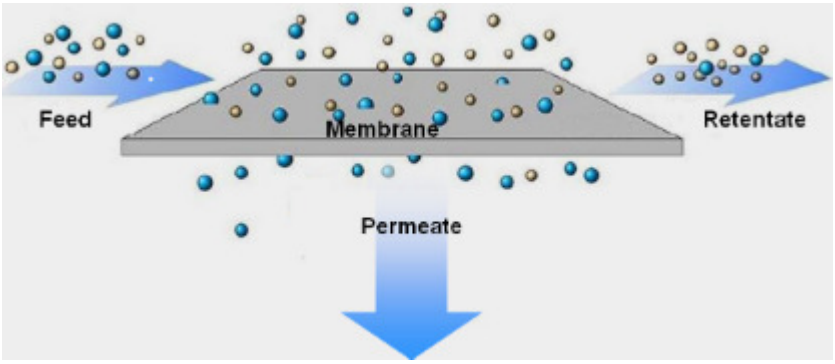


Figure 1.1: Membrane based separation process

1.2 Membrane separation processes

Membrane separation processes have very important role in separation industry. Nevertheless, they were not considered technically important until mid-1970. Membrane separation processes differ based on separation mechanisms and size of the separated particles. The widely used membrane processes include microfiltration, ultra-filtration, nano-filtration, reverse osmosis, electrolysis, dialysis, electro-dialysis, gas separation, vapor

permeation, pervaporation, membrane distillation, and membrane contactors (Pinnau and Freeman,1999). All processes except for pervaporation involve no phase change.

1.2.1 Classification of membrane separation processes

The membrane processes can be classified according to the driving force used in the process. Technically and commercially most relevant processes are pressure driven processes. Apart from this, concentration gradient and electrical potential also act as driving force for some of the membrane processes. Table 1.1 summarizes the classifications and general characteristics of various membrane processes.

Table 1.1 Classifications and characteristics of membrane processes (Nath, 2008; Dutta, 2007)

Driving force	**Membrane process**	**Permeate**	**Retentate**	**Membrane type**
Pressure difference	Micro-filtration (MF) (0.5-2 bar)	Dissolved solutes, water	Suspended solids	Symmetric micro-porous
	Ultra-filtration (UF)	Small molecules, water	Polymers, proteins, micelles, colloid particles	Asymmetric micro-porous
	Nano-filtration (NF)	Monovalent ions, water	Small molecules, divalent salts	Thin-film membrane
	Reverse osmosis (RO)	Small polar solvents, salts, water	All solutes	Asymmetric skin type
	Pervaporation (PV)	Volatile small molecules, water	Low volatility species; species less soluble in the membrane	Asymmetric homogenous polymer
Concentration difference	Diffusion dialysis (DD)	Small molecules, water	Large molecules	Nonporous or micro-porous
	Membrane extraction (ME)	Gases, solutes, vapours soluble in the extractant	Components of feed insoluble in extractant	-----
Electrical potential difference	Electro-dialysis (ED)	Ionized solutes, water	Non-ionic solutes	Ion-exchange membrane
Temperature difference	Membrane distillation (MD)		Molecules <1 nm	Micro-porous

The difference between the pressure driven processes (microfiltration, ultra-filtration, nano-filtration, reverse osmosis and pervaporation) are the trans-membrane pressure difference and pore sizes. The pore size is the most important parameter for size based membrane separation processes. The pore sizes of different types of membranes are compared in figure 1.2

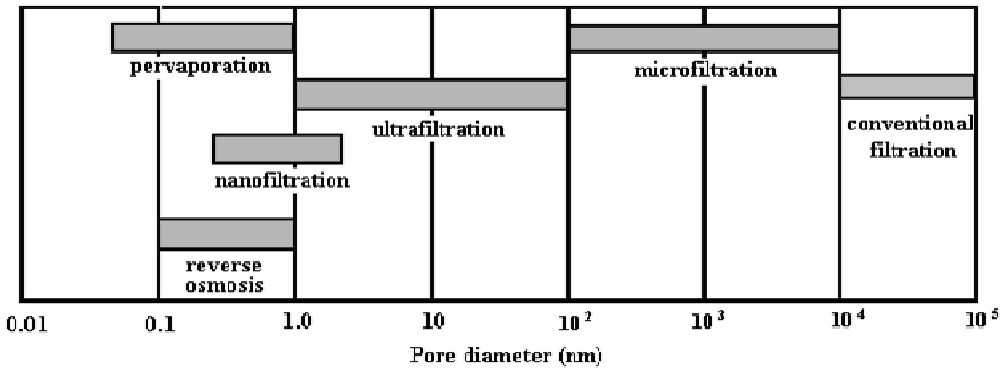


Figure 1.2 : Comparison of pore sizes of different types of membranes

1.3 Application and pressure range for different types of membranes

Membrane processes are no longer bound in the domain of laboratory but have found their way into industries as viable separation technique. These processes have achieved impressive industrial importance for the resolution of aqueous liquid mixtures, purification of chemical and biological products, wastewater reclamation, hydrometallurgical processing and many more. The principle characteristics of various commercialized membrane process separation processes can be specified based on several aspects:

- Size of the species to be retained.
- Nature of species to be transported through the membrane((i.e. volatile, electrolyte etc.).
- Mechanism of transport.
- Selectivity between the components.

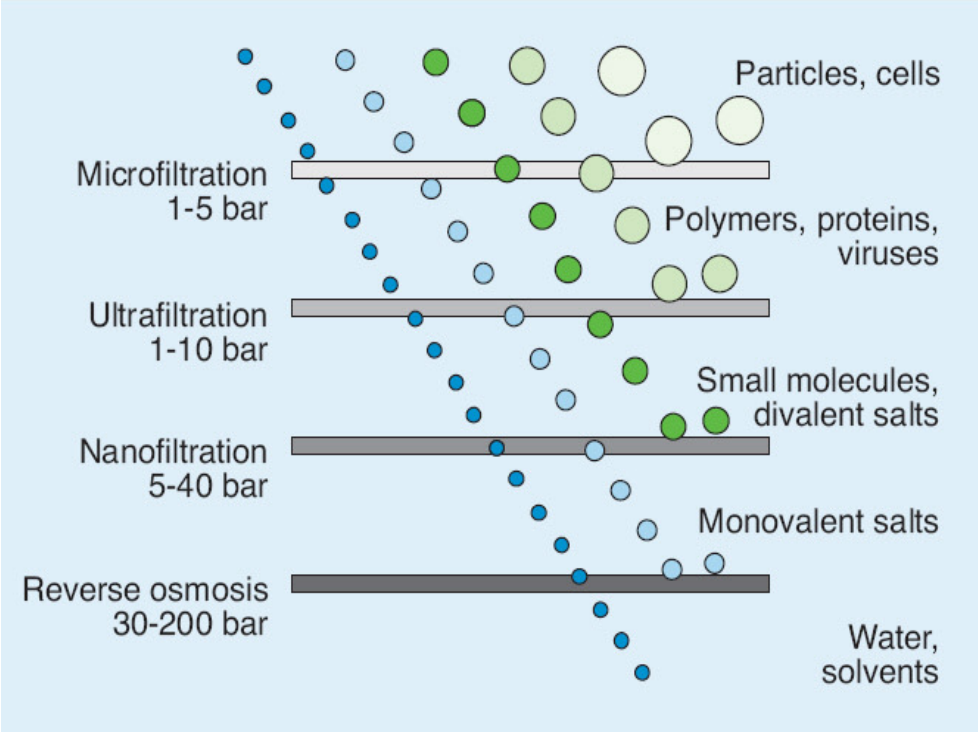


Figure 1.3: Application and pressure range for different types of membranes

1.4 Potential applications of membrane separation

1.4.1 Heavy metals separation

Membrane filtration has received considerable attention for the treatment of heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultra-filtration, nano-filtration and reverse osmosis can be employed for heavy metal removal from wastewater. Ultra-filtration (UF) utilizes permeable membrane to separate heavy metals, macromolecules and suspended solids from inorganic solution on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds (1000–100,000 Da). These unique specialties enable UF to allow the passage of water and low-molecular weight solutes, while retaining the macromolecules, which have a size larger than the pore size of the membrane. The application of both reverse osmosis (RO) and nano-filtration (NF) technologies for the treatment of wastewater has given good results. The disadvantage associated with reverse osmosis and nano-filtration is that they require high pressures.

1.4.2 Olefin/Paraffin mixtures

The separation of olefin/paraffin mixtures is rather difficult because of the small differences in physical properties, e.g., boiling points. Currently, such separations are carried out by energy intensive low temperature distillation. Huge splitter columns are necessary to separate the mixtures of saturated and unsaturated hydrocarbons. A hybrid process combining a membrane unit and a distillation column could lead, depending on the separation characteristics of the membrane material, to a significant reduction of the stream brought to the energy intensive splitter. Due to the fact that the separation train is more than half of the total cost of an olefin plant, a reduction of the splitter column is of high interest.

1.4.3 Aromatics/aliphatics separation

The separation of aromatics/aliphatics is receiving more and more attention, as the benzene content in gasoline is, by law in Europe, limited to less than 1% The separation factors achieved, using a conventional separation process (extraction and stripping unit) is between 2 and 3. In the hybrid process a membrane separation unit might be implemented into a conventional aromatic/aliphatic separation process. This design is advantageous because the complete extracting column is replaced by a single membrane unit. Therefore the process itself requires only minor changes. In the proposed hybrid process, the separation factors for the aromatics are twice as high using a membrane compared to the extractor.

1.4.4 Natural gas treatment

In the area of natural gas treatment a number of different applications are of great interest. In tertiary oil production supercritical CO_2 is introduced into the oil field, especially if the oil is distributed in porous layers. However, it is important to hold back the CO_2 present in this stream because it is well known that CO_2 is one of various compounds responsible for the greenhouse effect. A membrane unit can be implemented in such a process, so that the CO_2 is removed through the membrane and can then be re-used after compression. With this process not only could the emission of CO_2 be drastically reduced but also the natural gas can be recovered in this case instead of burning it which is generally carried out if the quantity and quality are too low.

Another very interesting application is the treatment of natural gas in offshore deposits. So far a huge number of gas resources are known worldwide, which cannot be exploited because of the high CO_2 content and the high pressure of the mixture. For economic reasons more and more membrane based processes in natural gas treatments are being developed.

1 .5 Types of flow patterns in membranes

1.5.1 Cross flow filtration

In cross-flow filtration the feed flow is tangential to the surface of membrane, retentate is removed from the same side further downstream, whereas the permeate flow is tracked on the other side. The tangential flow devices are more cost and labor intensive, but they are less susceptible to fouling due to the sweeping effects and high shear rates of the passing flow. Figure 1.4 below shows cross flow filtration.

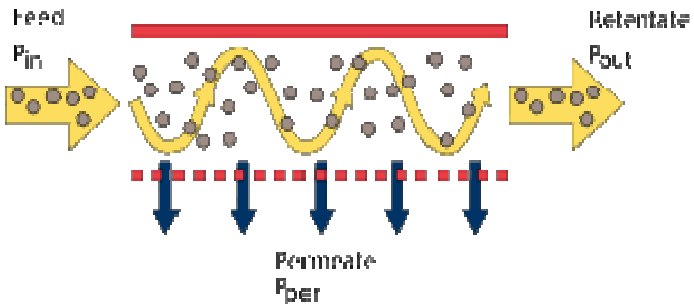


Figure 1.4: Cross-flow filtration

1.5.2 Dead end filtration

In dead-end filtration the direction of the fluid flow is normal to the membrane surface. The dead-end membranes are relatively easy to fabricate which reduces the cost of the separation process. The dead-end membrane separation process is easy to implement and the process is usually cheaper than cross-flow membrane filtration. The dead-end filtration process is usually a batch-type process, where the filtering solution is loaded (or slowly fed) into membrane device. The main disadvantage of a dead end filtration is the extensive membrane fouling and concentration polarization. The fouling is usually induced faster at the higher driving forces. Membrane fouling and particle retention in a feed solution also builds up a

concentration gradient and particle backflow (concentration polarization). Figure 1.5 below shows dead end filtration.

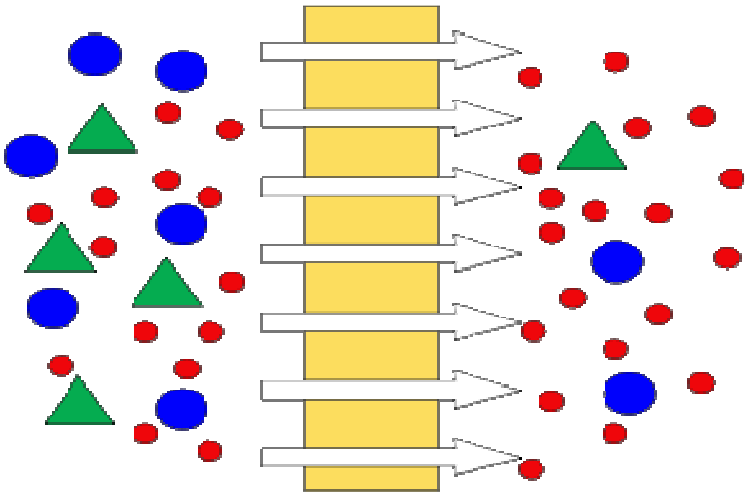


Figure 1.5: Dead-end filtration

1.6 Mass transfer in membranes

For the mass transfer at the membrane, two basic models can be distinguished: the solution diffusion model and the hydrodynamic model. In real membranes, these two transport mechanisms certainly occur side by side, especially during the ultra-filtration.

1.6.1 Solution-diffusion model

The transport is done only by diffusion. The component that need to be transported must be first dissolved in the membrane. This principle is more important for dense membranes without real pores such as those used for reverse osmosis and in a fuel cell. During the filtration process is formed on the membrane a boundary layer. This concentration gradient is created by molecules which cannot pass through the membrane. This effect is referred as concentration polarization. It occurs during the filtration and leads to a reduced trans-membrane flow(flux). The concentration polarization is in principle reversible by cleaning the membrane and the initial flux can be almost restored. Also the use of a tangential flow to the membrane (cross-flow filtration) minimizes concentration polarization.

1.6.2 Hydrodynamic model

Transport through pores - in the simplest case of pure transport convectively. This requires the size of the Pores to be smaller than the diameter of the components to be separated.

Membranes, which function according to this principle are used mainly in micro-and ultra-filtration. They are used to separate macromolecules from solutions, colloids from a dispersion or remove bacteria. During this process the not passing particles or molecules form on the membrane a more or less a pulpy mass(filter cake). This hampers the filtration due to blockage of the membrane. By the so-called cross-flow method(cross flow filtration) this can be reduced. This creates a shear stress that cracks the filter cake and lower the formation of fouling.

1.6.3 Membrane performance and governing equations

The selection of synthetic membranes for a targeted separation process is usually based on few requirements. Membranes have to provide enough mass transfer area to process large amounts of feed stream. The selected membrane has to have high selectivity(rejection) properties for certain particles; it has to resist fouling and should have high mechanical stability . It also needs to be reproducible and to have low manufacturing costs. The flux through the membrane can be generally expressed as:

$$Flux = \frac{Membrane\ \ permeability}{Membrane\, thickness} \times Driving\ \ force$$

This means that the flux depends linearly on both the permeability (a constant which indicates how tight the membrane is) and the driving force. The driving force may be difference in pressure, concentration, temperature, chemical potential and so on. The flux also depends inversely upon the thickness of the membrane. The thinner the membrane; the higher the flux. The main modeling equation for the dead-end filtration at constant pressure drop is represented by Darcy's law (Osada and Nakagawa,1992)

$$\frac{dV_p}{dt} = Q = \frac{\Delta p}{\mu} A(\frac{1}{R_m + R})$$

where V_p and Q are the volume of the permeate and its volumetric flow rate respectively (proportional to same characteristics of the feed flow), μ is dynamic viscosity of permeating fluid, A is membrane area, R_m and R are the respective resistances of membrane and growing deposit of the foulants. R_m can be interpreted as a membrane resistance to the solvent (water) permeation. This resistance is a membrane intrinsic property and expected to be fairly constant and independent of the driving force, Δp. R is related to the type of membrane

foulant, its concentration in the filtering solution, and the nature of foulant-membrane interactions. Hydraulic permeability is defined as the inverse of resistance and is represented by the equation (Osada and Nakagawa,1992)

$L_p = \frac{J}{\Delta P}$ where J is the permeate flux which is the volumetric flow rate per unit of membrane area.

1.7 Polymeric membranes

Polymeric membranes are thin films of 10 - 100 mm thickness. Different types of polymers such as polysulphone (PSU), cellulose acetate (CA), polyamide (PA), polyethersulphone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polytetrafluoroethylene (PTFE), polyetherimide (PEI), polypropylene (PP) are used widely to fabricate polymeric membranes.

Advantages for polymeric membranes are:

a) Wider ranges of pore sizes varying from MF to RO are available.

b) Both hydrophobic and hydrophilic membranes are available to minimize fouling during filtration.

c) Comparatively low cost than ceramic membrane.

d) They are easy to fabricate and use.

e) Ease to scale up.

Disadvantages of polymeric membranes are:

a) Low solvent resistance.

b) Lower applicable range of pH and hence low corrosion resistance.

c) Low temperature ranges.

d) Lower life span (12 – 18 months).

In the recent times, modified polymeric membranes have been developed that can cater towards wider pH ranges. However, their corrosion resistance and resistance to organic solvents have not been resolved to an extent of providing confidence in industrial applications.

1.8 Ceramic membranes

Typically ceramic membranes are made of various inorganic materials such as α - alumina, γ - alumina, zirconia, silica, titania, kaolin etc. Compared to polymeric membranes, ceramic membranes possess superior chemical, thermal and mechanical stability. The thickness of ceramic membrane is in the range of 2 - 5 mm and some times higher depending on the specific applications. Asymmetric ceramic membranes constitute thin film (10 - 100 mm) of ceramic coating over a thick porous symmetric support.

Advantages for ceramic membranes are :

a) Very high corrosion resistance. There exist very few chemicals such as hydrofluoric acid and phosphoric acid for which the ceramic membranes don't have high corrosion resistance. The most useful feature of the ceramic membranes is their ability to tolerate strong doses of chlorine.

b) Applicability to wider pH ranges (0.5 - 14).

c) Applicability to wider temperature ranges (350 – 500 ^{o}C). As a result they are used in industrial scale separations without any feed pre-conditioning steps.

d) Longer life span (5 - 10 years).

e) Less fouling tendency.

f) Inertness to common chemicals and solvents.

g) Higher mechanical strength.

Since these membranes do not get seriously affected by the frequency and nature of cleaning, they can be subjected to aggressive cleaning agents and regimes, which is very much prevalent in industrial chemical processing units.

Disadvantages of ceramic membranes are:

a) Most ceramic membranes are available in pore diameters within the MF and UF range (0.010 - 10 mm). In the recent years, few literatures presented the fabrication of NF membranes. Therefore, ceramic membranes are not generally applicable for separation schemes with NF and RO.

b) Comparatively higher cost. Though the price of ceramic membranes may have reduced in due course of time, these costs have not been very competitive with polymeric membranes.

c) They are brittle in nature. If dropped or subjected to undue vibrations it may be damaged.

1.9 Ceramic Vs. Polymeric membranes

Considering the advantages and disadvantages of both membranes, it can be observed that polymeric membranes are very much useful for laboratory scale use. For laboratory scale use, applicability of the membrane technology towards any particular separation is the main aim but not their life span and cost. However, for industrial scale applications, cost and life span are the most relevant matters along with the separation efficiency. Therefore, though ceramic membranes involve higher initial costs, their ability to provide higher flux and applicability to wide range of temperature and chemical processing conditions could favour them to be the choice in contrary to the polymeric membranes. Though ceramic membrane possesses separation characteristics similar to polymeric membranes, due to higher cost, they are not yet widely applied in industrial scale applications. Under these circumstances, the development and usages of comparatively low cost ceramic membranes with longer life span (10 - 15 years) is anticipated to drive the economic competitiveness of ceramic membranes in the industry.

1.10 Major research areas in membrane technology

Membrane technology research involves numerous issues. These are listed as follows:

a) Selection of suitable materials for membrane fabrication.

b) Parametric optimization of membrane preparation methods using trial and error approach in experimentation.

c) Characterization studies of the prepared membrane.

d) Identification of suitable application of the developed membrane.

e) Evaluation of optimal operating conditions (trans-membrane pressure, feed concentration, temperature etc.,) that enables longer lifespan of the membrane.

f) Evaluation of the best membrane module (tubular, disk, hollow fiber and spiral wound modules) and mode of application (dead-end, cross-flow etc.,).

g) Modelling and simulation of the membrane technology for design.

h) Cost and techno-economic analysis.

In the above list, materials research broadly constitutes (a) – (e).

Membrane materials research is central theme which facilitates the development of conventional and novel functional materials that ensure applicability, low cost and durable performance. The membrane materials must withstand operating environments such as pH of the feed solution, temperature, pressure etc., In addition, the membranes shall also possess chemical, thermal and mechanical durability. Once these membrane materials are identified, applications that suit the membrane are thoroughly investigated. After this, membrane module development studies including module fabrication and pilot plant studies follow. Module development studies target transformation of lab scale membrane technology to industrial scale systems. During this phase, the ease of operation along with the quality of the product and cost of the process are important matters for pursuing the research. Eventually, modelling and simulation of observed module performance is followed up for design purposes which are followed with techno-economic and cost analysis. While modelling and simulation aims to identify suitable models (both time dependent and independent) to correlate the experimental data with minimal error, cost estimation and techno-economic analysis provide insights upon the economics of the membrane process for its industrial and commercial feasibility. In all the above areas, membrane materials research is by far the most important and nearly two thirds of the total research activities are dovetailed towards the development of durable membranes at lower cost for both conventional as well as novel applications. Unless membranes are fabricated with effective functionality using materials research techniques, subsequent areas of research cannot be followed due to the pertinent evolutionary nature and hence industrial scale membrane separation schemes cannot be realized. Therefore, for any industrial application of membrane, emphasis is upon the development of suitable membrane materials. Ideally, the developed membrane shall possess a good combination of permeation and separation characteristics for the chosen application along with good corrosion resistance and mechanical strength.

Chapter 2

LITERATURE REVIEW

2.1 Background

Membranes processes are now more and more used in a number of industrial processes, which include different operating conditions and module designs. The use of membrane technology to replace a separation or purification step in an existing industrial process may reduce the overall consumption of energy and produce acceptable results. In the past two decades, significant advances in membrane technology research have already been reported. Numerous applications have been proposed of which micro-filtration and ultra-filtration are critical technologies in chemical and biochemical processing that are regarded economically competitive due to the availability of membranes with higher flux and lower process cost. Existing and continuing research in membrane technology aims to extend the horizons of membranes for high temperature processing (Sourirajan, 1970; Yoshino et al., 2005) and corrosive feed stocks (Wang et al., 2006) for which ceramic membrane development is targeted. These membranes are found to be capable for high temperature, corrosive and high pressure applications with good durability (Sourirajan, 1970; Meares, 1976; Cuperus and Nijhuis, 1993; DeFriend et al., 2003; Yoshino et al., 2005; Wang et al., 2006). The preparation of inorganic symmetric and composite membranes is focused towards fundamental research on the impact of the type of inorganic precursors on the morphology, stability and porous texture of the inorganic matrix. In addition, the aspiring feature of such research is to find optimal formulations of different ingredient to yield a thermally and chemically stable membrane with good separation characteristics.

Early research in inorganic membrane fabrication was focused towards the utilization of α-alumina which is an expensive precursor to fabricate the membrane (DeFriend et al., 2003; Yoshino et al., 2005). Research at a later stage, involved the utilization of inorganic materials such as γ-alumina, zirconia, titania and silica (Tsuru, 2001; Falamaki et al., 2004; Yoshino et al., 2005; Wang et al., 2006). Nonetheless, the cost of these precursors remains to be significantly high and therefore significantly contributes to the operating cost of membrane modules for industrial applications. To circumvent the issue of membrane cost, recent research in the fabrication of inorganic membranes is focused towards the utilization of cheaper raw materials such as apatite powder (Masmoudia et al., 2007), fly ash (Saffaj et al., 2004), natural raw clay (Saffaj et al., 2005, 2006), dolomite, kaolin (Almandoza et al., 2004;

Bouzerara et al., 2006). Potdar et al. (2002), Neelakandan et al. (2003) have provided optimal inorganic formulations (based on dry basis) using kaolin (12.7 wt.%), ball clay (16.1 wt.%), quartz (23.6 wt.%), feldspar (5.1 wt.%), $CaCO_3$ (28.1 wt.%) and pyrophallite (14.3 wt.%) for the fabrication of micro-filtration range inorganic membranes. In a similar approach, Belouatek et al. (2005) have reported optimal inorganic formulations (based on dry basis) using clay (21 wt.%), kaolin (35 wt.%), feldspar (20 wt.%) and sand (24 wt.%) for fabricating inorganic supports capable for liquid waste treatment. Of these precursors, quartz, feldspar and pyrophallite could be regarded as expensive materials when compared to kaolin, ball clay and calcium carbonate. Few literature were found for the fabrication of membrane supports using mixture of clays (Bouzerara et al., 2012; Jana et al., 2009).

In recent years, some researchers found that coal fly ash, a by-product of coal combustion in thermal power plants, was also a good candidate for preparing low-cost ceramic membrane due to its high percentage of alumina and silica. The other important physicochemical characteristics of fly ash such as bulk density, particle size, porosity, water holding capacity, and surface area make it suitable for ceramic membrane preparation . Indeed, this allows a good management of this sub product which represents a major problem in many parts of the world due to the resulting pollution. Fly ash consists of fine, powdery particles predominantly spherical in shape, either solid or hollow, and mostly glassy (amorphous) in nature. The carbonaceous material in the fly ash is composed of angular particles. The particle size distribution of most bituminous coal fly ash is generally similar to that of silt (less than a 0.075 mm or No. 200 sieve). Although sub-bituminous coal fly ash is also silt-sized, it is generally slightly coarser than bituminous coal fly ash. The specific gravity of fly ash usually ranges from 2.1 to 3.0, while its specific surface area may vary from 170 to 1000 m^2/kg (www.flyashindia.com; Roy et al., 1981; Tolle et al., 1982; Mattigod et al., 1990) . The colour of fly ash can vary from tan to gray to black depending on the amount of unburned carbon in the ash. Jo et al. (1996, 1997) prepared stainless steel/fly ash and stainless steel/fly ash/TiO_2 membranes for hot gas cleaning. Jedidi et al. (2009) prepared a mineral porous tubular ceramic membrane based on coal fly ash and applied it in the treatment of the dying effluents generated by the washing baths in the textile industry. Dong et al. (2006) investigated the development of cordierite based porous ceramic membranes made of waste fly ash and basic magnesium. Dong et al. (2010) developed mullite membrane by sintering fly ash with the addition of chemically pure titania. Although several literature

are available on the fabrication of ceramic membrane some of the most relevant and recent studies are presented below in table 2.1:

Table 2.1 Some recent and important studies on ceramic membranes

Author	**Materials**	**Sintering Temperature (^oC)**	**Average pore diameter (µm)**	**Observation**
Bouzerara et al. (2012)	Clay (74%), Amijel (2.5%), Methocel (2.5%), Calcium Carbonate (21%)	1150 ^oC 1300 ^oC	Average pore size 1.39 µm. Average pore size 4.89 µm.	Increase in average pore size with increase in sintering temperature.
Vasanth et al. (2012)	Kaolin (50%), Quartz (25%), Calcium carbonate (25%)	900 ^oC	Average pore diameter 1.32 µm.	Porosity of membrane was 30% while hydraulic permeability was 4.11×10^{-6} (m^3/m^2 s kPa)
Jedidi et al. (2011)	Fly ash powder (84%), Methocel (4%), Amijel (4%), Starch(8%)	1125 ^oC	Average pore diameter 4.5 µm.	1.Porosity and pore size are strongly dependent on sintering temperature. 2.Membrane was used for treating dying effluents.
Hasan et al. (2011)	Clay soil (80%), Rice bran (20%)	900 ^oC	Pore size 1 to 5 µm .	Ceramic membrane showed good promise as a membrane bioreactor for waste water treatment.

Mittal et al. (2011)	Clay (60%), Kaolin (30%), Boric acid (2.5%), Sodium metasilicate (2.5%), Sodium carbonate (5%)	1000 ^{o}C	Average pore diameter 1.24 μm.	Composite membrane was used to separate lower conc. of oil (<250 mg/L) from oil–water emulsion.
Monash et al. (2011)	Kaolin (14.5%), Ball clay (17.6%), Feldspar (5.6%), Quartz (26.6%), Pyrophyllite (14.7%), Calcium carbonate (11%), Titanium dioxide (6%), with PVA as binder	950 ^{o}C	Three different supports S1(without TiO_2), S2(3% TiO_2) and S3(6% TiO_2) gave average pore diameters of 0.98, 0.93, 0.83 μm respectively.	1.All membrane supports gave higher permeability for non polar solvents than polar solvents. 2.All supports showed higher rejection at lower pressure and high feed concentration.
Majouli et al. (2011)	Perlite (volcanic glassy rock) (81.7%), Methocel (4%), Amijel (4%), Starch of corn as porosity agent (10%), PEG 1500 (Prolabo) as binder (0.3%)	1000 °C	Average pore diameter of 6.64 μm.	Progressive reduction in porosity is observed with increase in temperature.
Bulasara et al. (2010)	Kaolin (40%), Boric Acid (5%), Quartz (15%), Sodium carbonate (10%), feldspar (15%), Sodium metasilicate (5%), Pyrophyllite (10%)	900 ^{o}C	Average pore size 0.275 μm.	Lowest pore size was obtained which is desirable but the raw materials used such as Quartz, Feldspar and Pyrophyllite are highly expensive.

Jana et al. (2010)	Clay (70%), Water (24%), Boric Acid (1.5%), Sodium metasilicate (1.5%), Sodium carbonate (3%)	800 to 1000 ^{o}C	Average pore size 4.08 to 4.92 μm.	1.Porosity decrease with increase in sintering temperature. 2.Membrane showed good promise for treating waste water containing heavy metals.
Nandi et al. (2009)	Kaolin (50%), Boric Acid (5%), Quartz (15%), Sodium carbonate (10%), feldspar (15%), Sodium metasilicate (5%)	900 ^{o}C	Average pore diameter 0.285 μm.	This work inferred that low cost ceramic membranes are promising for mosambi juice processing.
Belouatek et al. (2008)	Barbotine (Algerian clay) consisting of Hycast clay (21%), KR kaoline (7%), LPC kaoline (20%), Tamazirt kaoline (8%), Feldspar (Incusa) (13%), Feldspar (NM) (7%), Sand (24%)	1100 ^{o}C	Mean pore diameter between 0.8 and 1.3 μm.	Porosity varied with support composition ranging from 12% for double layered ceramic support to 47% for activated carbon filled support.
Nandi et al. (2008)	Kaolin (40%), Quartz (15%), Calcium Carbonate (25%), Boric Acid (5%), Sodium metasilicate (5%), Sodium carbonate (10%)	800 to 1000 ^{o}C	Maximum pore size 5 μm.	Pore size of the membrane increases with rise in sintering temperature.

2.2 Literature review summary

Early literature reports the preparation of ceramic membranes using α alumina, γ alumina, zirconia, titania and silica. The cost of these membranes are significantly high due to the higher costs of the precursors used for the preparation of these membranes. Therefore, these membranes posses higher installation costs that may not be affordable for industrial separation schemes. To circumvent the higher costs of these membranes, existing and ongoing research in the preparation of low cost inorganic membranes are dovetailed towards the usage of low cost inorganic precursors and lower sintering temperature (below 1000 ^{o}C). However, these variants in ceramic membrane research need to guarantee cheaper membranes that have the inherent ability to provide consistent performance along with longer life time, in similarity to the existing expensive ceramic membranes. Recently, much work have been reported for the fabrication of inorganic membranes using cheaper raw materials such as apatite powder, natural raw clay, kaolin, dolomite and fly ash. From the table 2.1 it can be observed that for many of the cases, the sintering temperature used was more than 1000 ^{o}C. The maintenance of high sintering temperature during fabrication process demands higher electrical energy and hence operating costs during fabrication. In addition, higher sintering temperature may also give rise to enhancement in furnace power specifications and installed cost. Another challenge, because of which, the economic competitiveness of the inorganic membranes has not been appreciable till date, has been the development of membranes with pores sizes in the submicron range. It is well known that MF membranes with pore size in the submicron range (pore sizes < 1 mm) are preferred for the industrial application to obtain excellent solute separation efficiency. Submicron range ceramic membranes (pore sizes ranging from 0.1 – 0.5 mm) available so far, are membranes consisting of an asymmetric membrane structure. These asymmetric membranes typically consist of a submicron skin layer on either single or several layers of macro-porous structures. The utilization of expensive precursors such as zeolite and alumina for fabricating the submicron skin layer contributes to the overall cost of membrane. Moreover, the process of fabrication of asymmetric membranes in comparison to fabrication of symmetric membranes involves additional complexities because of which the cost of membrane is increased manifold. Therefore, the preparation of low cost symmetric membranes with submicron pore size would be economically more beneficial to the membrane based process industries.

2.3 Scope for further research

A critical review of the above publications and other relevant research findings convey the following conclusions for the fabrication of inorganic membranes. Firstly, there is a need to develop alternate formulations that could provide breakthrough to the development of symmetric inorganic membranes possessing pore size of about 0.5 - 1 mm without using expensive inorganic precursors. Secondly, if a ceramic membrane is prepared by using expensive inorganic precursor formulation, such formulation should contain small quantities of expensive inorganic precursors and larger quantities of inexpensive inorganic precursors. Thirdly, the fabrication of the inorganic membrane with a processing temperature below 1000 ^{o}C needs to be experimentally tested and verified. The reduction in maximum sintering temperature to values below 1000 ^{o}C would be beneficial for additional cost reduction of membrane fabrication process. Fourthly, the prepared ceramic membrane should provide excellent combination of thermal, mechanical and chemical stability in addition to good separation characteristics for chosen MF and UF applications. In a similar way, the fabrication of a symmetric ceramic MF membrane possessing lower submicron range average pore size (0.1 - 0.5 mm) using low cost inorganic precursors and sintering temperature lower than 1000 ^{o}C also needs to be addressed.

2.4 Objectives

The main aim of this work is to fabricate low cost ceramic membranes suitable for microfiltration applications using fly ash as the major constituent. The specific objectives of this work are as follows:

- To formulate a low cost raw material composition based on fly ash for making microfiltration membranes.
- To study the effect of sintering temperature on membrane porosity and corrosion resistance.
- To study the dependence of pore size distribution and morphology on sintering temperature.

Chapter 3

EXPERIMENTAL METHODOLOGY

3.1 Raw materials

This work has utilized five inorganic raw materials such as fly ash, sodium carbonate, calcium carbonate, boric acid, sodium metasilicate. Different raw materials used for fabricating membranes serve different functional attributes . Fly ash has been used as physicochemical characteristics of fly ash such as bulk density, particle size, porosity, water holding capacity, and surface area make it suitable for ceramic membrane preparation. Sodium carbonate and boric acid act as colloidal agent improving the dispersion properties of the membrane and addressing homogeneity in the membrane structure. Boric acid also improves the mechanical strength of membrane by forming metallic metaborates at sintering temperature. Sodium metasilicate acts as binder by creating silicate bonds thereby inducing higher mechanical strength. Calcium carbonate under sintering conditions would dissociate into CaO and CO_2 gas .The path created by the release of CO_2 gas gives porous structure to the membrane and contributes to membrane porosity.

All chemicals (sodium carbonate, calcium carbonate, boric acid and sodium metasilicate) except fly ash were obtained from CDH India. Fly ash was obtained from Bhatinda thermal plant. Sodium carbonate, calcium carbonate, boric acid and sodium metasilicate all were graded at least 99.5% pure so all of them were used without any pre-treatment. On the Other hand fly ash was heated to 550 ^{o}C and kept at this temperature for 4 hours to remove any un-burnt carbon and organic impurities. After this treatment the colour of fly ash changed from grey to tan.

3.2 Membrane preparation

The membrane fabrication process starts by thorough mixing and grinding of raw materials like fly ash, sodium carbonate, sodium metasilicate, calcium carbonate and boric acid in a ball mill for 1 hour. Composition of raw material used both in dry basis and wet basis for membrane fabrication is given in Table 3.1 and 3.2 respectively. Grinding of raw materials is then followed by paste preparation by addition of distilled water. The paste is then casted in a circular ring of diameter 55 mm and thickness 5.5 mm. After this casted membrane rings are placed under distributed load of 2 Kg for 12 hours to prevent deformation and drive

homogeneity in the inorganic matrix followed by drying at room temperature. This step is followed by heating the casted membranes upto 100 ^{o}C in a muffle furnace and then keeping these membranes at this temperature for about 12 hours. After 12 hours the membranes are again heated upto temperature 250 ^{o}C maintaining a heating rate of 50 ^{o}C/ hour . The membranes are then kept at 250 ^{o}C for about 2 hours. After 2 hours, membranes are heated again upto the desired sintering temperature maintaining heating rate of 100 ^{o}C/ hour. Four sintering temperature have been used in this work 800 ^{o}C, 850 ^{o}C, 900 ^{o}C, 1000 ^{o}C to study the effect of sintering temperature on porosity and pore size. The membranes after heating upto desired sintering temperature are kept at this temperature for about 5 hours. This is followed by slow cooling from sintering temperature to below 100 ^{o}C. After sintering the membranes achieve rigid, hard, porous texture. Then the membranes are polished by using silicon carbide paper (C-220) and (C-100) to obtain membranes with smooth surface. Thereafter, the membranes are sonicated in an ultrasonic bath to remove the loose particles that might have adhered on the surface of membranes during polishing. Flow chart depicting steps involved in membrane preparation is shown on the next page.

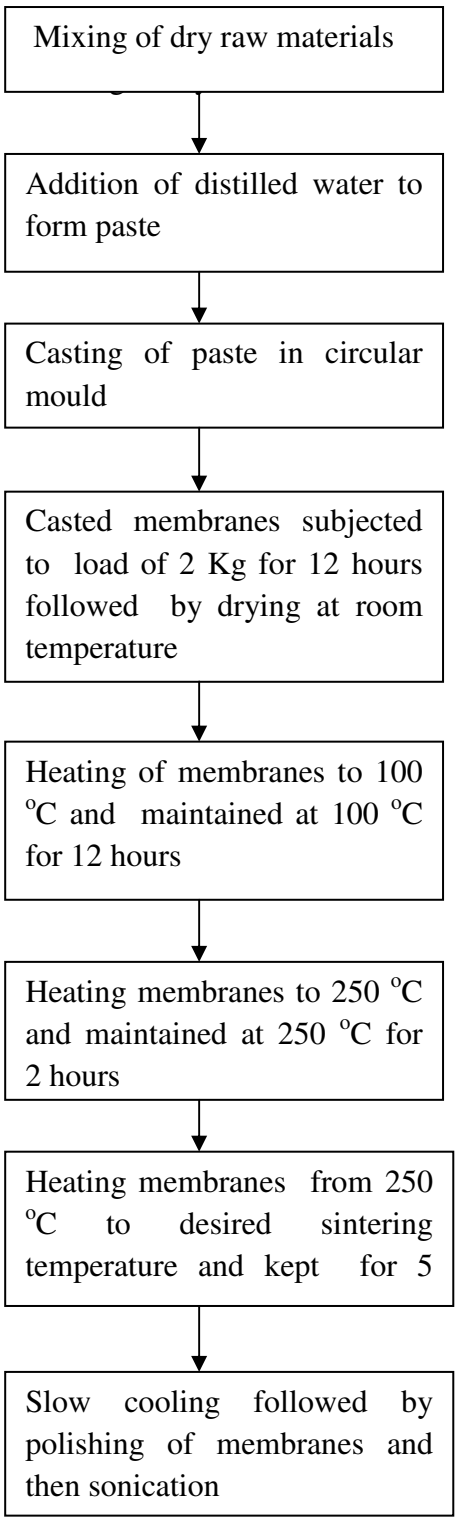
Table 3.1 Composition of raw material used for membrane fabrication (dry basis)

Material	Composition dry basis (wt%)
Fly ash	65
Sodium carbonate	10
Sodium metasilicate	2.5
Calcium carbonate	20
Boric acid	2.5

Table 3.2 Composition of raw material used for membrane fabrication (wet basis)

Material	Composition wet basis (wt%)
Fly ash	50.00
Sodium carbonate	7.69
Sodium metasilicate	1.92
Calcium carbonate	15.38
Boric acid	1.92
Water	23.08

Flow chart depicting steps involved in membrane preparation



3.3 Characterization techniques

Characterization techniques involve the structural characterization of the membranes by thermo-gravimetric analysis (TGA), XRD and morphological study by scanning electron microscope (SEM), porosity determination and chemical stability.

- TGA of the sample mixture was conducted using (EXSTAR TG/DTA 6300) to identify the various thermal transformations of the material during sintering condition.
- XRD analysis of membranes was conducted on (D8 Advance Bruker AXS) diffractometer using Cu- K_{α} radiation and wavelength 1.540598 Å to evaluate the extent of phase transformations.
- SEM was carried out using (JEOL JSM-6610LV) to analyze the presence of possible defects and estimate pore size.
- Porosity of the membranes was determined by the pycnometric method using water as wetting liquid.
- Chemical stability of the membrane was checked by subjecting membranes to HCl (pH1) and NaOH (pH13) solution for 7 days.

Chapter 4

RESULTS AND DISCUSSIONS

4.1 Physical observations

1. Fly ash, before it was used for preparing paste for membrane preparation, was heated to 550 ^{o}C and kept at this temperature for 4 hours to remove any un-burnt carbon and organic impurities. After this treatment the colour of fly ash changed from light grey to tan.

2. In the prepared membranes sintered at four different temperature (1000 ^{o}C, 900 ^{o}C, 850 ^{o}C, 800 ^{o}C) variation in colour was observed . While the membranes sintered at 900 ^{o}C, 850 ^{o}C and 800 ^{o}C were similar in colour on the other hand the membranes sintered at 1000 ^{o}C were light brown in colour. The variation in colour of these membranes sintered at four different temperature is shown in picture below:

Figure 4.1: Picture of membranes sintered at four different temperature
(from left to right 800 ^{o}C, 850 ^{o}C, 900 ^{o}C and 1000 ^{o}C)

3. The membranes sintered at 1000 ^{o}C appeared more rigid and hard than membranes sintered at 900 ^{o}C, 850 ^{o}C and 800 ^{o}C.

4.2 Corrosion test results

The membranes sintered at four different temperature were subjected to HCl (pH1) and NaOH (pH13) solution for 7 days to check their chemical stability. Firstly, the weight of the membranes before leaving them in contact with acid and base solutions was measured. Then the membranes were left in contact with acid and base solutions for seven days under atmospheric conditions. Thereafter, the wet membranes were dried. Lastly, the weight of dried membranes after seven days of acid and base treatment was taken into account. The difference in the weights of membranes before and after acid and base treatment gave the weight loss. Based on the experimental results obtained, it can be inferred that for all sintering temperature the membranes showed good stability against both acid and base treatment. The weight loss for all membranes for both acid and base solutions turned out to be less than 2%. Table 4.1 and 4.2 show results obtained for % weight loss exhibited by membranes sintered at different temperature in acid and base solutions respectively. As expected, the membranes sintered at 1000 ^{o}C performed slightly better than membranes sintered at 900 ^{o}C, 850 ^{o}C and 800 ^{o}C for both acid and base solutions. Figures 4.2 and 4.3 show % weight loss of the membranes sintered at various temperature when subjected to acid and base solutions respectively.

Table 4.1 Corrosion test results for membranes sintered at different temperature for HCl solution pH(1)

Membrane sintering temperature	Initial weight (W_1) gm	Final weight (W_2) gm	Weight loss = (W_1 - W_2) gm = ΔW	Weight loss (%) = ($\Delta W/W_1$)*100
800 ^{o}C	2.35	2.31	0.04	1.702
850 ^{o}C	2.09	2.06	0.03	1.435
900 ^{o}C	4.1	4.06	0.04	0.976
1000 ^{o}C	3.04	3.02	0.02	0.658

Table 4.2 Corrosion test results for membranes sintered at different temperature for NaOH solution pH(13)

Membrane sintering temperature	Initial weight (W_1) gm	Final weight (W_2) gm	Weight loss = (W_1 - W_2) gm = ΔW	Weight loss (%) = ($\Delta W/W_1$)*100
800 °C	2.18	2.15	0.03	1.376
850 °C	3.04	3.00	0.04	1.316
900 °C	1.78	1.76	0.02	1.124
1000 °C	2.91	2.88	0.03	1.031

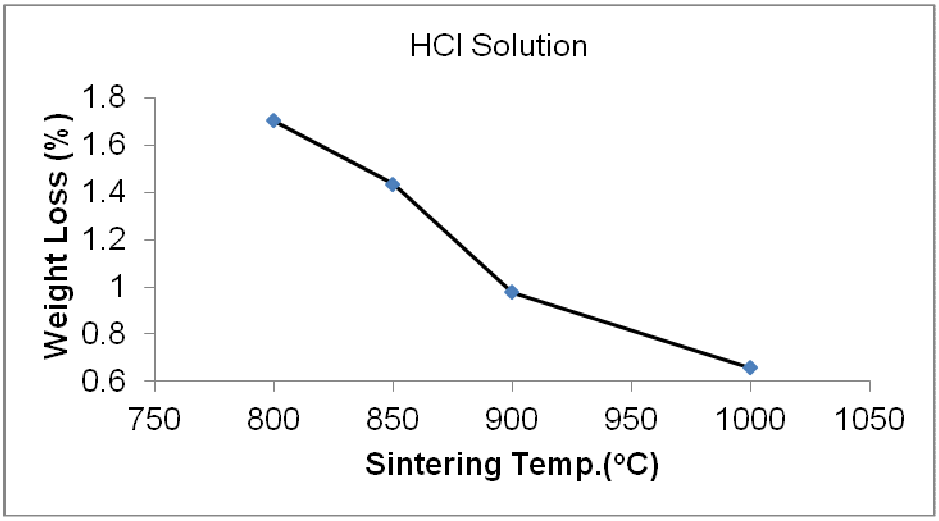


Figure 4.2: Weight loss (%) of membranes sintered at four different temperature for HCl solution

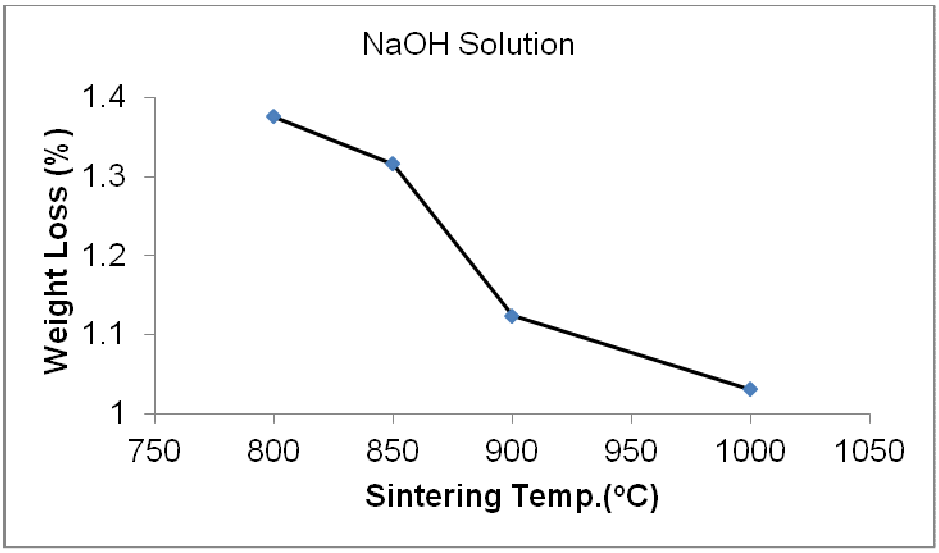


Figure 4.3: Weight loss (%) of membranes sintered at four different temperature for NaOH solution

4.3 Porosity results

The porosity (ε) of the membranes was determined by the pycnometric method using water as wetting liquid. Firstly thickness and diameter of sintered membranes were measured. To take into account the variation in thickness and diameter of membranes due to polishing, thickness and diameter of membranes were measured at different locations and then their average values were taken for calculating porosity. The second step involved taking dry weight of sintered membranes. The membranes were then kept for sonication in an ultrasonic bath for 15 minutes. Then the membranes were removed from ultrasonic bath and their wet weight was taken. Difference between the wet weight and dry weight of membranes divided by the density of water gave the volume of pores. The total volume of membranes was calculated using the formula $V_t = \pi/4d^2\, t$, where d = average diameter of membrane (cm), t = average thickness of membrane (cm). Finally porosity was calculated by using the following relation:

$$\text{Porosity (\%)} = \frac{\text{Volume of pores}}{\text{Volume total}} * 100 \qquad (1)$$

The different steps involved in calculation of porosity are given in Tables 4.3 to 4.7

Table 4.3 Calculation of average thickness for membranes sintered at different temperature

S no.	Sintering temperature			
	800 ^{o}C	850 ^{o}C	900 ^{o}C	1000 ^{o}C
1	5.36	4.81	5.26	4.64
2	5.45	4.79	4.63	4.53
3	5.22	4.85	5.04	4.43
4	5.16	4.8	5.49	4.37
Average thickness (mm)	5.297	4.812	5.105	4.492

Table 4.4 Calculation of average diameter for membranes sintered at different temperature

S no.	Sintering temperature			
	800 ^{o}C	850 ^{o}C	900 ^{o}C	1000 ^{o}C
1	5.3	5.4	5.4	5.5
2	5.4	5.4	5.5	5.5
Average diameter (cm)	5.35	5.4	5.45	5.5

Table 4.5 Calculation of volume of pores

Membrane sintering temperature	Dry Weight (gm) W_1	Wet Weight (gm) W_2	Volume of pores $= V_p$ (cm^3) $= (W_2-W_1)/1$ gm/(gm/cm^3)
800 ^{o}C	15.316	19.85	4.534
850 ^{o}C	13.508	17.688	4.18
900 ^{o}C	14.565	18.704	4.139
1000 ^{o}C	12.399	16.638	4.239

Table 4.6 Calculation of total volume

Membrane sintering temperature	t = average thickness (cm)	d = average diameter (cm)	Total volume = V_t (cm^3) = (πd^2 t)/4
800 °C	0.529	5.35	11.909
850 °C	0.481	5.4	11.022
900 °C	0.510	5.45	11.909
1000 °C	0.449	5.5	10.673

Table 4.7 Calculation of porosity

Membrane Sintering temperature	Volume total (cm^3) = V_t	Volume pores (cm^3) = V_p	Porosity (%) = (V_p/V_t) *100
800 °C	11.909	4.534	38.073
850 °C	11.022	4.18	37.925
900 °C	11.909	4.139	34.755
1000 °C	10.673	4.239	39.716

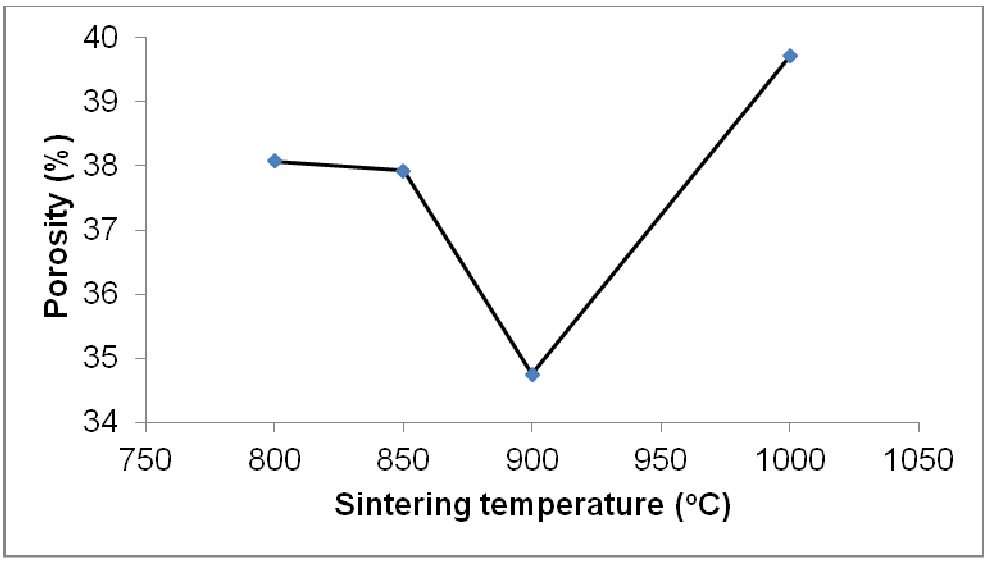


Figure 4.4: Variation of porosity with sintering temperature

From figure 4.4 it is clear that porosity is almost constant between temperature 800 ^{o}C and 850 ^{o}C then it decreases at sintering temperature 900 ^{o}C. At 1000 ^{o}C the porosity increases sharply. This sharp increase can be explained on the basis of disappearance of crystalline phase anorthite at sintering temperature 1000 ^{o}C although it is the major dominating phase present in the un-sintered membrane and membranes sintered at 800 ^{o}C, 850 ^{o}C, 900 ^{o}C as shown by xrd graphs of five membranes. The disappearence of phase anorthite has given way to appearence of phase dmisteinbergite which is a polymorph of anorthite i.e. dmisteinbergite has the same formula as anorthite but different structure.

4.4 Structural characterization

4.4.1 Thermo-gravimetric analysis

Thermo-gravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The objective of thermal analysis is to identify temperature regimes where predominant weight losses (and hence transformations) occur in the membrane. Thereby, an understanding could be developed for analyzing the effect of various temperature regimes on the porous structure, pore diameter and mechanical strength of the membrane. TGA (EXSTAR TG/DTA 6300) of the dry sample mixture was conducted to identify the various thermal transformations of the material during sintering conditions. Figure 4.5 presents the TGA curve of the powder mixture when subjected to thermo-gravimetric analysis by heating the dry inorganic mixture from room temperature to 1000 °C at a heating rate of 10 °C/min.

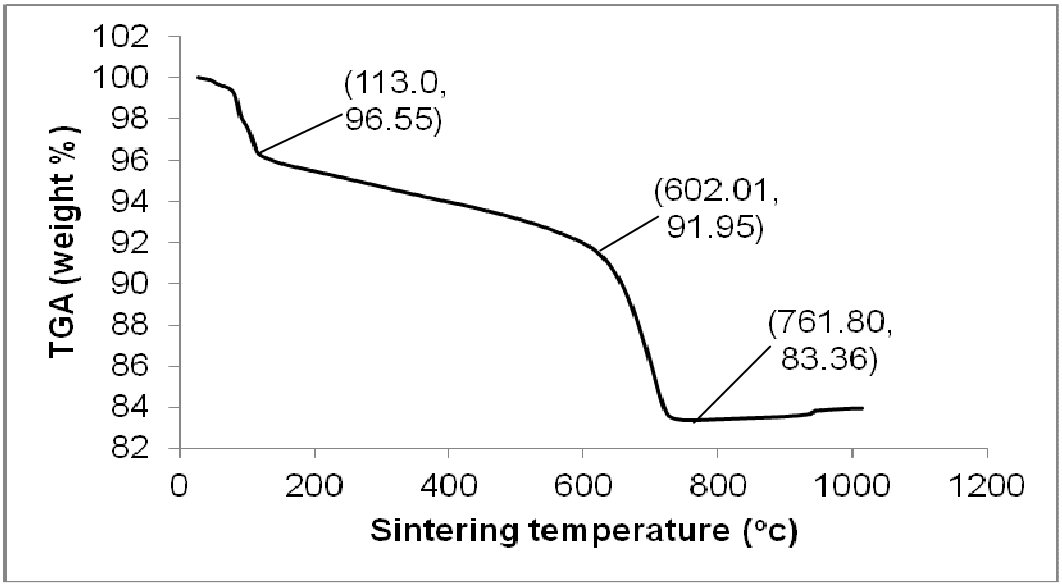


Figure 4.5 : TGA curve

The figure 4.5 conveys that a highly non-linear variation exists due to the presence of complex phase transformations and interactions. The total weight loss of the sample was observed to be 17%. About 3.45% weight loss is observed below 113 °C due to the removal of weakly bonded water molecules in the sample mixture. The weight loss of sample between 113 ^{o}C to 602 ^{o}C was 4.6% which can be attributed to burning of small impurities and unburned mineral coal powder and also because of evaporation of boric acid whose boiling point is 300 ^{o}C. In the temperature regime between 602 ^{o}C to 761 ^{o}C maximum weight loss happened about 8.59%. This is the region where the formation of CO_2 (and hence enhancement of the porous structure of the membrane) occurred due to calcination of $CaCO_3$. Beyond 761 ^{o}C very insignificant weight loss happened as conveyed by TGA curve so minimum sintering temperature for the membrane fabrication should be above 761 °C.

4.4.2 Phase characterization by XRD analysis

X-ray diffraction was used to identify the formed phases. XRD analysis was done on (D8 Advance Bruker AXS) diffractometer using Cu K_{α} radiation and wavelength 1.540598 Å. The observation of peaks and trends in the XRD graphs convey that major dominating phase present is Anorthite ($CaAl_2Si_2O_8$) while other significant phases present were Mullite ($2Al_2O_3.SiO_2$), Nacrite and Dickite both polymorphs of Kaolinite $Al_2Si_2O_5(OH)_4$ (having same formula as Kaolinite but different structures). Apart from these small quantities of Quartz (SiO_2), Iron (III) oxide (Fe_2O_3), Aluminium oxide(Al_2O_3), Gehlenite ($Ca_2Al[AlSiO_7]$)

were also present. Comparisons of XRD graphs for five different samples also indicated that continuous phase transformations were taking place during sintering conditions. Anorthite which was a major constituent in 4 samples at temperature 25 ^{o}C, 800 ^{o}C, 850 ^{o}C and 900 ^{o}C disappeared in sample sintered at 1000 ^{o}C and gave way to Dmisteinbergite which is a polymorph of anorthite. Similarly other phases were also undergoing transformations and their content also varied during sintering conditions. Figures from 4.6 to 4.10 show XRD graphs for five different samples four of them sintered at 800 °C, 850 ^{o}C, 900 °C and 1000 °C and one un-sintered membrane.

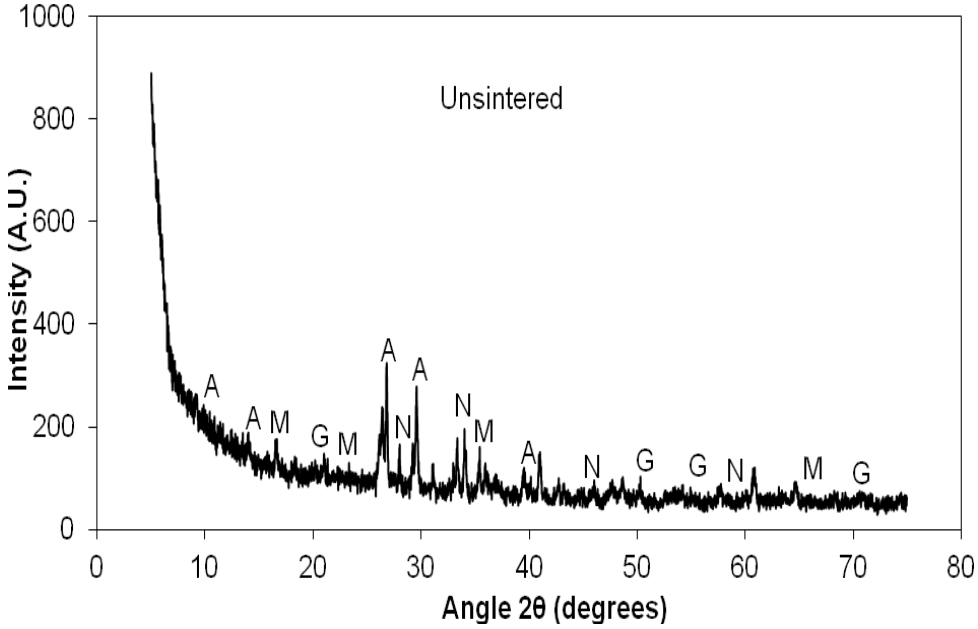


Figure 4.6 : XRD graph for un-sintered membrane A: Anorthite (96-900-0362), M: Mullite (96-710-5576), N: Nacrite (96-101-1063), G: Gehlenite (96-101-1003)

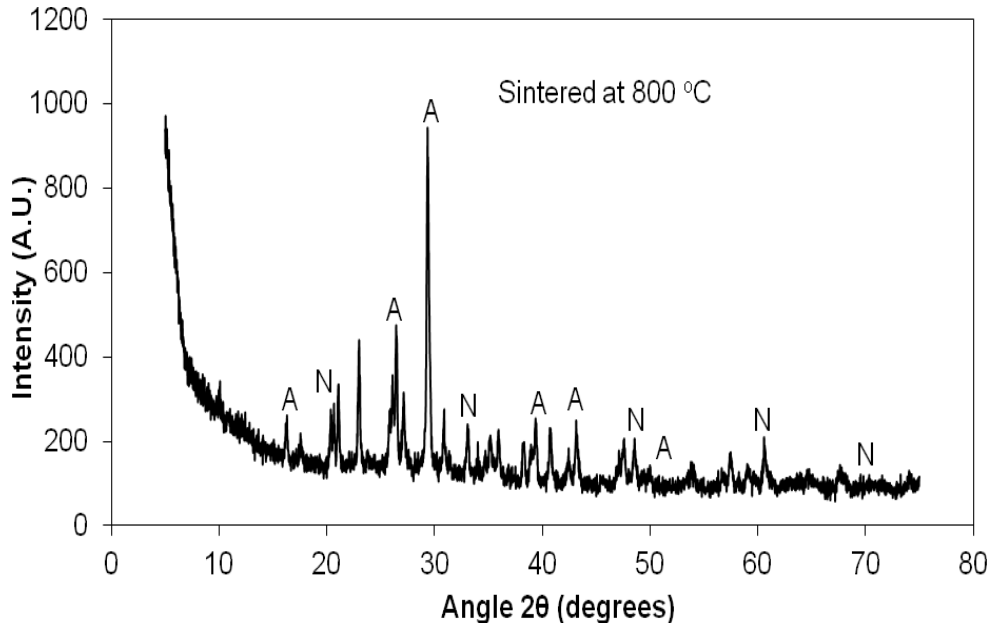


Figure 4.7 : XRD graph for membrane sintered at 800 °C A: Anorthite (96-900-1260), N: Nacrite (96-101-1081)

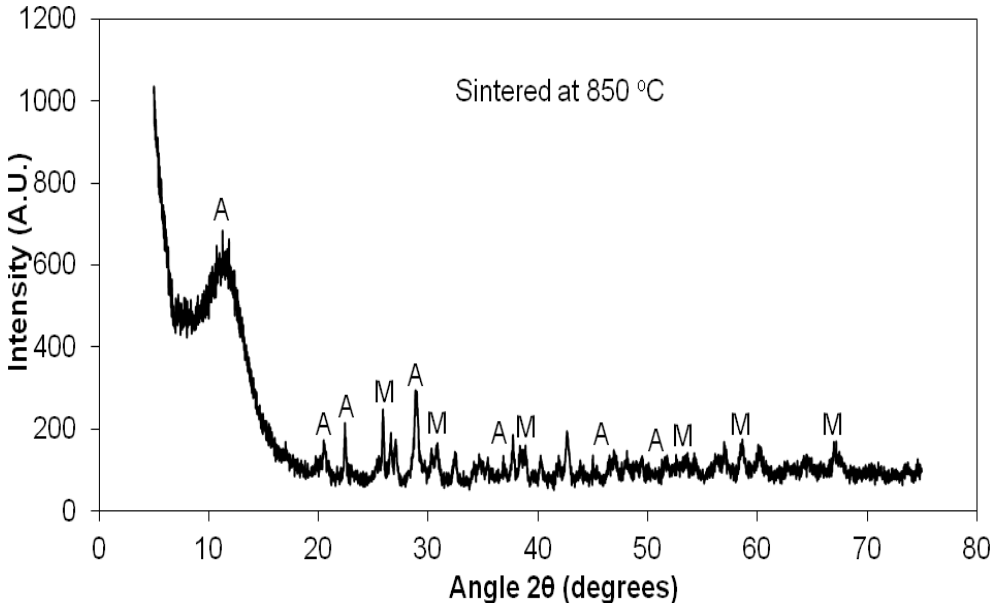


Figure 4.8 : XRD graph for membrane sintered at 850 °C A: Anorthite (96-900-0362), M: Mullite (96-710-5576)

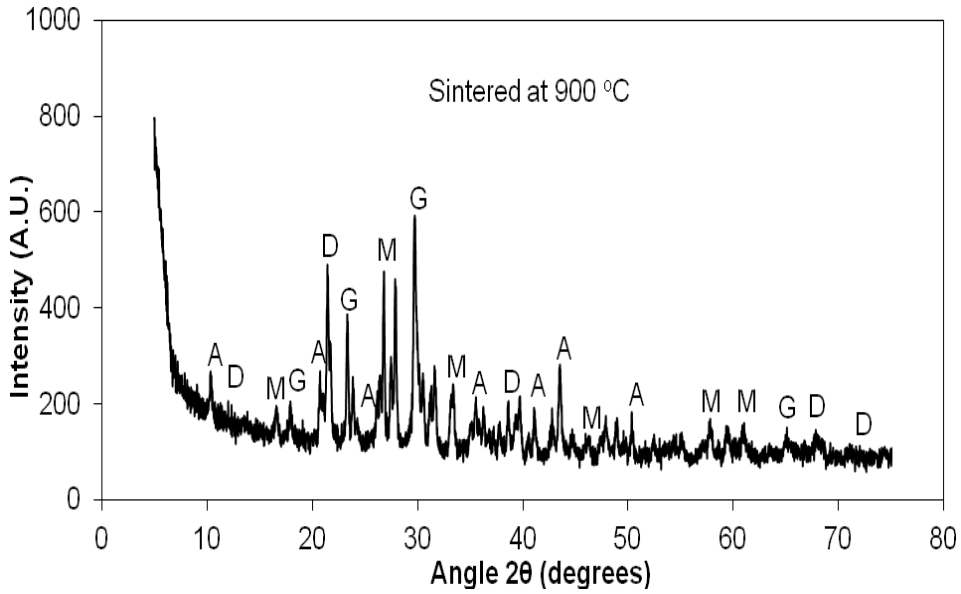


Figure 4.9 : XRD graph for membrane sintered at 900 °C A: Anorthite (96-900-0362), M: Mullite (96-710-5576), D: Dickite (96-900-3083), G: Gehlenite (96-100-0049)

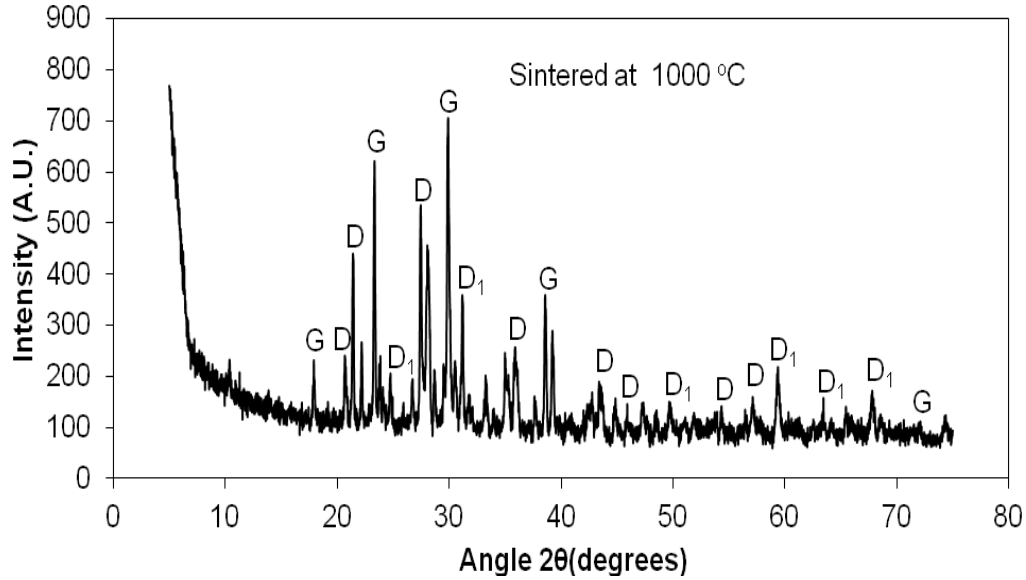


Figure 4.10 : XRD graph for membrane sintered at 1000 °C D: Dickite (96-900-3082), D_1: Dmisteinbergite (96-901-1036), G: Gehlenite (96-101-1003)

4.4.3 Surface morphology

Figures 4.11 to 4.14 illustrate SEM pictures for the membrane sintered at four different temperature considered in this work. Observation of the SEM pictures indicate that for all sintering temperature the membranes did not show any cracks or surface defects. Individual

pore diameters were measured for about 100 pores for each membrane using Image J software for different pores visible in the SEM. Since pore size distribution and average pore size distribution values are critically dependent on the sampling procedure, four SEM pictures are evaluated using the software for each membrane. These micrographs are taken from the randomly selected sections of the membrane. These ensure that the pore size distribution represent the existing porous texture of the membrane. Based on this method it was found that up-to 900 ^{o}C average pore size decreased with increasing sintering temperature while it increased for membrane sintered at 1000 ^{o}C. Table 4.8 shows the variation of average pore size of the membrane with sintering temperature.

Table 4.8 Variation of average pore size of the membrane with sintering temperature

Sintering temperature	Minimum pore size	Maximum pore size	Average pore size
800 ^{o}C	0.271	5.602	1.524
850 ^{o}C	.336	4.891	1.458
900 ^{o}C	.399	13.689	1.202
1000 ^{o}C	0.636	9.634	2.301

Figures 4.12, 4.14, 4.16 and 4.18 present the surface pore size distribution of the membranes sintered at 800, 850, 900 and 1000 ^{o}C respectively.

For the membranes sintered at 800 ^{o}C, about 31% pores are lying between 0.5 and 1.0 μm diameter while another 33% pores are lying between 1.0 and 1.5 μm. Therefore, 64% of the pores have diameters in the range of 0.5 – 1.5 μm.

For the membranes sintered at 850 ^{o}C, about 36% pores are lying between 0.5 and 1.0 μm diameter while another 28% pores are lying between 1.0 and 1.5 μm. Therefore, 64% of the pores have diameters in the range of 0.5 – 1.5 μm.

For the membranes sintered at 900 ^{o}C, about 51% pores are lying between 0.5 and 1.0 μm diameter while another 27% pores are lying between 1.0 and 1.5 μm. Therefore, 78% of the pores have diameters in the range of 0.5 – 1.5 μm.

For the membranes sintered at 1000 ^{o}C, pores are widely distributed and about 30% pores are lying between 1.0 and 1.5 μm diameter.

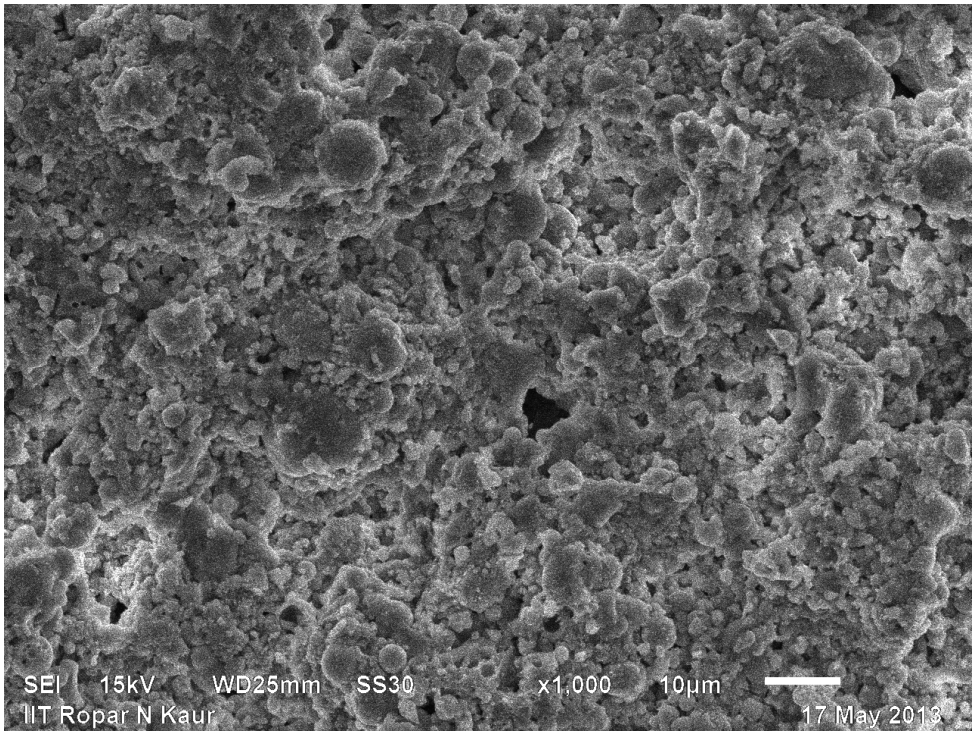


Figure 4.11 : SEM picture of membrane sintered at 800 ^{o}C

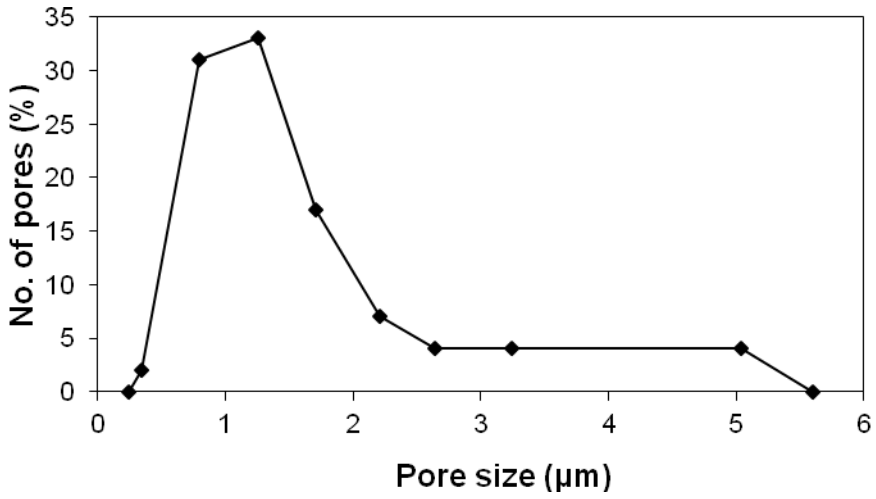


Figure 4.12 : Surface pore size distribution of membrane sintered at 800 ^{o}C

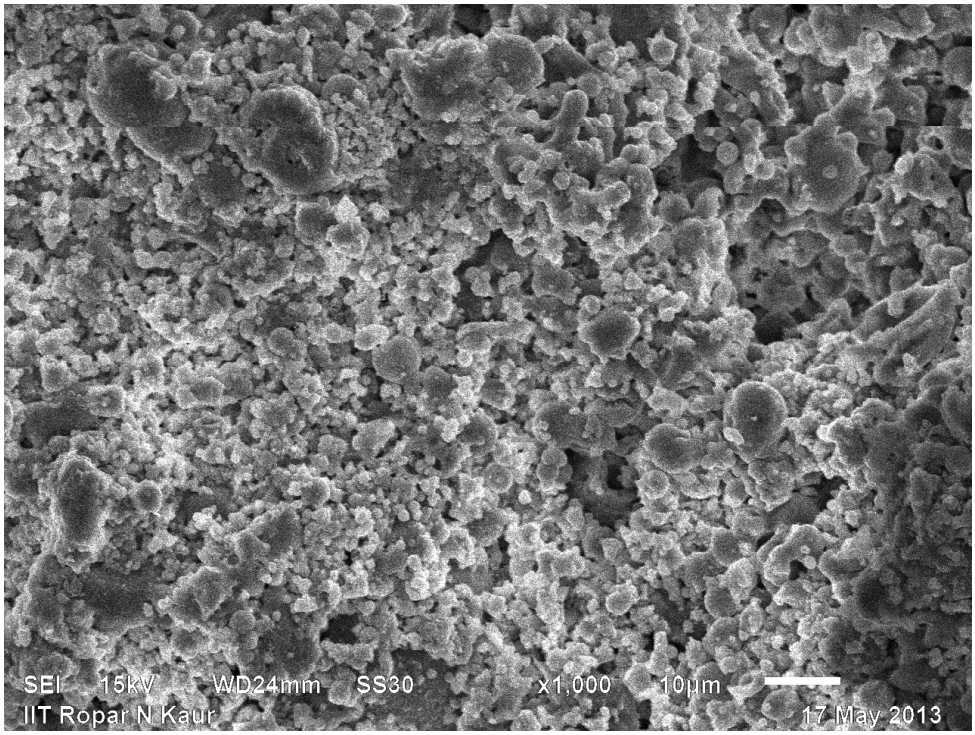


Figure 4.13 : SEM picture of membrane sintered at 850 ^{o}C

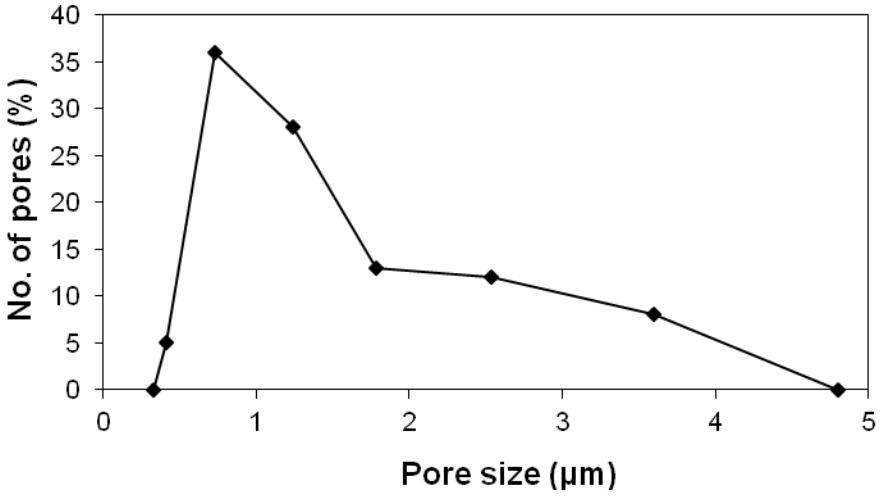


Figure 4.14 : Surface pore size distribution of membrane sintered at 850 ^{o}C

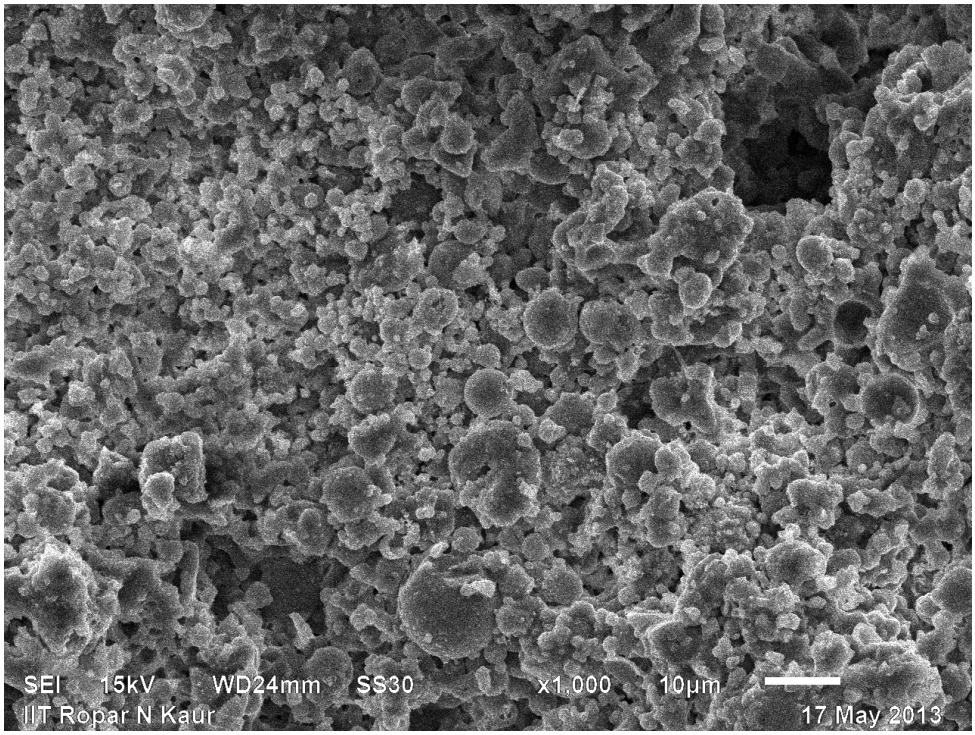


Figure 4.15 : SEM picture of membrane sintered at 900 ^{o}C

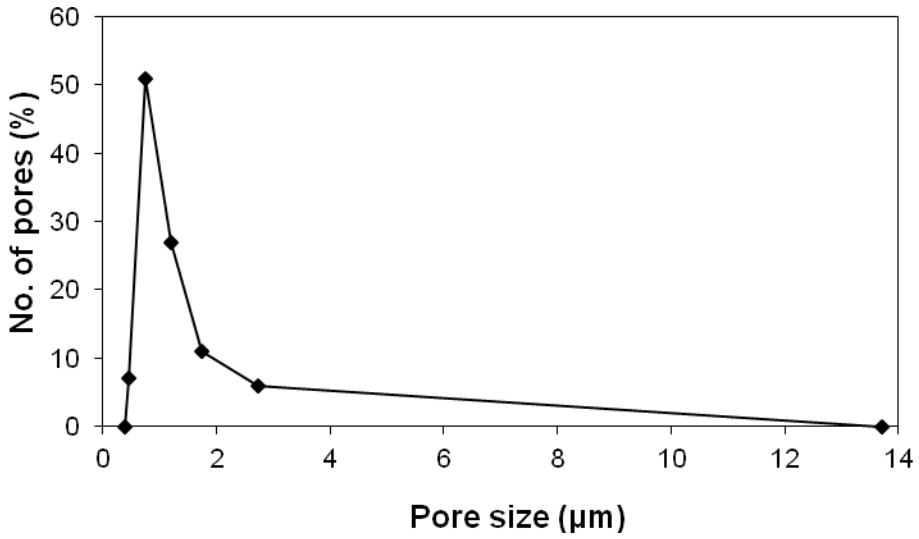


Figure 4.16 : Surface pore size distribution of membrane sintered at 900 ^{o}C

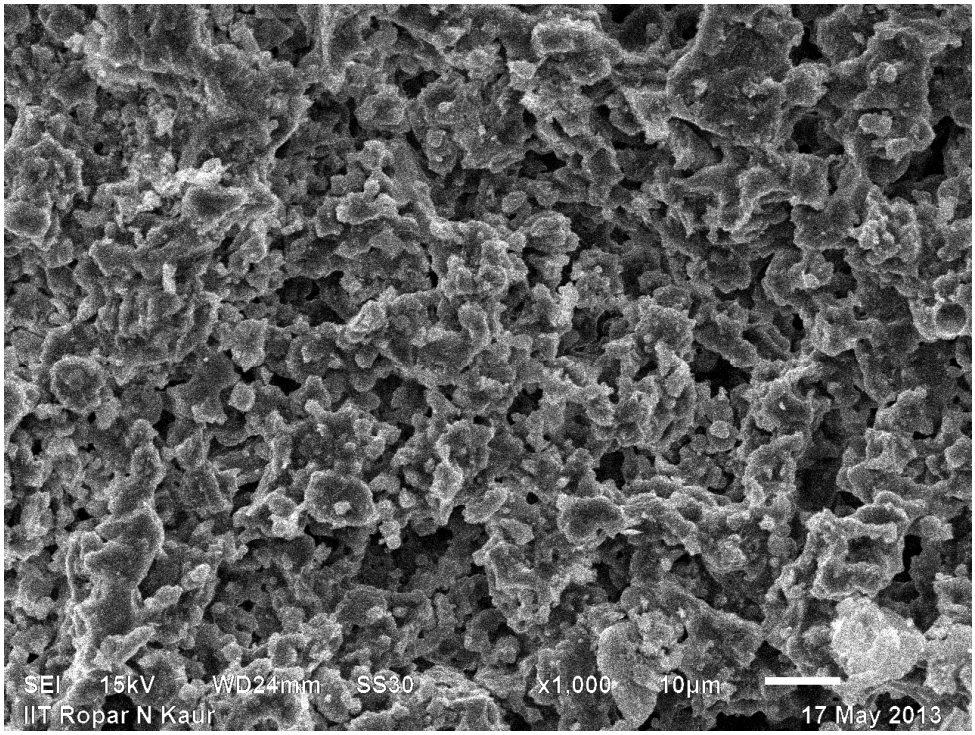


Figure 4.17 : SEM picture of membrane sintered at 1000 ^{o}C

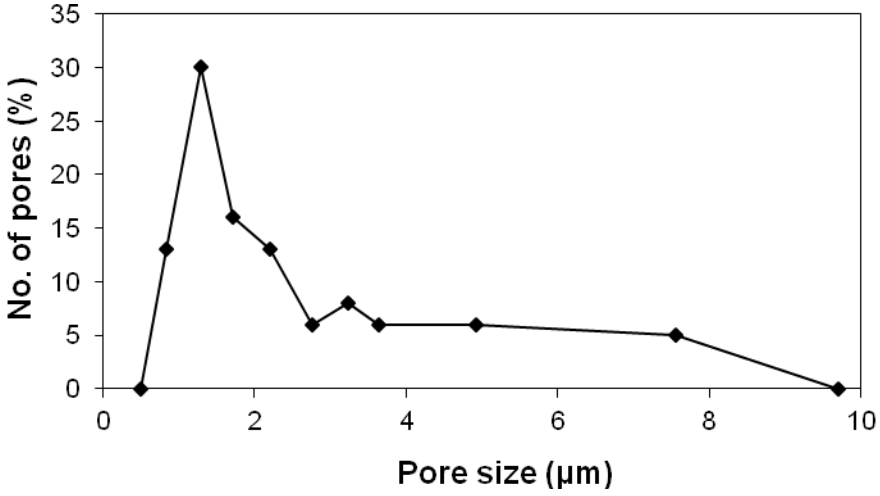


Figure 4.18 : Surface pore size distribution of membrane sintered at 1000 ^{o}C

Chapter 5

CONCLUSIONS and FUTURE WORK

5.1Conclusions

This study indicates that a defect-free low cost microfiltration range ceramic membrane can be fabricated by using fly ash as major constituent along with inorganic precursors such as calcium carbonate. Based on the XRD and TGA analysis it can be inferred that the sintering temperature of membrane should be above 760 ^{o}C. The membranes fabricated at four different sintering temperature showed porosity in the range 34.755 to 39.716 % which is considered as good. The average pore size of the sintered membranes varied in the range 1.458 to 2.301 μm. The fabricated membranes showed excellent chemical resistance exhibiting less than 2% weight loss for both acid and base solutions. These results provide significant opportunities to develop low cost ceramic micro-filtration membranes with flexible pore sizes from a potentially environmental hazardous material such as fly ash for industrial applications.

5.2 Future work

The present work deals with preparation and characterization of low cost ceramic microfiltration membranes using fly ash. In this study effect of sintering temperature on membrane characteristics has been studied. However, there is lot of scope for further research as outlined below:

- Effect of heating rate can be studied.
- Application of prepared membranes for separation of oil water emulsions can be studied.
- Polymer ceramic composite membranes can be prepared by dip coating a thin polymer layer on the fly ash based membranes for ultra-filtration applications.
- Micellar/Polymer enhanced micro/ultra filtration experiments can be performed to separate dyes and heavy metal ions from waste water streams.

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