PREPARATION AND CHARACTERIZATION OF MEMBRANES MADE OF POTTERY CLAY

Thesis submitted in partial fulfilment of the requirements
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CHEMICAL ENGINEERING

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CERTIFICATE

This is certified that the thesis entitled **"Preparation and Characterization of Membranes Made of Pottery Clay"** 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.

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ABSTRACT

Membrane separation works on the physical principle of size cut-off, wherein the particles larger in diameter cannot permeate while fluid (solvent) can. Membranes used in micro to ultra filtration have been prepared from refined inorganic materials. Some researchers have used low-cost natural materials such as clay, fly ash and apatite, these need lower firing temperature than metal oxide materials and have high flux performance to treat large volumes of process fluids. The kiln-fired earthen pottery is in use for building homes, storage vessels since earliest civilizations, the strength combined with the porosity and pore sizes in micro-filtration range makes clay suitable for membrane fabrication. The pores are formed when the water evaporates, giving macro-pores, use of additional porosity agents like calcium carbonate gives micro-pores along with higher porosity. The firing temperature determines final strength, porosity and pore size, reason being materials in use have crystalline constituents that have vitreous properties like forming semi-solid phases, restructuring, and reduction of volume known as sintering at temperatures beyond 750^{o}C. Sintering gives membrane strength and reduced pore sizes which can be used as is in micro-filtration or with polymer coating for ultra-filtration.

Membranes with pore-size lying in micro filtration regime were prepared using local pottery clay of Patiala. Two membranes sets were prepared by paste casting followed by sintering at different temperatures, viz. 850^{o}C, 900^{o}C, 1000^{o}C varying the primary and porosity components compositions. Using 68% clay, 20% calcium carbonate, 10% sodium carbonate (membrane A) and the second one using 76% clay, 20% calcium carbonate (membrane B) with small amounts of sodium metasilicate. Both the membranes were characterized by TGA, SEM, XRD, porosity test with water as wetting liquid and acid–base treatment. The effect of sintering temperature on porosity and pore size has been studied, with pore size data taken from SEM imaging analysis. The composition of membrane is also important as amount of calcium carbonate determines amount of CO_2 escaping per gram of membrane bulk, porosity increases with increase in $CaCO_3$ amount/g of membrane, but larger $CaCO_3$ concentration can be damaging as pressure of CO_2 increases with increased percentage of $CaCO_3$.

From the experimental results, it was found that with the increase of sintering temperature, pore size was increasing while porosity was decreasing. The overall performance of membrane B was better than membrane A.

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List of Symbols/Abbreviations

h_∞ Coating thickness (cm)

μ Viscosity

ρ Density

σ Surface tension

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 filtration ranges

Ceramic membranes are a type of artificial membranes made from inorganic materials such as alumina, titania, zirconia oxides, some glassy materials or even a combination of these. A summary of pore size cut-offs of different membrane processes and materials that can be separated is shown in Figure 1.1.

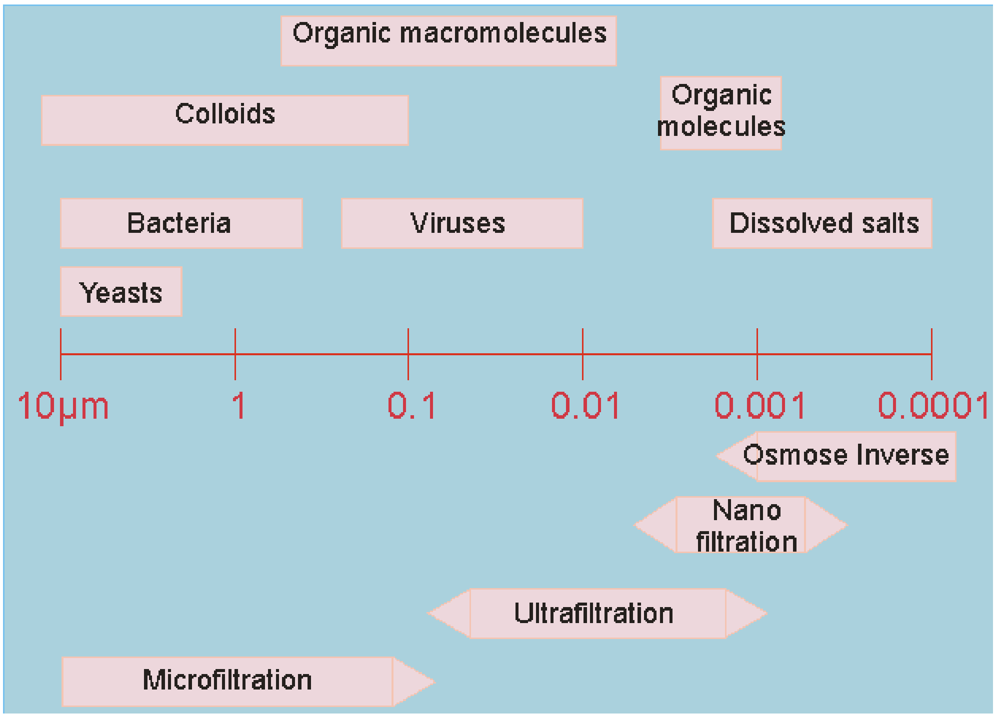

Figure 1.1: Summary of the membrane cut-offs

1.2 Structure of Ceramic Membranes

Ceramic membranes normally have an asymmetrical structure composed of at least two, mostly three, different porosity levels. Indeed, before applying the active, micro-porous top layer, a meso-porous intermediate layer is often applied in order to reduce the surface roughness. The macro-porous support ensures the mechanical resistance of the nano-filter.

The ceramic membranes are often formed into an asymmetric, multi-channel element. These elements are grouped together in housings, and these membrane modules can withstand high temperatures extreme acidity or alkalinity and high operating pressures, making them suitable for many applications where polymeric and other inorganic membranes cannot be used.

Several membrane pore sizes are available to suit specific filtration needs covering the micro-filtration, the ultra-filtration, and nano-filtration ranges (from 5 mm down to 1000 Dalton).

1.3 Materials of Construction

Ceramic membranes today run the gamut from A to Z in terms of materials (from alpha alumina to zircon). The most common membranes are made of Al, Si, Ti or Zr oxides, with Ti and Si being more stable than Al or Si oxides. In some less frequent cases, Sn or Hf are used as base elements. Each oxide has a different surface charge in solution. Other membranes can be composed of mixed oxides of two of the previous elements, or are established by some additional compounds present in minor concentration.

1.3.1 Advantages of Ceramic Membranes

- Chemical, Mechanical and Thermal stability.
- Ability of steam sterilisation and back flushing.
- High abrasion resistance.
- High fluxes.
- High durability.
- Bacteria resistance.
- Possibility of regeneration.
- Dry storage after cleaning.

1.4 Classification - Based on Pore Size

- Dense
- Porous

Dense membranes are used in gas separation process, e.g., separation of oxygen from air, or the separation of hydrogen gas from a mixture (de Vos and Verweij, 1998).

Porous ceramic membranes are chiefly used for gas separation and micro- or nano-filtration. They can be made from both crystalline as well as amorphous solids.

1.5 Applications of Ceramic Membranes

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 and recycling of organic solvents

Metal industry / Surface engineering:

- recycling and disposal of degreasing and rinsing bathes
- treatment of oil/water emulsions
- recovery of heavy metals
- cleaning of wastewater from grinding processes
- treatment of wastewater form glass and glass fibre production

Textile / Pulp and paper industry:

- concentration, fractionation, isolation and sterilization for antibiotics, enzymes, proteins, amino acids and vitamins
- separation, concentration and dewatering of biomass 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 and fractionation of milk and whey ingredients
- desalination 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 microorganism
- retention of heavy metals and radioactive substances
- recycling of water form swimming pools
- purification of the drain of sewage plants.

1.6 Ceramic Membrane Preparation Methods:

- ➢ Slip Casting
- ➢ Tape Casting
- ➢ Pressing
- ➢ Extrusion
- ➢ Sol-Gel Process
- ➢ Dip Coating
- ➢ Chemical Vapour Deposition (CVD)
- ➢ Preparation of Hollow Fibre Ceramic Membranes

1.6.1 Sol-Gel Process:

- ➢ Hydrolysis
- ➢ Condensation
- ➢ Gelation
- ➢ Ageing
- ➢ Drying
- ➢ Densification

A sol-gel preparation involves first the formation of a sol, which is a suspension of solid particles in a liquid, and then of a gel, which is a diphasic material with a solid encapsulating a liquid. The liquid can be removed from a gel by either conventional drying (such as by using an oven) to obtain a product known as a xerogel, or by drying with supercritical extraction (often referred to as supercritical drying for short) to give an aerogel. Preparing catalytic materials with the sol-gel method has received increasing attention in recent years because of its versatility and excellent control over a product’s properties (Cauqui and

Rodriguez-Izquierdo, 1992). In fact, there are a host of experimental variables, generally referred to as the sol-gel parameters, which can impact on the physical and chemical characteristics of a sample. To date, most studies have focused on sol-gel parameters that are important in the first step which is the formation of a gel. There has been relatively less work on the subsequent processing steps: aging, drying, and heat treatment. Because these steps are often interrelated (Brinker and Scherer, 1990), one should take a broader viewpoint and consider all of them in fine-tuning a sol-gel product.

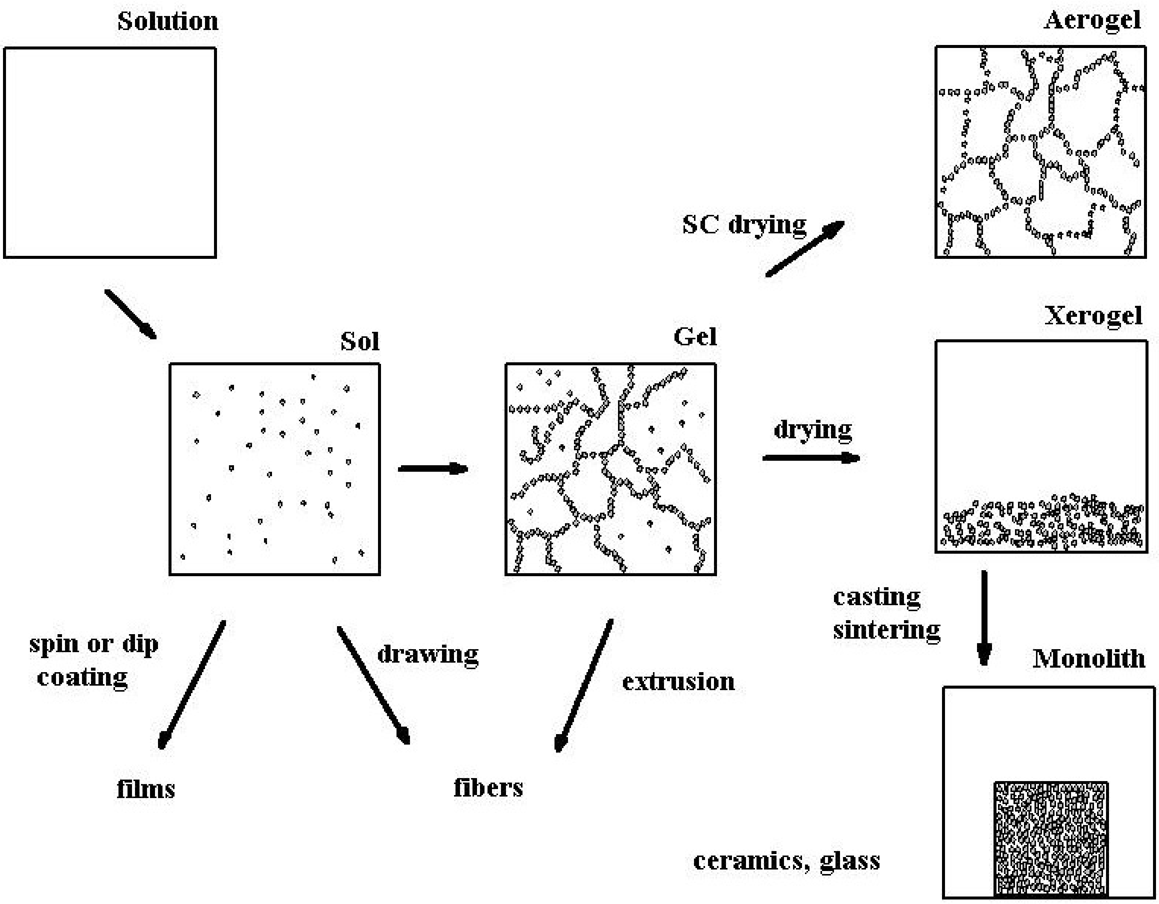

Figure 1.2: Sol-gel process

The sol-gel process (Figure 1.2) has four key steps namely gel formation, ageing, drying, and heat treatment. Furthermore, these steps are interrelated in that what is happening in one step usually affects the next step. The initial gel structure will dictate the extent to which it is influenced by drying conditions. Differently dried gels will have different structural evolution with heat treatment, and so on. However, it is important to view these complexities as opportunities in using the sol-gel method to prepare catalytic materials with desirable properties. There are three specific parameters that affect the surface area, pore volume, and crystal structure of zirconia. Although these are physical and not chemical properties, results in our laboratory have shown that they have important catalytic implications. More systematic studies are necessary to identify the key parameters in each sol-gel step and to understand the underlying physical and chemical processes. Extension to multi-component systems is of particular interest because of their widespread applications.

1.6.2 Dip Coating Process

Dip coating (Figure 1.3) is used for creating thin layers. Uniform films can be applied onto flat or cylindrical substrates.

The dip coating process (Figure 1.4) can be separated into five stages:

- **Immersion:** The substrate is immersed in the solution of the coating material at a constant speed (preferably jitter-free).
- **Start-up:** The substrate has remained inside the solution for a while and is starting to be pulled up.
- **Deposition:** The thin layer deposits itself on the substrate while it is pulled up. The withdrawing is carried out at a constant speed to avoid any jitters. The speed determines the thickness of the coating (faster withdrawal gives thicker coating material).
- **Drainage:** Excess liquid will drain from the surface.
- **Evaporation:** The solvent evaporates from the liquid, forming the thin layer. For volatile solvents, such as alcohols, evaporation starts already during the deposition & drainage steps.

Figure 1.3: Dip coating machine (continuous)

If the withdrawal speed is chosen such that the sheer rates keep the system in the Newtonian regime, the coating thickness can be calculated by the Landau Levich equation (Eq. (1)):

$$h_{\infty} = 0.945 l_c Ca^{2/3} \qquad (1)$$

Where, $$l_c = \sqrt{\frac{\sigma}{\rho g}}, Ca = \frac{\mu U}{\sigma}$$

h_{∞} = coating thickness, μ = viscosity, ρ = density, σ = surface tension, U = withdrawal speed, g = gravity.

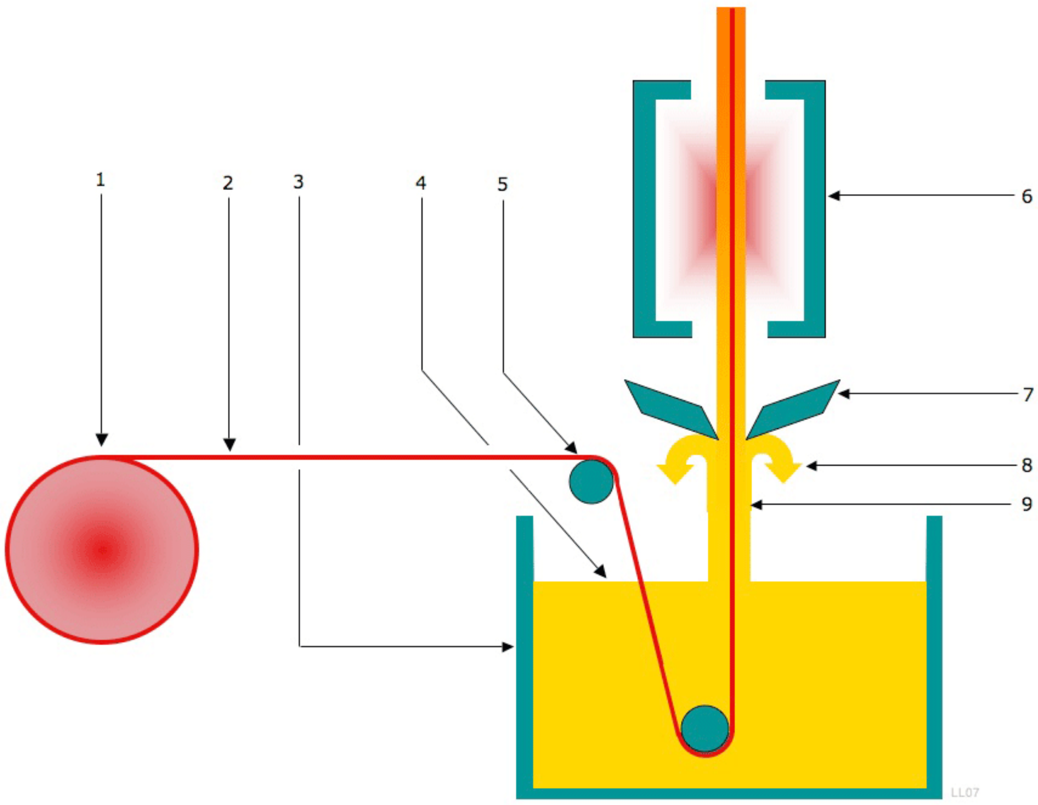

Figure 1.4: Continuous dip coating process

1.7 Ceramic Membranes Materials

Inorganic materials have advantages over polymeric materials for their thermal stability, good chemical resistance to solvents, high mechanical strength and long lifetime (Bhave, 1991; Hsieh, 1996; Burggraaf et al, 1996; Tsuru, 2001). Commonly used materials for ceramic membranes are Al_2O_3, TiO_2, ZrO_2, SiO_2 etc. or a combination of these materials.

The combined Al_2O_3–TiO_2 membranes have been developed in order to obtain the specific properties of both materials, namely the possibility of obtaining membrane layers with a high thickness, without defects and a good thermal, mechanical and chemical stability (Van Gestel et al., 2002).

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.

α-Al_2O_3 was used as primary component in initial microfiltration membrane fabrications, (DeFriend et al., 2003). Subsequently, γ-Al_2O_3, zirconia, titania, and silica were used by (Yoshino et al., 2005). Apatite powder (Masmoudia et al., 2007) has also been used as precursor for micro-filtration membrane preparation. Moroccan clay porous ceramic membranes deposited on tubular support and a pore size of 9.25 to 10.5 μm was reported (Saffaj et al., 2006). Mechanical strength of support was 10 MPa at 1250 °C sintering temperature. Ceramic microfiltration membranes made of Tunisian clay had a pore size of around 10 μm (Khemakhem et al., 2009).

Although, several literatures are available on the fabrication of ceramic membranes, 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 Temp. (^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.
Khemakhem et al., (2009)	Tunisian clay,	900 ^oC	Around 10 μm	Porosity of membrane was 30%
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.
Bulasara et al. (2010)	Kaolin (40%), Boric Acid (5%), Quartz (15%), Na_2CO_3 (10%), Feldspar (15%), Sodium metasilicate (5%), Pyrophyllite (10%)	900 ^oC	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.
Nandi et al. (2009)	Kaolin (50%), Boric Acid (5%), Quartz (15%), Sodium carbonate (10%), Feldspar (15%), Sodium metasilicate (5%)	900 ^oC	Average pore diameter 0.285 μm.	This work inferred that low cost ceramic membranes are promising for mosambi juice processing.
(Saffaj et al.,2006)	Moroccan clay porous ceramic membranes	1250 °C	Mean pore size of 9.25 to 10.5 μm	Mechanical strength of support was 10 MPa
Nandi et al. (2008)	Kaolin (40%), Quartz (15%), $CaCO_3$ (25%), Boric Acid (5%), Sodium metasilicate (5%), Na_2CO_3 (10%)	800 to 1000 ^oC	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 has been reported for the fabrication of inorganic membranes using cheaper raw materials such as apatite powder, natural raw clay, kaolin, dolomite & 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. The submicron range ceramic membranes (pore sizes ranging from 0.1 – 0.5 mm) available in the market consist 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 Objectives

The following objectives were laid out during the course of whole work.

- Preparation of low cost membranes from pottery clay in microfiltration range.
- Study of sintering temperature on membrane porosity and corrosion resistance.
- Study of membrane porosity with variation in membrane compositions.
- Phase characterization of membrane using XRD and pore size distribution using SEM.

Some of the advantages of pottery clay membranes are superior structural strength of fired pottery clay, combined with the low cost and good availability of raw materials.

Chapter 3

EXPERIMENTAL METHODOLOGY

3.1 Raw materials

The raw materials used in this work were pottery clay, calcium carbonate, sodium carbonate, sodium metasilicate and boric acid. Different raw materials used for fabricating membranes were chosen for their different physical and chemical attributes, all serve different functional purposes.

Pottery Clay: Pottery clay was obtained locally; the color of the clay was reddish brown. The clay was cleaned and screened for organic impurities and other foreign rock debris. Paste was made using ordinary water. The paste was then dried in hot air blow drier, crushed in ball mill for half an hour. Clay was screened using screening meshes with cut-off of 150 standard mesh size. The clay powder thus obtained was then used according to the need in membrane preparation batch. Clay was used as a major component in fabrication of membranes. It provided the bulk structure of the membrane. It served as basic support structure.

Calcium Carbonate: Calcium Carbonate was used as porosity agent, it was used for it's calcination property, calcium carbonate decomposes to give calcium oxide and carbon dioxide when heated upwards of 550 ^{o}C, the release of CO_2 through the membrane bulk in its semi solid, inversion states gives pores or network of pores. The release path formed micro-pores.

Sodium Carbonate: Sodium carbonate was used as dispersant or surfactant to homogenize the membrane components throughout the membrane bulk.

Boric Acid: Boric acid acts both as a dispersant and a binder. Boric acid forms metallic metaborates at sintering temperatures, which help improving the mechanical strength of the membranes.

Sodium Metasilicate: Sodium Metasilicate was used as a primary binder. It binds membrane constituents by forming silicate bonds with other components. It provides the structural strength and compactness of membrane, reducing the average pore size availability.

All chemicals used were obtained from CDH India. Sodium carbonate, calcium carbonate, boric acid & sodium metasilicate all were graded at least 99.5% pure so all were used without any pre-treatment.

3.2 Membrane preparation

The membrane fabrication is similar to brick-kilning in general concept but with required emphasis on important phases through out whole process.

The raw materials were taken according to composition requirements and thoroughly ground using mortar-pestle. For larger batches raw materials were ground in a ball mill for 1 hour. Compositions with amounts of raw material used both in dry basis & wet basis for membrane fabrication is given in table 3.1. The powder was used to make a thick paste by adding small doses of distilled water. It is safe to use distilled water to avoid ionic constituents in local water. The membranes are then cast in a circular ring mould of diameter 55 mm and thickness 5.5 mm, the ring was made out of non corrosive 316 grade steel. The cast discs were then subjected to static load of 2-5 kg for about 12 hours to avoid deformation in shape as the discs dry, followed by open air drying at room temperature. The membrane discs were then heated in a controlled heat muffle furnace.

The membranes were heated to 120^oC in a muffle furnace and kept at this temperature for about 12 hours. After 12 hours heat treatment to evaporate the water, the membranes were then heated to a temperature of 250^oC with step increment in heat rate at $50^oC/hr$. The membranes were kept at 250^oC for about 2 hours. Subsequently the membranes were heated again up to the desired sintering temperature maintaining heating rate of $100^oC/hr$. After desired sintering temperature was reached the membranes were heated for 5 hrs at sintering temperature. Three membrane sets were prepared with sintering temperatures 850^oC, 900^oC, 1000^oC to study the effect of sintering temperature on porosity & pore size.

The membranes were allowed to cool down in the furnace itself without allowing convective heat loss by preventing air from entering in. The membranes were allowed to cool to temperatures ranging $100\text{-}150^oC$. The membranes achieved rigid, hard, porous texture. The membranes were then polished using silicon carbide abrasive paper of grades C-220 and C-100 to remove top layers and obtain a smooth surface. The membranes are subjected to sonication in an ultrasonic bath to remove the loose particles that might have adhered on the surface of membranes during polishing.

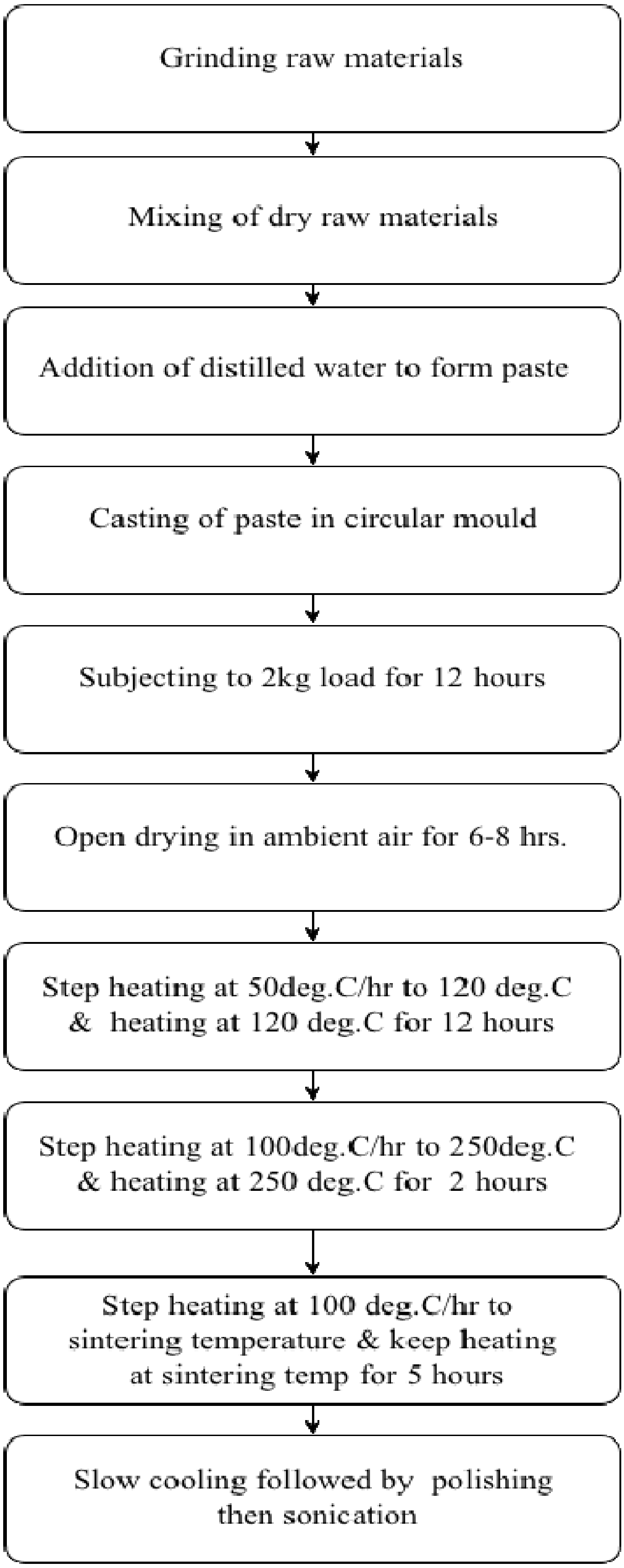

Figure 3.1: Flow chart steps involved in membrane preparation

Table 3.1 Composition of raw material used for membrane fabrication

Material	Comp. A dry (wt%)	Comp. A wet (wt%)	Comp. B dry (wt%)	Comp. B wet (wt%)
Clay	68	54.4	76	60.8
Calcium carbonate	20	16	20	16
Sodium metasilicate	2	1.6	4	3.2
Sodium carbonate	10	8	-	-
Boric acid	-	-	-	-
Water	-	20	-	20

3.3 Characterization techniques

Characterization techniques undertaken are the structural characterization of the membranes by Thermo-Gravimetric Analysis (TGA), X-ray Diffration and morphological surface analysis using Scanning Electron Microscopy (SEM) Imaging, porosity calculation and chemical stability.

- TGA was conducted using (EXSTAR TG/DTA 6300) to study the phenomenon and processes that membrane undergoes by monitoring the weight loss with increase in temperature.
- XRD analysis of membranes was conducted on (D8 Advance, Bruker AXS) diffractometer using Cu K_{α} radiation and wavelength 1.540598 Å to know the final composition of the membrane.
- SEM was carried out using (JSM-7600F) to study the surface morphology and determine the pore size.
- Porosity of the membranes was determined by the pycnometric method using water as wetting liquid.
- Chemical stability of the membrane was tested using corrosion tests, by subjecting membranes to HCl (pH = 2) and NaOH (pH = 13) solution for 8 days.

Chapter 4

RESULTS AND DISCUSSION

4.1 Physical observations

1. The clay used was muddy-pottery clay, reddish brown in color, indicating significant ferric oxides present, with silt-like shining flakes.

2. Difference in color and texture were observed in the membranes after heating, polishing and sonication. The membranes sintered to 900^{o}C, 850^{o}C were brownish red in color, the ones sintered to 1000^{o}C had creamy red surface. The membranes sintered to 850^{o}C was easier to polish using silicon carbide abrasive paper, the surface was smooth and soft. Those sintered to 1000^{o}C had a hard whitish-yellow coating.

4.2 Corrosion test results

The membranes sintered at different temperature were subjected to HCl (pH = 2) and NaOH (pH = 13) solutions for 8 days, and were then dried and weighed to test any weight loss due to chemical activity with acid/base solutions. Initially dry weight of the membranes was measured. Then the membranes were submerged in HCl and NaOH solutions for 8 days. Finally the membranes were taken out, washed with water, dried in hot air blower and weighed again. Table 4.1 and 4.2 show the results obtained for percent weight loss exhibited by membranes sintered at different temperature in acid and base solutions respectively. It can be inferred that for all sintering temperature the membranes showed good stability against both acid & base treatment. The weight loss for all membranes in both acid and base solutions was found to be less than 1%. 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 percent weight loss of the membranes sintered at various temperature when subjected to acid and base solutions respectively.

Table 4.1 Corrosion test (NaOH, pH = 13) results for membranes sintered at different temperatures.

Membrane (sintering temp.°C)	Initial weight (W_i) gm	Final weight (W_f) gm	Weight loss = (W_i - W_f) gm = ΔW	Weight loss (%) = (ΔW/W_i) ×100
A(850)	4.64	4.62	0.02	0.43
B(900)	3.72	3.70	0.02	0.53
B(1000)	4.73	4.72	0.01	0.21

Table 4.2 Corrosion test (HCl, pH = 2) results for membranes sintered at different temperatures.

Membrane (sintering temp.°C)	Initial weight (W_i) gm	Final weight (W_f) gm	Weight loss = (W_i - W_f) gm = ΔW	Weight loss (%) = (ΔW/W_i) ×100
A(850)	6.44	6.40	0.04	0.62
B(900)	3.87	3.85	0.02	0.51
B(1000)	5.23	5.20	0.03	0.57

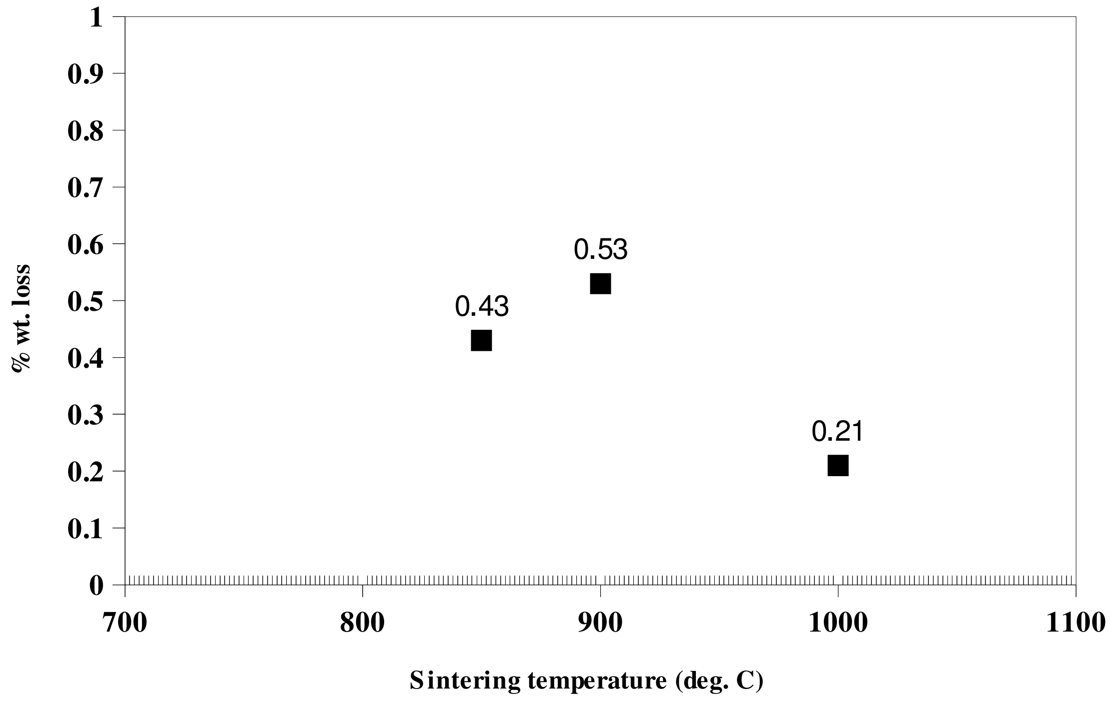

Figure 4.1: Weight loss (%) of membranes sintered at different temperatures after corrosion test (NaOH solution)

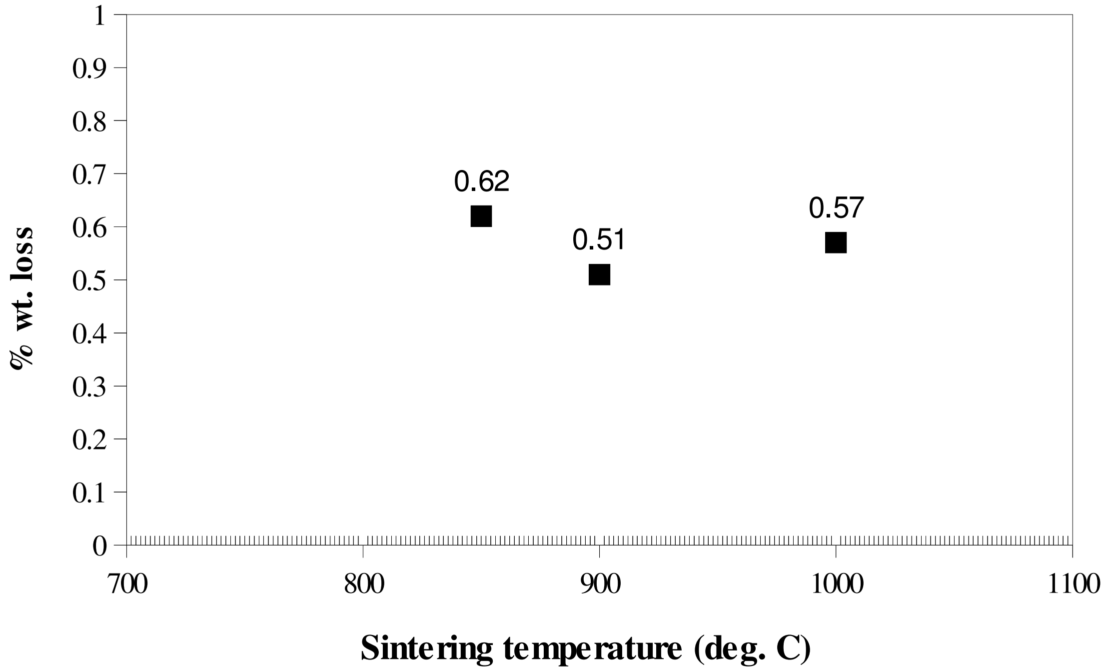

Figure 4.2: Weight loss (%) of membranes sintered at different temperatures after corrosion test (HCl solution)

4.3 Porosity results

The porosity (ε) of the membranes was determined by the pycnometric method using water as wetting liquid. Thickness and diameter of sintered membranes were measured using vernier callipers, which were then used to calculate membrane volume. Initially, the dry weights of membranes were measured, and then the membranes were dipped in water bath and subsequently sonicated for half an hour. The membranes were taken out and immediately wet weights were measured. The difference in weight gives water weight which occupied the pore volume. Using density correlation volume of water was calculated. Since membrane was circular disc, cylinder volume relation was used taking average diameter (d) and thickness (t).

d = average diameter of membrane (cm), t = average thickness of membrane (cm).

Porosity was calculated using the following relation (Eq. (2)):

$$\text{Porosity } (\%) = \frac{\text{Volume of pores}}{\text{Volume of membrane}} \times 100 \qquad (2)$$

Volume of pores is given by weight of water divided by density of water at 30°C = 0.995 g/cc The different steps involved in calculation of porosity are given in table 4.3.

Table 4.3 Diameter, thickness and volume of membranes

Membrane (temp ^oC)	Diameter, d (cm)	Thickness, t (cm)	Volume, V_t (cm^3)
A (850)	5.460	0.545	12.76
A (900)	5.266	0.545	11.87
B (900)	5.440	0.505	11.65
A (1000)	5.365	0.536	12.12
B (1000)	5.236	0.435	9.37

Table 4.4 Calculation of pore volume

Membrane (temp ^oC)	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)
A (850)	16.62	20.81	3.19
A (900)	15.83	19.69	3.86
B (900)	18.30	21.47	3.17
A (1000)	16.47	20.12	3.65
B (1000)	14.31	17.01	2.70

Table 4.5 Calculation of porosity

Membrane (temp ^oC)	Volume total (cm^3) = V_t	Volume pores (cm^3) = V_p	Porosity (%) = $(V_p/V_t) \times 100$
A (850)	12.76	3.19	25.0
A (900)	11.87	3.80	32.5
B (900)	11.65	3.17	27.2
A (1000)	12.12	3.64	30.1
B (1000)	9.37	2.70	28.8

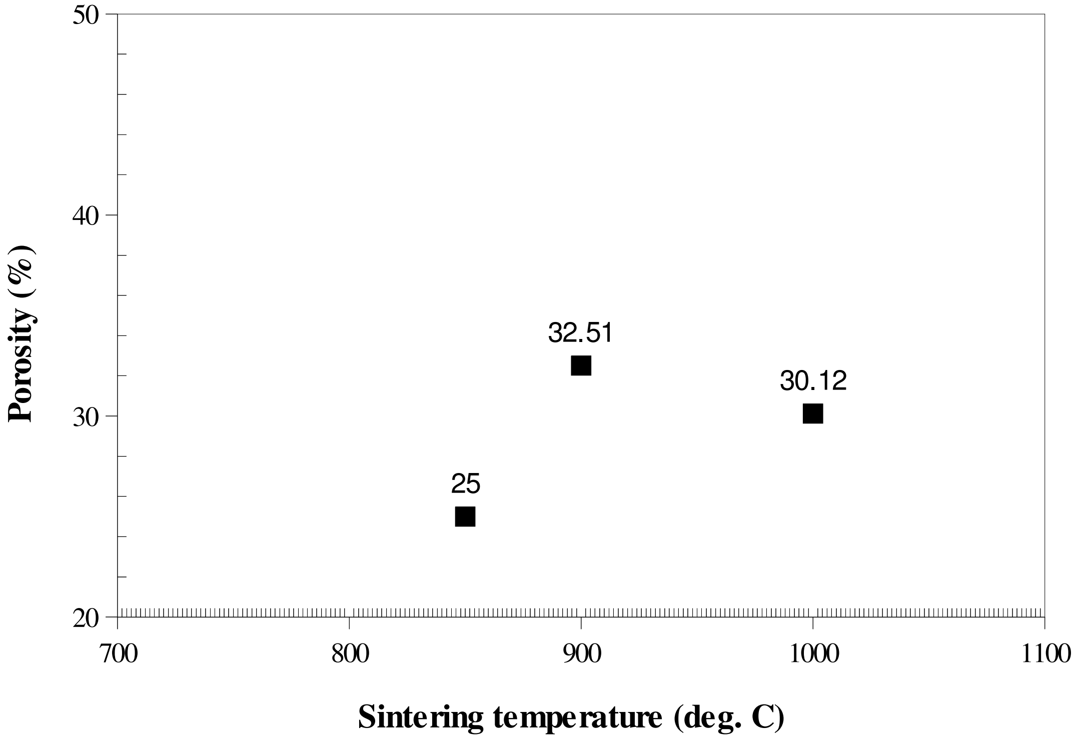

Figure 4.3: Variation of porosity with sintering temperature of composition A membranes

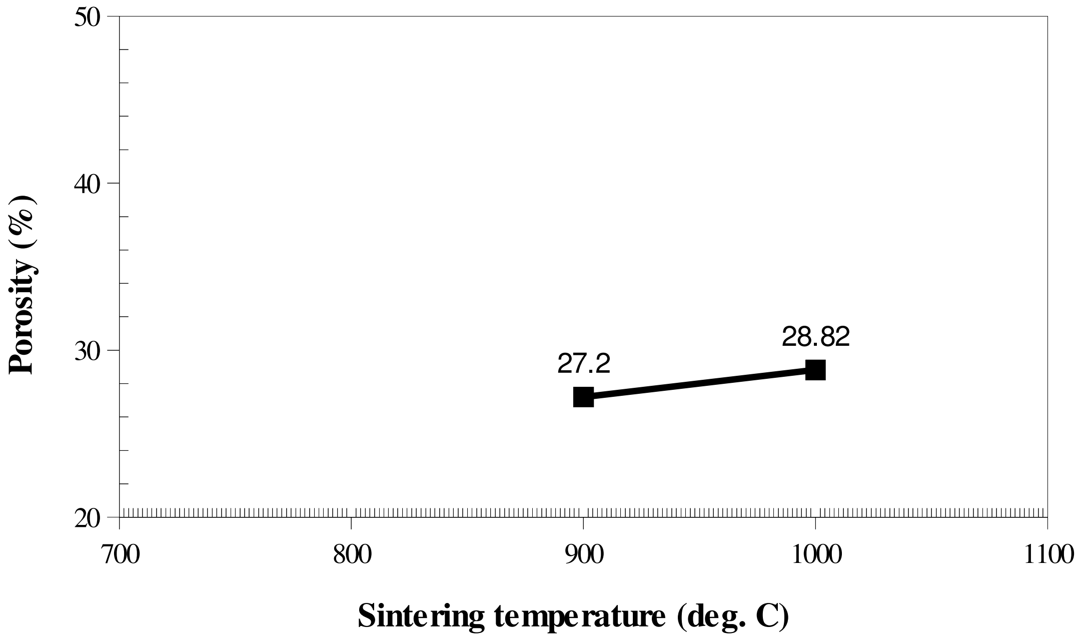

Figure 4.4: Variation of porosity with sintering temperature of composition B membranes

4.4 Thermal and 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 4.6 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.

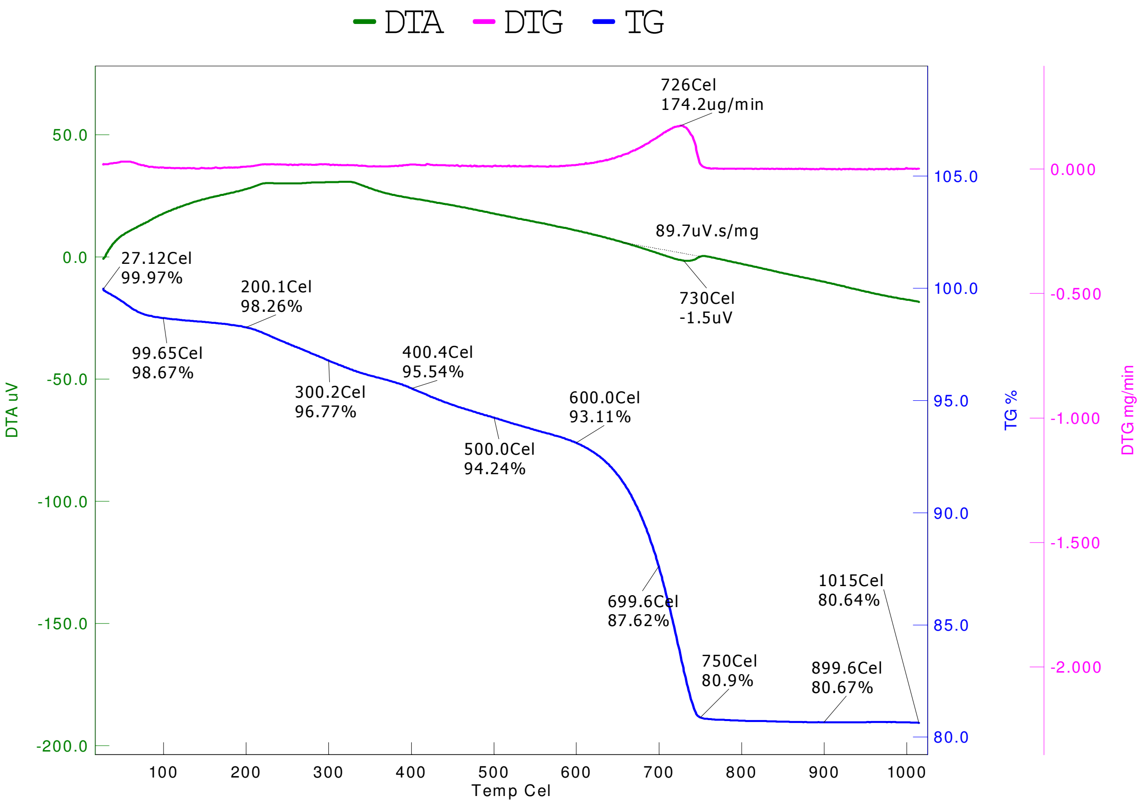

Figure 4.5: TGA curve

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 19.3%. About 1.3% weight loss is observed up to 99 °C due to the removal of weakly bonded surface water molecules in the sample mixture. The weight loss of sample between 100 ^{o}C to 600 ^{o}C was 6.86% which can be attributed to burning of small impurities and unburned mineral carbon and also because of evaporation of hydrated water. In the temperature regime between 600 ^{o}C to 750 ^{o}C maximum weight loss happened about 12%. This is the region where the dissociation of CO_2 from calcium carbonate happens (and hence enhancement of the porous structure of the membrane) occurred due to calcination of $CaCO_3$. Beyond 750 ^{o}C, very insignificant weight loss happened as conveyed by TGA curve so minimum sintering temperature for the membrane fabrication should be above 750 °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 Kα 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 poly-morphs of Kaolinite [$Al_2Si_2O_5(OH)_4$]. Julienite [$Na_2Co(SCN)_4 \cdot 8(H_2O)$], along with Diopside [$CaMgO_6Si_2$] were also found. Apart from these, silicon oxide $-alpha (quartz low) (96-101-1098), iron (III) oxide [Fe_2O_3], aluminium oxide [Al_2O_3], Gehlenite [$Ca_2Al(AlSiO_7)$] were also present. Oxides of magnesium and manganese were also found. Comparison of XRD graphs for four different samples also indicated that continuous phase transformations were taking place during sintering conditions. Similarly other phases were also undergoing transformations and their content also varied during sintering conditions. Figures 4.7 to 4.10 show XRD graphs for four different samples. Three of them sintered at 850 ^{o}C, 900 °C and 1000 °C and one un-sintered membrane. The reference data against which the XRD graphs, profiles and peaks were tested was taken from Crystallography Open Database (COD) for inorganics. Match 2 from CRYSTAL IMPACT (Brandenburg et al., 2013) was used for matching the data to known datasets.

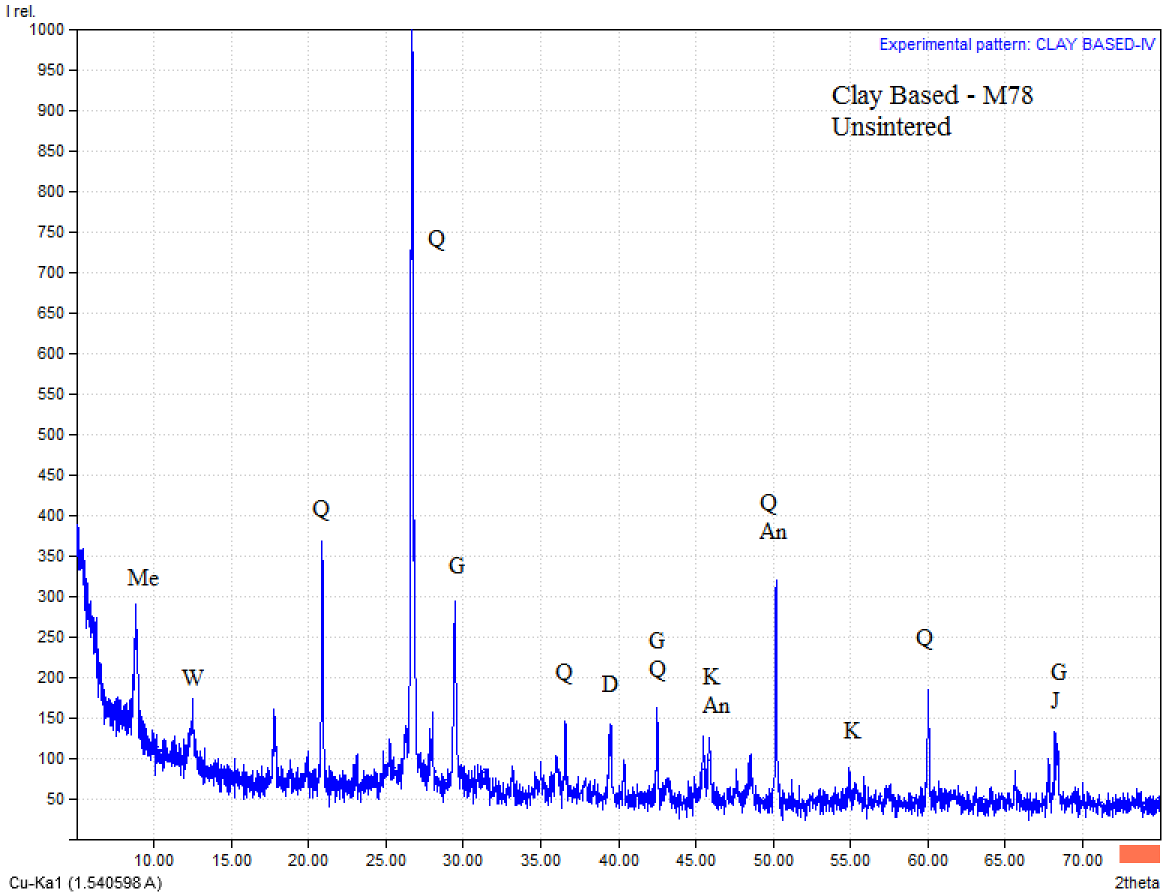

Figure 4.6: XRD graph for un-sintered membrane. An: Anorthite (96-900-0362), D: Diopside (96-101-1048), G: Gehlenite (96-101-1003), J: Julienite, K: Kaolinite, Me: Metavanuralite, Q: Silicon Oxide $-alpha (Quartz low) (96-101-1098), W: Wheatleyite.

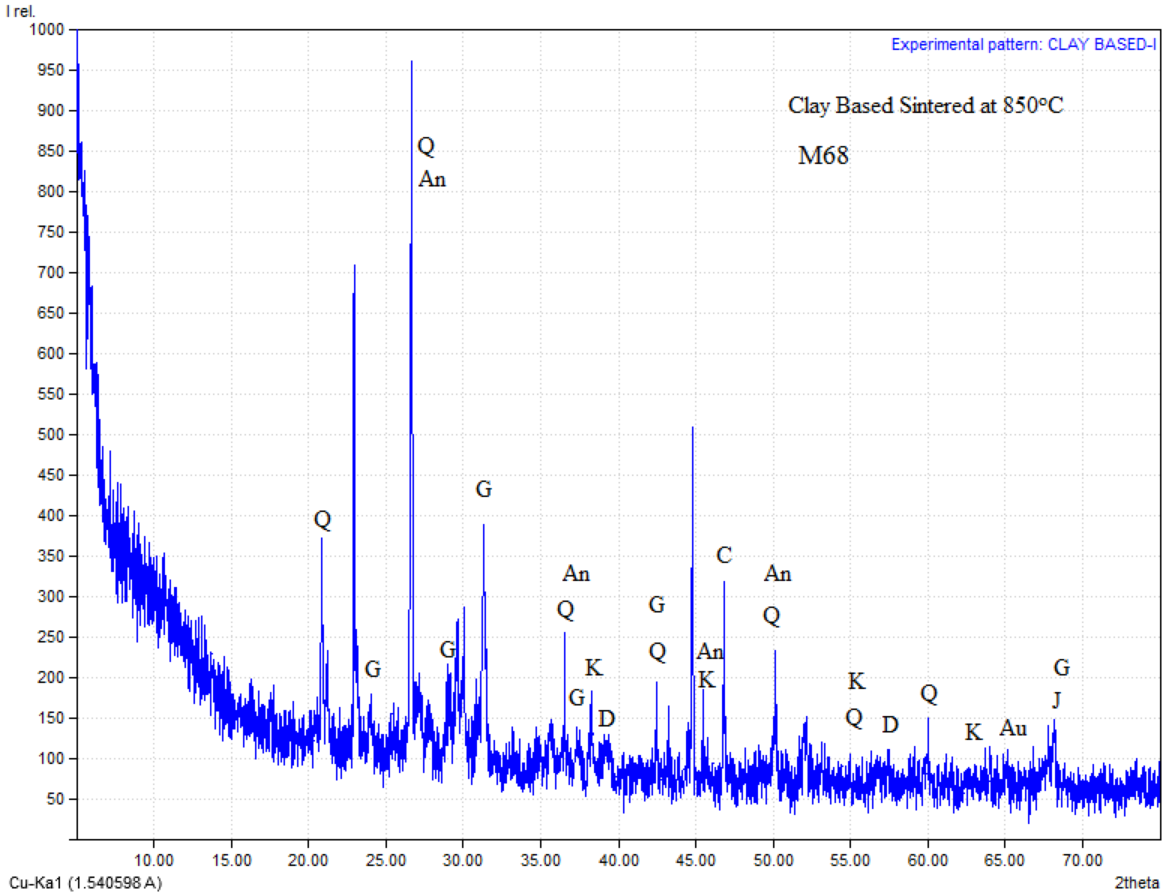

Figure 4.7: XRD graph for membrane sintered at 850 °C An: Anorthite (96-900-0362), D: Diopside (96-101-1048), G: Gehlenite (96-101-1003), J: Julienite, K: Kaolinite, Q: Silicon Oxide $-alpha (Quartz low) (96-101-1098)

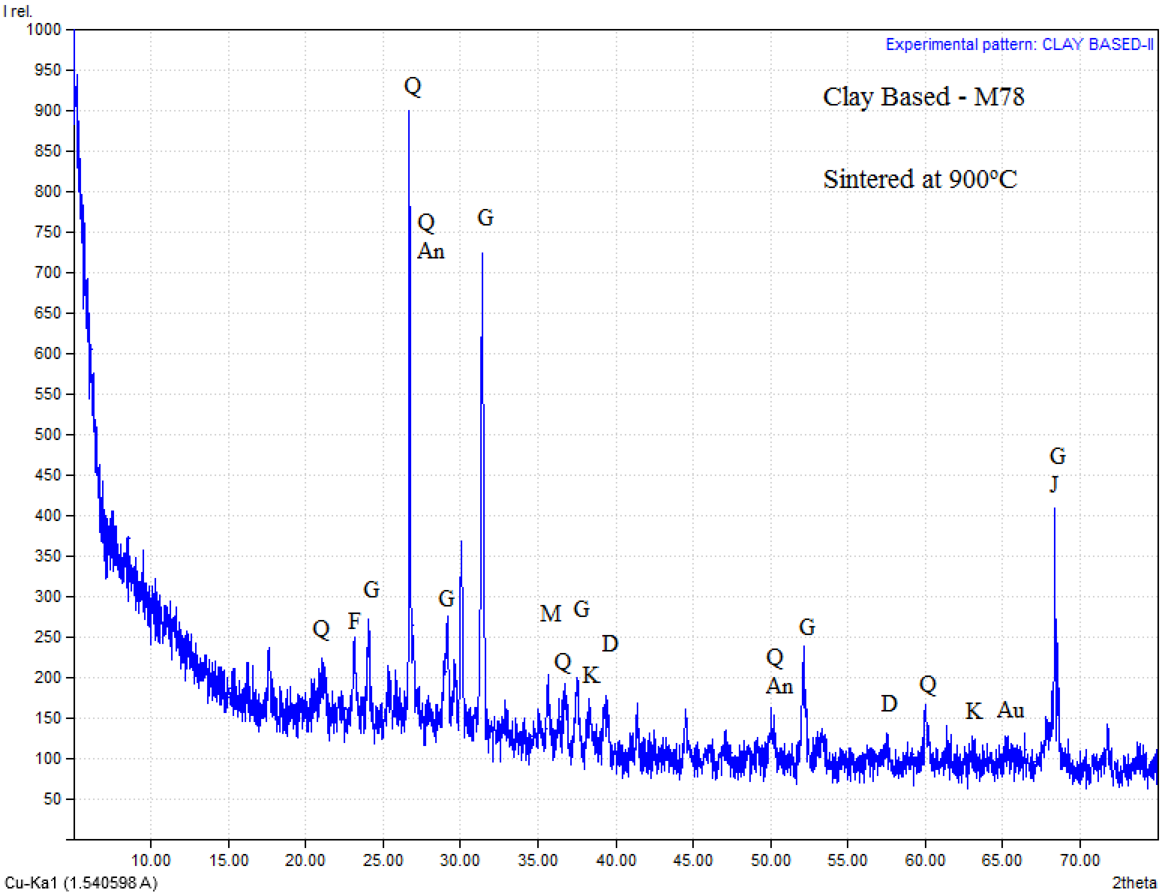

Figure 4.8: XRD graph for membrane sintered at 900 °C An: Anorthite (96-900-0362), Au: Augite, D: Diopside (96-101-1048), G: Gehlenite (96-101-1003), J: Julienite, K: Kaolinite, M: Muscovite, Q: Silicon Oxide \$-alpha (Quartz low) (96-101-1098)

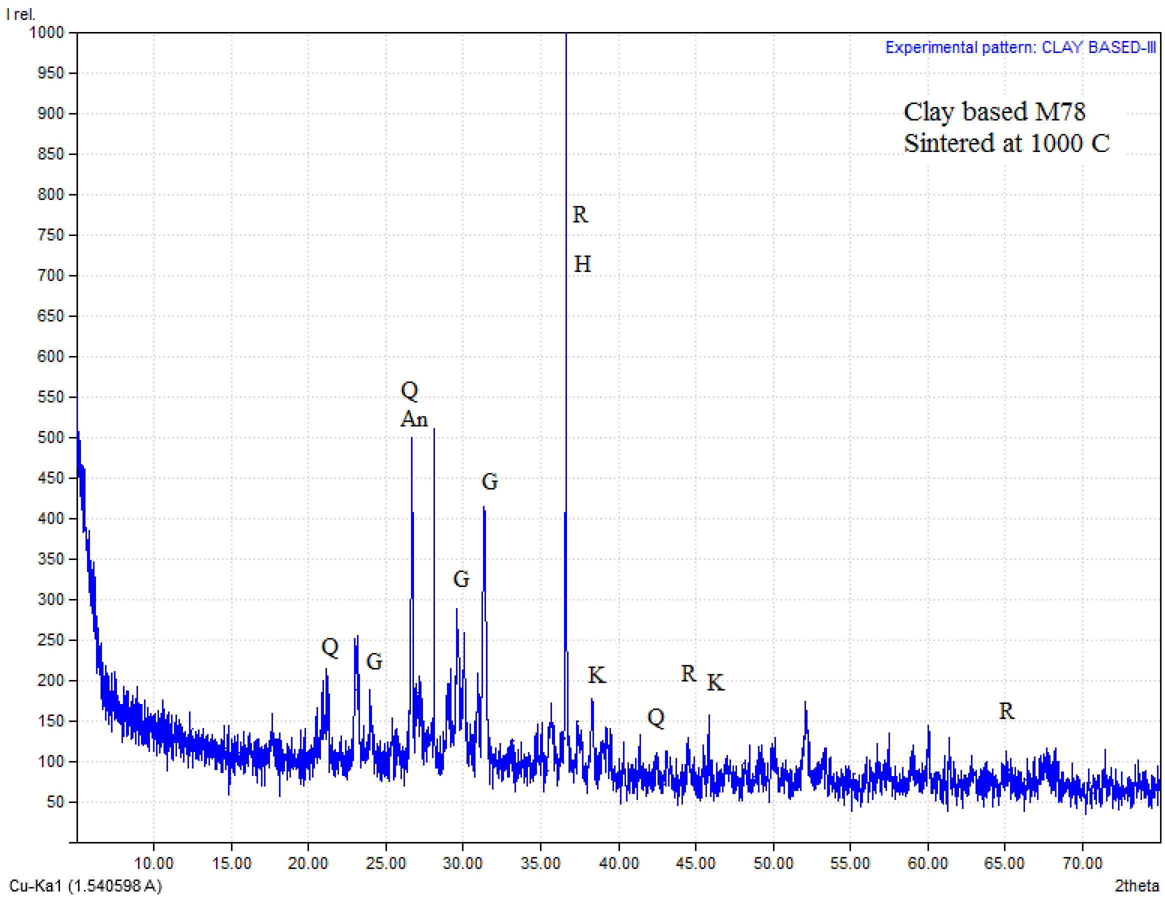

Figure 4.9: XRD graph for membrane sintered at 1000°C An: Anorthite (96-900-0362), G: Gehlenite (96-101-1003), H: Heterosite (96-900-0261) K: Kaolinite, Q: Silicon Oxide $-alpha (Quartz low) (96-101-1098), R: Ringwooodite (96-900-0270)

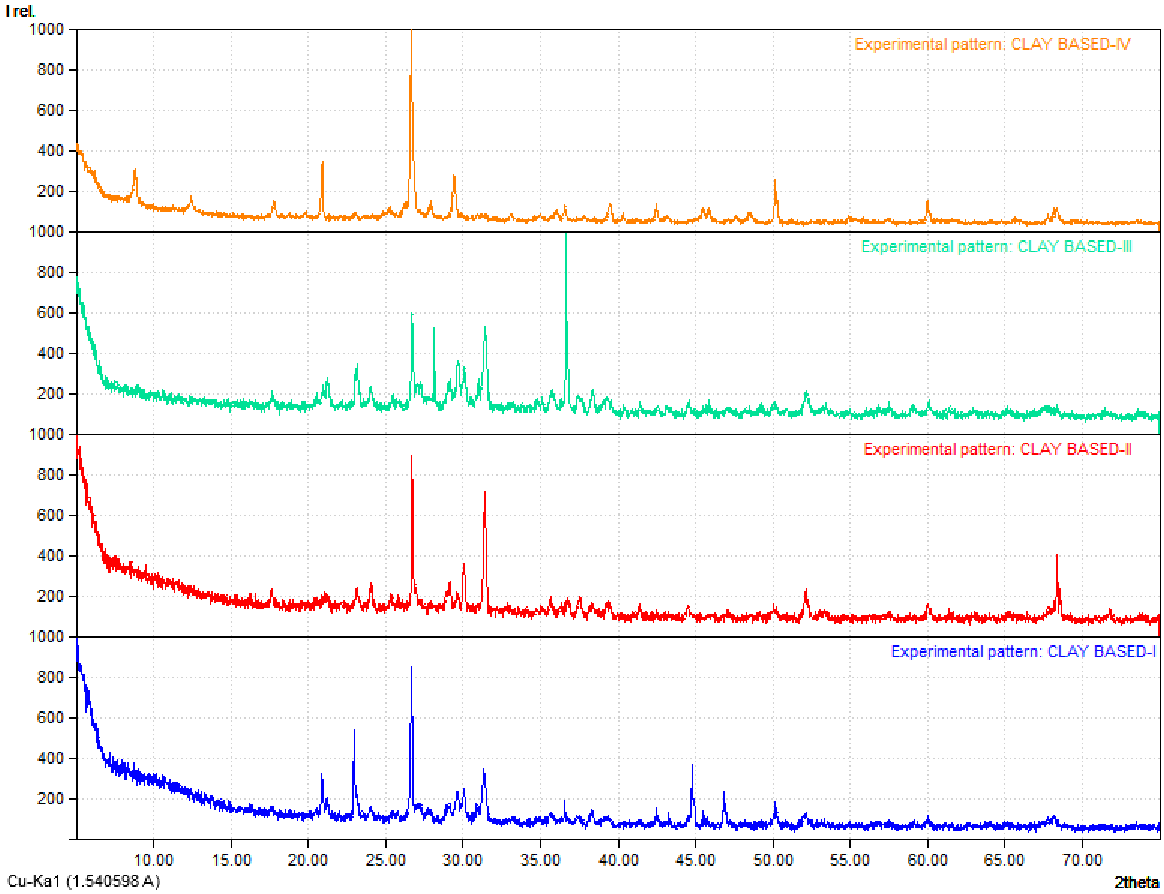

Figure 4.10: Comparative XRD graphs for membranes sintered at 850°C, 900°C, 1000°C and un-sintered membrane shown as Clay based -I, II, III, and Clay based-IV respectively.

4.4.3 Surface morphology

Figures 4.11 to 4.14 illustrate SEM pictures for the membrane sintered at four different temperatures considered in this work. Observation of the SEM pictures indicates 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 °C average pore size decreased with increasing sintering temperature while it increased for membrane sintered at 1000 °C. Table 4.8 shows the variation of average pore size of the membrane with sintering temperature.

Table 4.6 Variation of average pore size of the membrane with sintering temperature

Sintering temperature	Min. pore size (µm)	Max. pore size (µm)	Avg. pore size (µm)
850 °C	0.35	3.86	1.633
900 °C	0.11	4.78	1.290
1000 °C	0.46	2.72	1.189

Figures 4.14, 4.17 and 4.20 present the surface pore size distribution of the membranes sintered at 850°C, 900°C and 1000°C respectively.

For the membranes sintered at 850°C, about 25% pores are lying between 0 and 0.5µm (diameter) while another 52% pores are lying between 0.5 and 1.0 µm. Some 7% pores lie within 1.0 to 2.0 µm. So, about 78% of the pores have diameters in the range of 0 – 2.0 µm.

For the membranes sintered at 900°C, about 40% pores are lying between 0 and 0.5 µm diameter while another 28% pores are lying between 0.5 and 1.0 µm. About 8% lie within 1.0 to 2.0 µm. Therefore, 78% of the pores have diameters in the range of 0.0 – 2.0 µm.

For the membranes sintered at 1000°C, pores are widely distributed and about 48% pores are lying between 0 and 1 µm diameter. And 18% between 1 and 2 µm, a total of 66% pores lie within 0 and 2.0 µm.

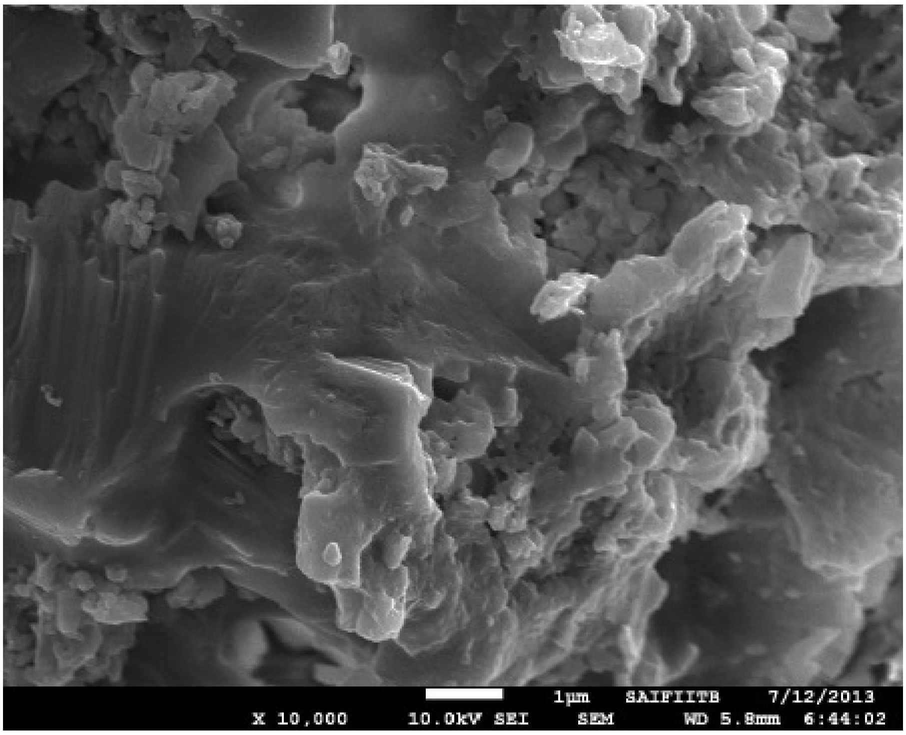

Figure 4.11: SEM picture of membrane sintered at 850 °C

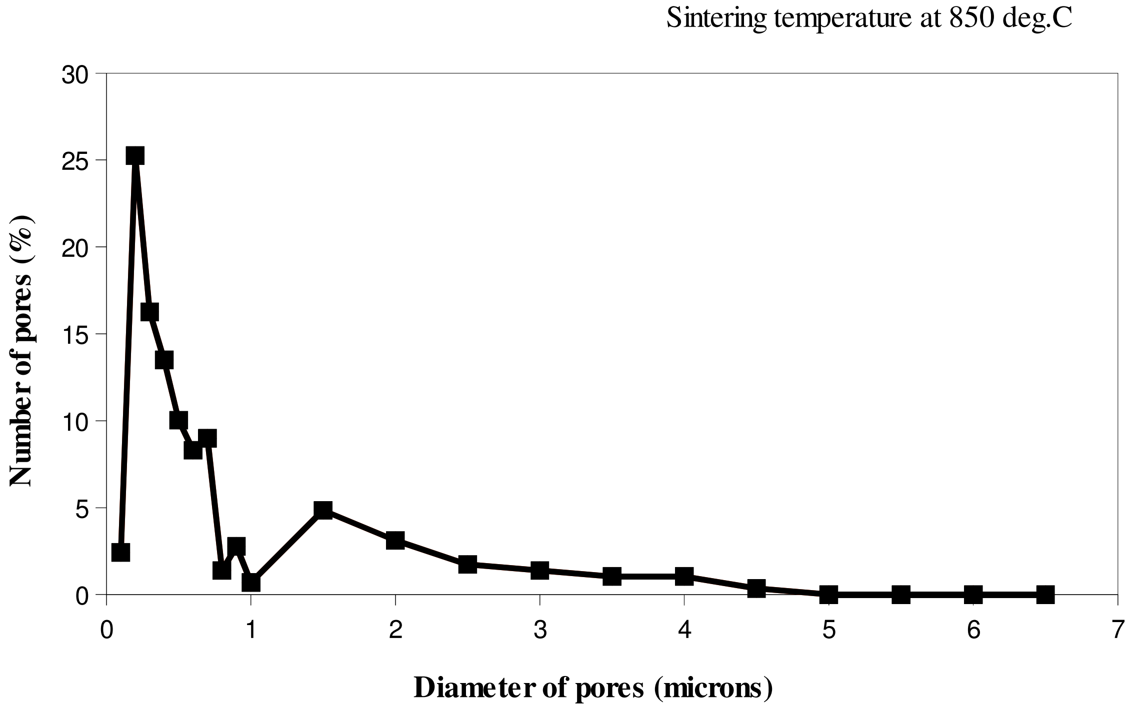

Figure 4.12: Surface pore size distribution of membrane sintered at 850 ^{o}C

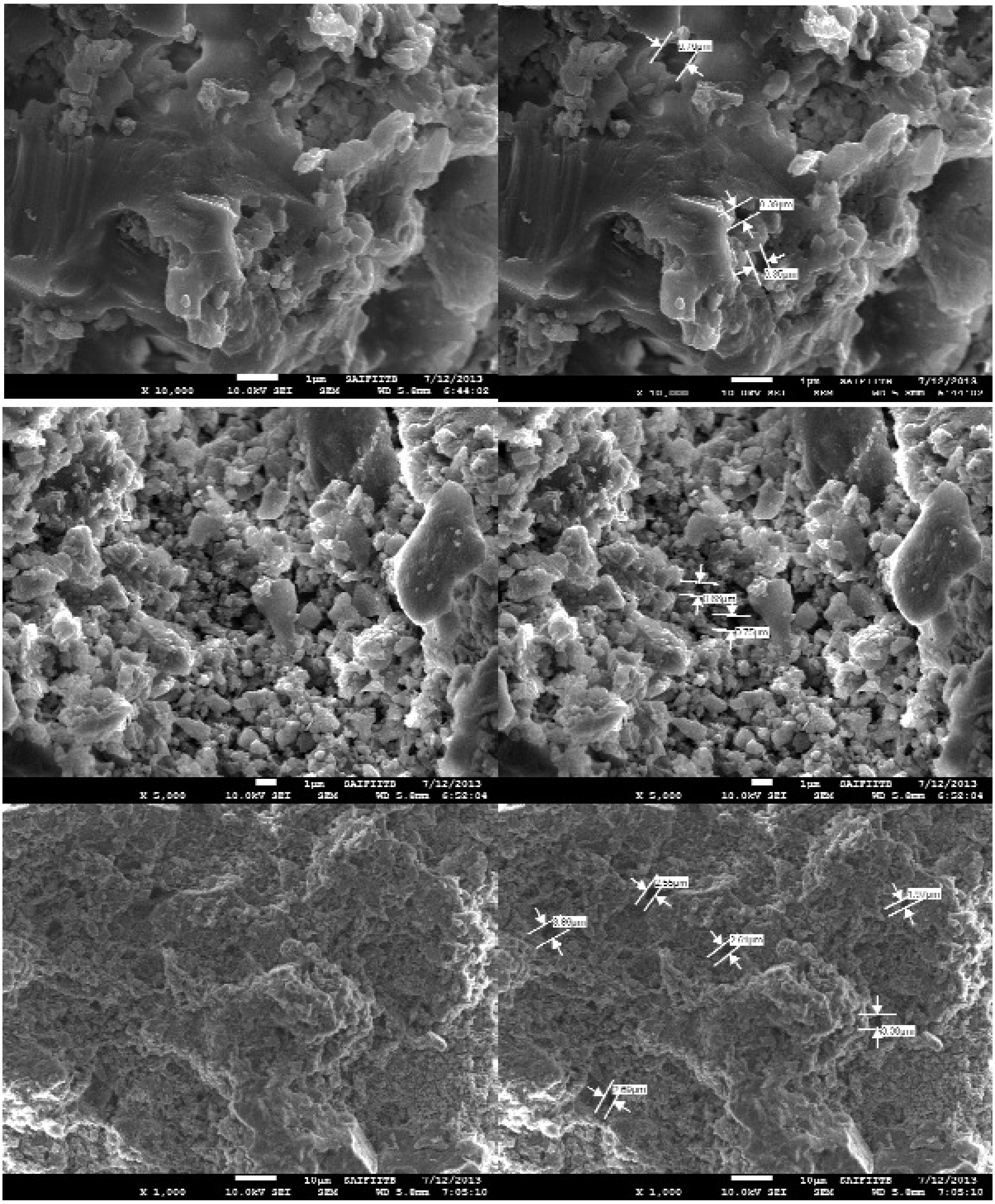

Fig 4.13: Pore sizes comparison of composition A sintered to 850^{o}C at 10kx, 5kx, 1kx magnification levels.

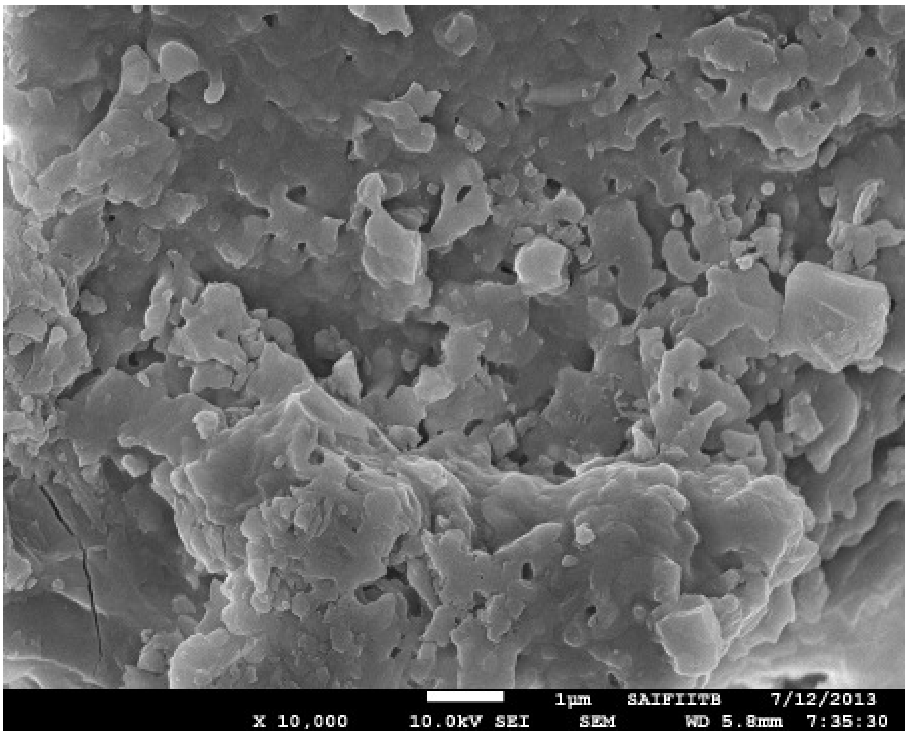

Figure 4.14: SEM picture of membrane sintered at 900 °C

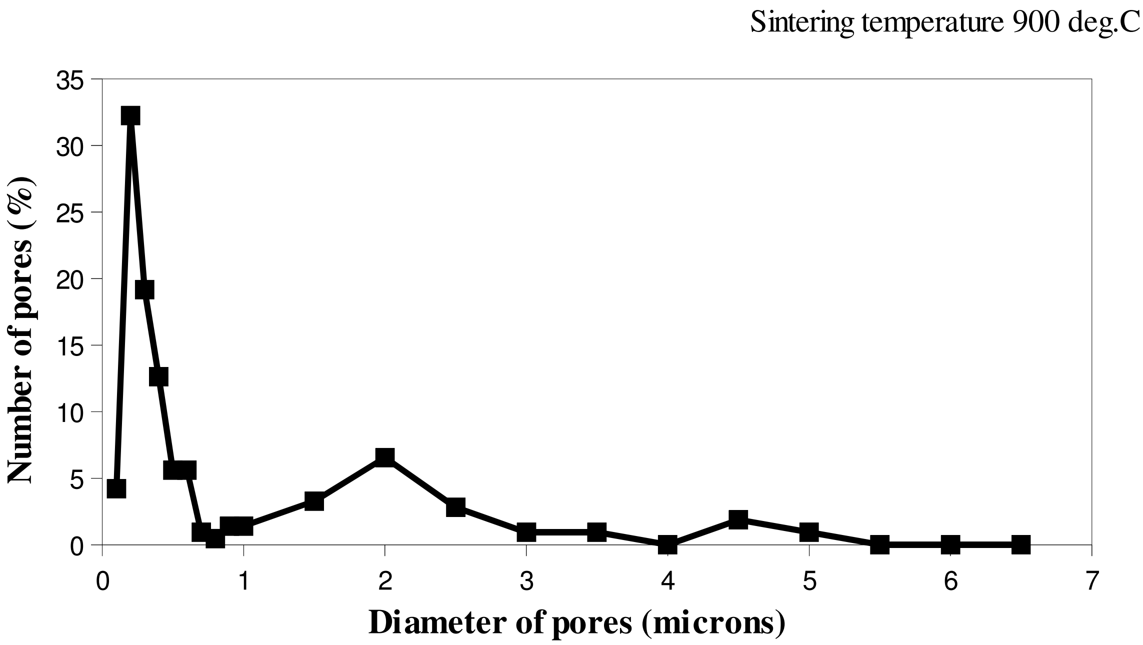

Figure 4.15: Surface pore size distribution of membrane sintered at 900 °C

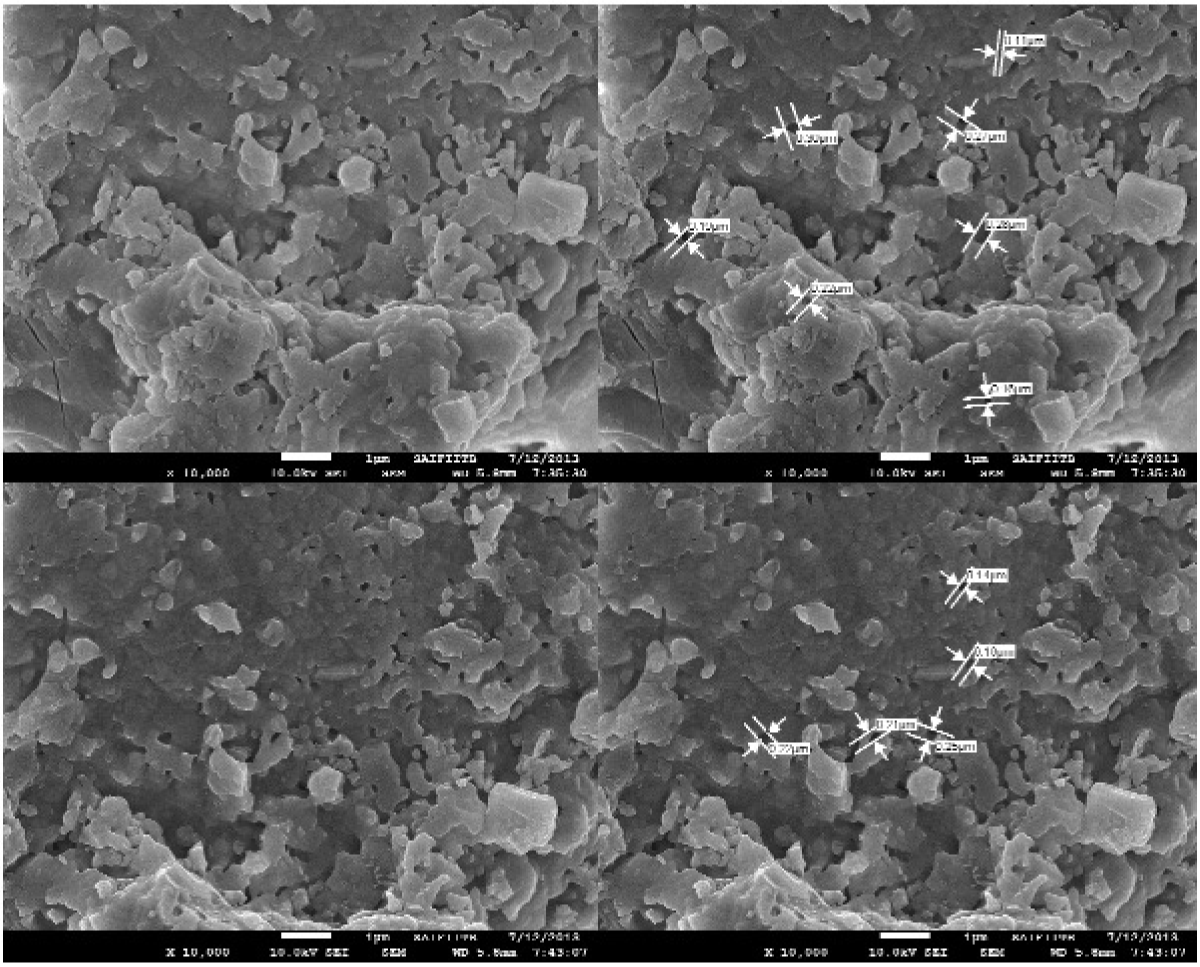

Fig 4.16: Pore sizes comparison of B sintered to 900^{o}C at 10kx magnification levels.

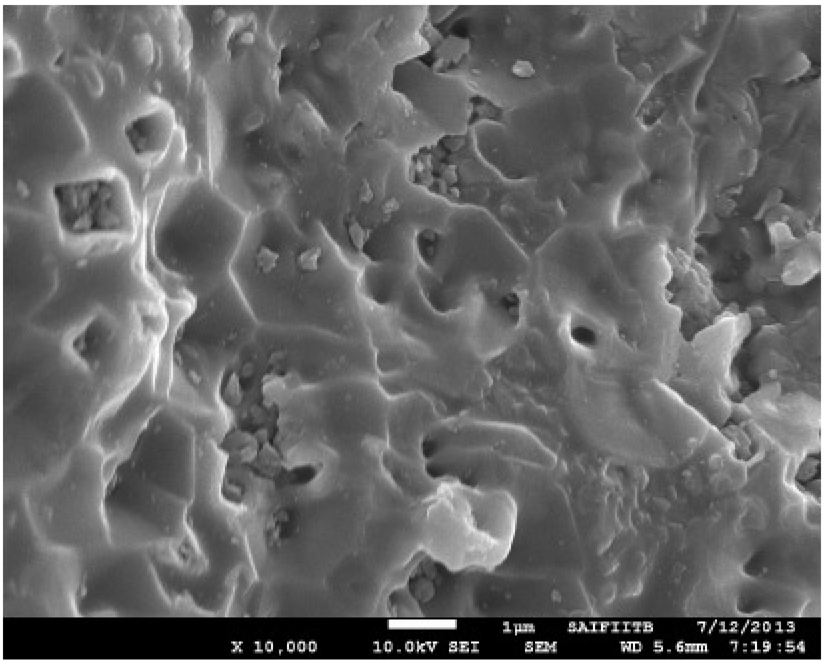

Figure 4.17: SEM picture of membrane sintered at 1000^{o}C

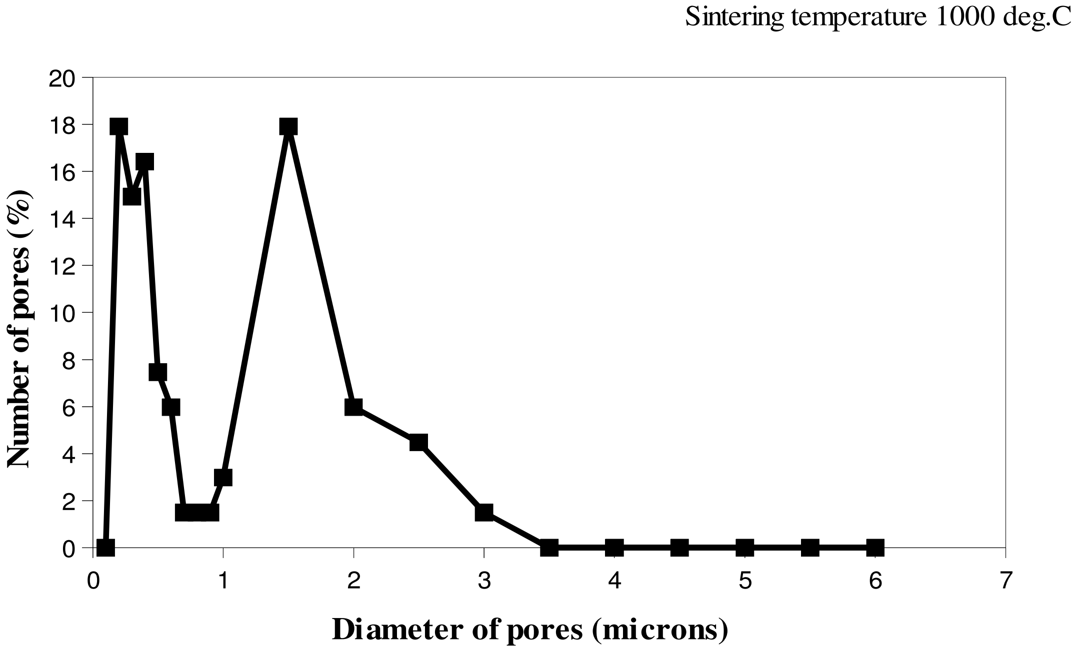

Figure 4.18 : Surface pore size distribution of membrane sintered at 1000°C

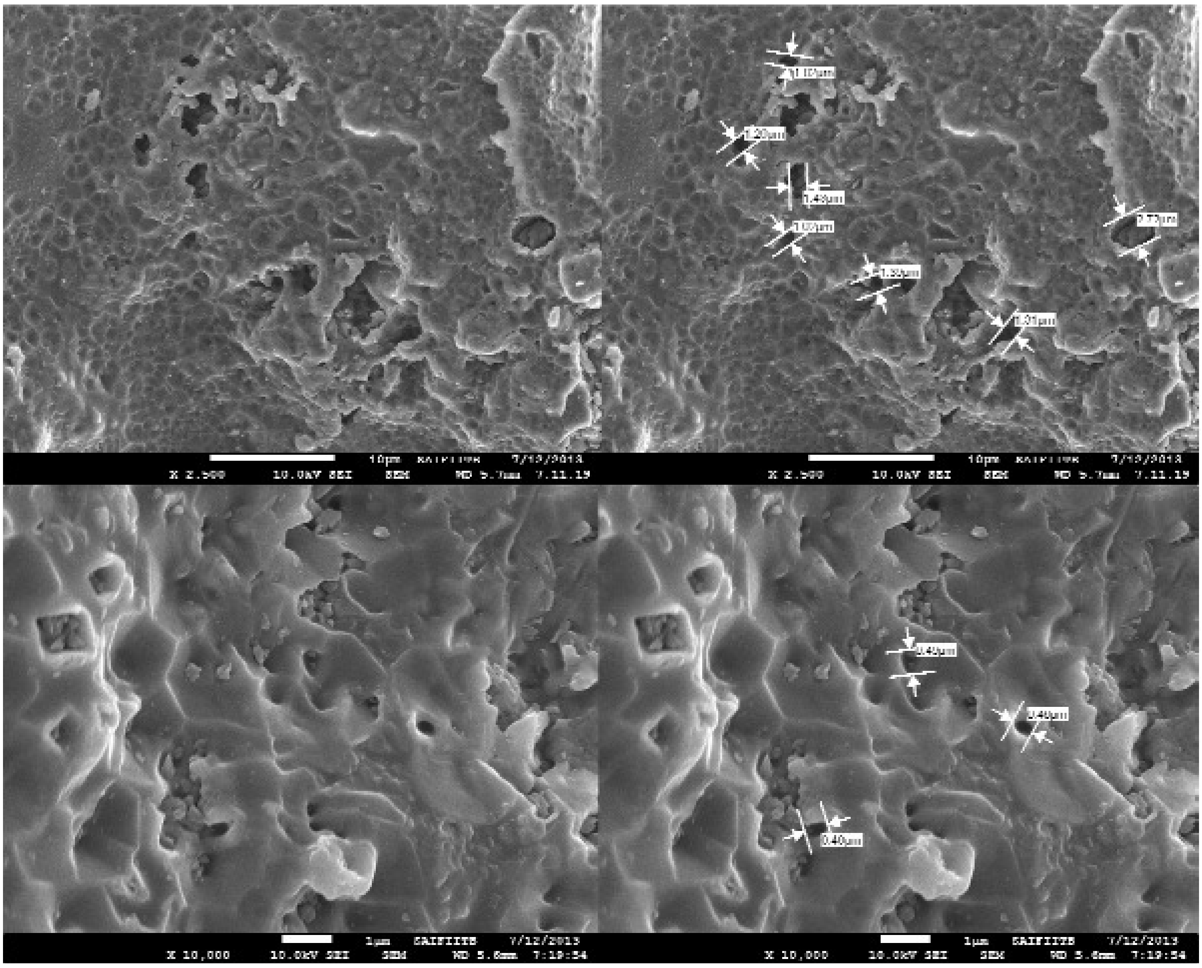

Fig 4.19: Pore sizes comparison of B sintered to 1000°C at 2.5kx, 10kx, magnification levels.

Chapter 5

CONCLUSIONS & FUTURE WORK

5.1 Conclusions

This study indicates that a micro-filtration range ceramic clay based membranes can be fabricated along with inorganic constituents such as calcium carbonate, sodium carbonate. Based on the XRD and TGA analysis it can be inferred that the sintering temperature of membrane should be above 750 ^{o}C. However for better, lower pore size distribution, sintering at 900 ^{o}C temperature is advisable. The membranes fabricated at three different sintering temperature showed porosity in the range 25 to 32% which is considered as moderately good. The average pore size of the sintered membranes varied in the range 1.29 to 1.63 μm. The fabricated membranes showed excellent chemical resistance exhibiting less than 1% weight loss against both acid and base solutions.

5.2 Future work

This work deals with preparation and characterization of ceramic micro-filtration membranes based on pottery clay. In this study, effect of sintering temperature on membrane characteristics has been studied. However, there is lot of areas this work can be improved. Following areas can be worked upon:

- Effect of per gram porosity agent in the membrane composition on the porosity of fabricated membranes can be studied.
- The effect of dispersant's amount per unit weight on pore distribution throughout the membrane can be studied.
- Effect of thickness on the porosity and its possible relation with heat rate, and temperature in general.
- The membranes can be prepared for ultra-filtration range using polymer coating.
- Effect of sintering duration on the overall pore size can be studied.

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