# Fabrication and characterization of micro-porous ceramic membrane based on kaolin and alumina

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Kaolin and α-alumina powders are used to synthesise microporous ceramics using starch as an organic pore-former, and phosphoric acid as an inorganic binder. This work has been carried out to further develop microporous ceramic materials based on alumina-kaolin for filtration purposes. The membranes are characterized using SEM, XRD, permeability, porosity, density, average pore size, chemical stability, shrinkage, and solvent permeation. The ceramics sintered at 1200°C, after being compacted at 14.7 MPa, exhibit porosity of about 32.2±3%. These ceramics show reasonably good permeability as well as mechanical strength. The average pore sizes of these supports found to be approximately between 0.5–1.5 μm and are hydrophilic in nature.

**Keywords:** Alumina, Ceramic membrane, Kaolin, Microporous, Phosphoric acid

The membranes manufactured for microfiltration (MF) and ultrafiltration (UF) can be composites, symmetric or asymmetric fabricated from polymeric or inorganic materials. They are manufactured with various geometric configurations: tubular, flat, monolithic, etc. Ceramic membranes can be fabricated by classical techniques using powdered compaction and/or using sol-gel technique using hydrated oxide salts as precursors (colloidal suspension route) or by employing alkoxides (polymeric gel route)[1].
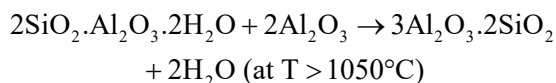
Membranes made of inorganic precursors have better chemical and temperature stability compared to polymeric-based membranes, making them a promising candidate in industries[2]. A great deal of research is being conducted in developing new types of composite inorganic membranes including α- and γ-$Al_2O_3$[3-5], zeolite[6,7], carbon[8-10], kaolin, and dense metals[11,12]. Porous ceramic supports have been fabricated from a variety of materials, viz., carbon[13], glass[14], kaolin, and alumina-based ceramics[15]. Various methods such as slip casting, extrusion, dry pressing, tape casting, and gel casting have been reported for making supports followed by sintering[16]. Aluminosilicate porous ceramics fabricated from partially sintered, dry-pressed powder compacts are excellent candidates for membrane supports from the standpoint of raw material cost, simple processing, chemical stability, and excellent mechanical properties[15-17].
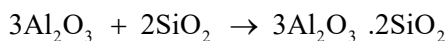
Inorganic membranes are gaining importance due to their endurance to high temperature, strong acids and alkalis, as well as corrosive systems[17-20]. Amongst all kinds of inorganic membranes, either $Al_2O_3$- or kaolin-based membranes are widely used as support for their stability and raw material availability[21-23].

Aksay and Pask[24] have reported the equilibria in $Al_2O_3$–$SiO_2$ system, and indicated that after sintering at high temperature, mullite became the only stable compound. Moreover, mullites grown by a solid state reaction was of 3:2 type ($3Al_2O_3 \cdot 2SiO_2$), and that formed in the liquid phase by exsolution was of 2:1 type ($2Al_2O_3 \cdot SiO_2$). Kaolin is the most popular raw material for aluminosilicate-based ceramics due to its easy availability and occurrence in nature[25,26]. In addition, kaolin undergoes some desirable reactions during the sintering process (Scheme 1).

A few papers have reported the effects of $SiO_2$ and kaolin on $Al_2O_3$ hollow fibre membrane properties, like mechanical strength and pore size distribution. Therefore, it was thought desirable to study the reaction of $Al_2O_3$ and $SiO_2$ as well as $Al_2O_3$ and kaolin, in ceramic field, to make further improvements. The reactions are as follows:

$$2SiO_2.Al_2O_3.2H_2O + 2Al_2O_3 \rightarrow 3Al_2O_3.2SiO_2$$
$$+ 2H_2O \text{ (at } T > 1050°C)$$

mullite

$$3Al_2O_3 + 2SiO_2 \rightarrow 3Al_2O_3.2SiO_2$$

mullite

Scheme —1

The current work has incorporated the above reaction scheme in the preparation of $Al_2O_3$-kaolin-based ceramic membranes.

The alumina–silicate structures are produced by sintering powdered compacts of α-alumina and kaolin (clay mineral composed of kaolinite ($Al_2O_3.2SiO_2.2H_2O$), small amounts of silica, and minor impurities). Such compositions are definitely advantageous because they are produced from relatively inexpensive materials and processed at comparatively lower temperatures (< 1300°C) as compared to formulations based on pure alumina[27].

α-Alumina-kaolin powder mixture undergoes several physical and chemical changes during sintering. The kaolinite phase undergoes initial dehydroxylation above ~500°C. Later, an intermediate metakaolin phase is formed at ~ 1000°C, in which silica is rejected from the structure. Gradual further increase in temperature causes the structure to transform into an aluminosilicate spinel phase, and finally to mullite ($3Al_2O_3 \cdot 2SiO_2$) at ~1250°C and above[28]. Free silica can react with α-alumina and other impurities to form a liquid phase, which further promotes sintering and eventually form the mullite phase. Past research has shown grain growth and pore coarsening commonly occurring along with the formation of a mullite phase in kaolin as well as kaolin-alumina mixtures[29,30]. The mullite phase has an effect on densification and grain growth; the reactions involved have an effect on the pore size and shape, as well as membrane strength.

The raw materials used in this work for the fabrication of inorganic support membranes have specific and distinct functional attributes. Kaolin provides plasticity and high refractory properties to the membrane[31,32]. Regulation of porous texture is realized by starch, which under sintering conditions would dissociate and release $CO_2$[33]. The path followed by the released $CO_2$, thereby renders porous texture to the membrane, and thus contributes to the porosity during sintering. On the other hand, phosphoric acid acts as a binder that increases the mechanical strength.

Although the binder constitutes a small amount, 7 wt.%, in the entire mass, it is critical to the mechanical property and permeability of the membrane so formed[34]. For these reasons, acid phosphate and phosphoric acid binders are commonly used in the refractory industries. The reactivity of several aluminas with orthophosphoric acid has been studied and been shown to be effective for bonding castables comprised of aluminium oxide. The reactivity of calcined aluminas with orthophosphoric acid has been studied. These studies proved the presence of $AlPO_4$ phase (meta phase) and $Al(PO_3)$ (ortho phase), both of which are effective bonding phases. Phosphoric acid was shown to be effective for bonding refracting supports of calcined $Al_2O_3$. These supports have high bond strength and excellent corrosion resistance over a wide temperature range[35,36].

The current study deals with fabrication of alumina-kaolin-based membrane using an inorganic binder orthophosphoric acid and an organic pore former, potato-starch.

## Experimental Section
### Materials
The raw materials were α-alumina (Sigma Aldrich, India), kaolin (extra pure), orthophosphoric acid (Thomas Baker Chemicals Pvt. Ltd., India), and potato-starch (SD Fine Chemicals Pvt. Ltd., India).

### Methodology
Ceramics of flat configuration were prepared by dry compaction method using kaolin, α-alumina, potato-starch, and phosphoric acid in its composition. α-alumina, kaolin, and starch were dry-mixed initially. Binder mixture of orthophosphoric acid and distilled water was added to this dry mix and mixed thoroughly to form a homogeneous paste. The percentage weight compositions of the paste are as given in Table 1. The paste was kept for ~36 h for maturation, under ambient conditions (~30°C). During maturation of the paste,

Table 1 — Percentage and individual weight compositions of sample pastes

| Components | Wt % (dry) | Actual Wt. | Wt % (wet) | Actual Wt. |
|---|---|---|---|---|
| Kaolin | 50 | 25 | 38.46 | 25 |
| α- Alumina | 38 | 19 | 29.23 | 19 |
| Phosphoric acid | 7 | 3.5 | 5.38 | 3.5 |
| Potato starch | 5 | 2.5 | 3.84 | 2.5 |
| Water | – | – | 23.07 | 15 |
| Sample Wt. | | **50** | | **65** |

some amount of the total water content got evaporated. The remaining water was removed by heating it in an oven at 110°C. This dry mass was cooled to room temperature and then grinded to fine powder in a ceramic mortar pestle.

The resulting powder was sieved using 50 mesh screen. Requisite amount of powder was put in a die unit (similar to those used in making IR pellets). This die unit was then placed in a hydraulic press machine for compaction under 14.7 MPa, designed for single ended compaction. After the press, circular pallets (or discs) were removed carefully from the die unit, whose dimensions were 48.5 mm diameter and 3.5 mm thickness. These ceramic discs were later placed in a programmable muffle furnace and sintered at temperatures viz., 1200 and 1300°C for 3 h, starting from 100°C giving a ramp of 2°C/min throughout. The heating rate was programmable whereas the cooling was natural.

After cooling, the fired ceramic was polished with silicon carbide abrasive paper so as to give it an even surface. The final dimensions of these circular discs were 47 mm in diameter and 3 mm in thickness. The discs were washed with distilled water in an ultrasonic bath to remove the loose particles, if any.

**Membrane characterization**

*Membrane density and porosity measurement*

The ceramic disc was immersed in deionised water for 24 h. Excess water was wiped with tissue paper. The wet membrane was weighed. Thereafter, membrane was vacuum dried in an oven at 100°C for 5 h. After drying, the membrane was weighed again. Membrane density was calculated as per [Eq. (1)].

$$\rho = \frac{m_{dry}}{V} = \frac{m_{dry}}{\frac{\pi}{4}.d^2 l} \qquad \ldots (1)$$

where, $\rho$ is defined as density (g/m$^3$), $m_{dry}$ as weight of dry ceramic disc (g), d diameter of the sintered disc and *l* thickness of disc.

Membrane porosity, $\varepsilon$ (%) has been defined as the volume of the pores over the total volume of the porous ceramic disc. It usually is determined by gravimetric method, considering the weight of liquid water contained in the membrane pores, and is shown in its equation Eq. (2).

$$\varepsilon = \frac{\Delta m}{V.H_2O} \times 100 = \frac{m_{wet} - m_{dry}}{\frac{\pi}{4}.d^2 l} \qquad \ldots (2)$$

*Pore size and Hydraulic permeability calculation*

The permeation experiments (pure water flux as well as solvent flux tests) were carried out in a standard dead-end filtration setup. Pore size and hydraulic permeability calculations, r and $L_h$, were evaluated from the slopes of the water-flow through the membranes versus pressure graph, in accordance with the Hagen-Poiseuille equation mentioned [Eq. (3)]:

$$J = \frac{n - .\pi r^4 \Delta P}{8 \mu l} = L_h \Delta P \qquad \ldots (3)$$

*Chemical stability test*

Chemical stability test of alumina-kaolin support was tested by noting the mass loss after keeping it separately in the acidic (*p*H 3) and alkaline solutions (*p*H 9). The synthesised supports were placed separately in HCl and NaOH media (3 days). At the end of each day, the supports were taken out from the solution (acid and alkali), washed with DI water, patted with tissue paper to partially dry the support, and finally dried in an oven at 100°C for about an hour. From the difference in the weight (before and after), the chemical stability was determined, i.e. if there was weight loss, the samples were considered unstable.

*Shrinkage*

The shrinkage of the discs was evaluated by noting the differences in the membrane diameters, before and after sintering. Membrane diameters were also studied by varying the sintering temperature.

*Solvent permeation study*

The solvent permeation was studied using solvents listed in Table 3. Both polar and non-polar solvents were used. Methanol, acetone, benzene, hexane, and water were the solvents used. The synthesized membrane was flushed with the solvent under study, so as to remove previously used solvent. The solvent flux was determined at 3 bar pressure. The hydraulic and solvent permeability of the ceramic membrane was evaluated using linear regression of the flux versus applied pressure. All the experiments were conducted for at least three different membrane samples prepared, and general membrane performance and characteristics were evaluated.

*SEM and XRD study*

Fired ceramic was investigated by XRD (Bruke D8, advanced X-ray diffraction measurement system) and SEM (Leo 1430 vp) to study the phase changes during sintering and to determine surface porosity. SEM images from different sections of the membrane (and in different magnification) were studied.

## Results and Discussion

### Membrane density and porosity measurement

Membrane density was calculated for all the sample ceramics post sintering by using Eq. (1). The density of ceramic discs sintered at 1200°C varied between 658.4 kg/m$^3$ to 705.6 kg/m$^3$ and between 520.2-586.5 kg/m$^3$ for those sintered at 1300°C.

Membrane porosity was calculated using Eq. (2). The porosity values of discs sintered at 1200°C varied between 32 to 35% consistently and those sintered at 1300°C showed porosity above 40%.

### Pore size and Hydraulic permeability calculation

The PWF depends on the porous nature of the membranes. A better PWF will be obtained in a porous membrane structure, while a denser structure would provide a controlled PWF. The permeation studies were carried out in a dead-end filtration setup. The results of permeation property tested by pure water flux (PWF) experiment, at different trans-membrane pressures, as shown in the Table 2 (for ceramics sintered at 1200°C). Effective membrane area was calculated to be $1.261 \times 10^{-3}$ m$^2$. The flux experiments were carried out till 450 kPa beyond which the discs developed cracks. This was observed consistently and hence can be concluded that these ceramic discs are functional till 450 kPa which means they are mechanically strong up to 450 kPa. Based on the PWF values (Table 2), Fig. 1 was plotted. Figure 1 is a plot showing flux versus pressure, which was used for calculation of the average pore size (r) of the sintered membrane. Since the graph shown in Fig. 1 satisfies Eq. (3), slope can be represented as SLOPE = $r^2/(8\mu L)$, where r was calculated to be ~ 1.5 μm. This is a theoretically calculated value of the average pore size. For other

ceramic membrane trials as well similar r values were calculated. Average pore size values ranged between 0.5-1.5 μm.

Similar pore-size calculation was carried out for ceramic discs sintered at 1300°C and ranged anywhere between 4-10 μm. In the PWF experiments carried out using these ceramics, there was no controlled flow rate and also no consistency was observed. No visible cracks were observed for these membrane discs till 650 kPa. Micro cracks were observed as pressure was increased beyond 650 kPa.

It can hence be stated though ceramics of 1300°C are mechanically stronger than those of 1200°C, they show inconsistent flux results. 1200°C ceramics are better for carrying out the flux experiments within a pressure range of 0-450 kPa which provide controlled flow rates.

### Chemical stability test

The chemical stability was quantified in terms of mass loss after leaving the ceramic in contact with acid and alkali solutions, individually, for a stipulated time period. The weight loss in acid was found to be less than ~5-6% for all the sintered membranes, whereas, the weight loss in alkali was found to be negligible. The results reveal that these membranes exhibit good corrosion resistance in acidic and basic media, and resistance towards basic media is much better.

### Shrinkage

There was negligible difference in the before and after diameters of membranes sintered at 1200°C. Figure 2 shows two sintered membranes at two different temperatures, viz., 1200 and 1300°C. The ceramics sintered at 1300°C showed significant changes in diameter when compared to those sintered at 1200°C. Ceramics sintered at 1200°C measured a

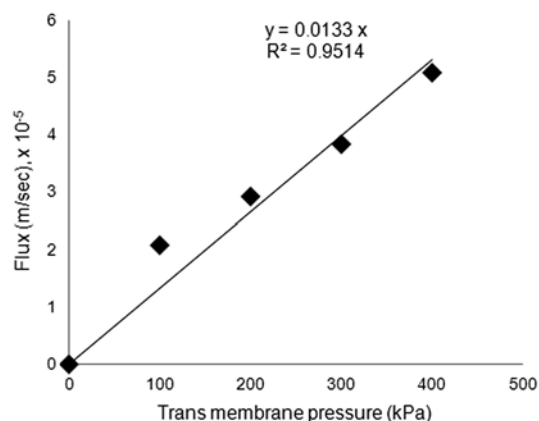| Table 2 — Pure water flux values of one sample ceramic membrane | | | |
|---|---|---|---|
| Trans-membrane pressure (ΔP), kPa | flow rate m$^3$/s | Flux (J), m$^3$/(m$^2$.s) | Permeability m$^3$/(m$^2$.s.kPa) |
| 0 | 0 | 0 | 0 |
| 100 | $2.36 \times 10^{-8}$ | $1.879 \times 10^{-5}$ | $1.879 \times 10^{-7}$ |
| 200 | $3.32 \times 10^{-8}$ | $2.639 \times 10^{-5}$ | $1.319 \times 10^{-7}$ |
| 300 | $4.35 \times 10^{-8}$ | $3.461 \times 10^{-5}$ | $1.153 \times 10^{-7}$ |
| 400 | $5.76 \times 10^{-8}$ | $4.589 \times 10^{-5}$ | $1.147 \times 10^{-7}$ |



Fig. 1 — Pure water permeation study by plotting flux v/s ΔP

diameter of 47.5 mm whereas those sintered at 1300°C showed 45 mm diameter. Figure also depicts negligible change in thickness for the both ceramics.

**Solvent permeation study**

Figure 3 shows the permeability trend of pure solvents for the ceramics sintered at 1200°C. Pressure difference is the only driving force for the solvent permeation here. It is seen that polar solvents have higher permeability than non-polar solvents. This proves that the ceramic membrane used for permeability experimentation is hydrophilic in nature. It was also noted that applied pressure, solvent viscosity, and surface tension (Table 3) influence the transport of solvent through membrane.
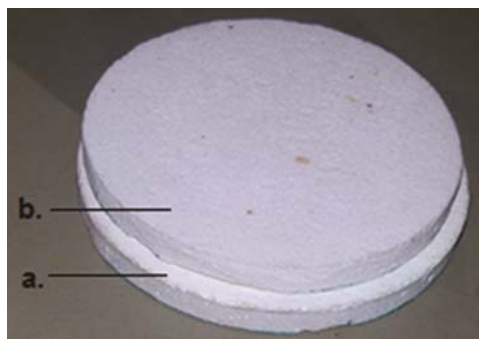


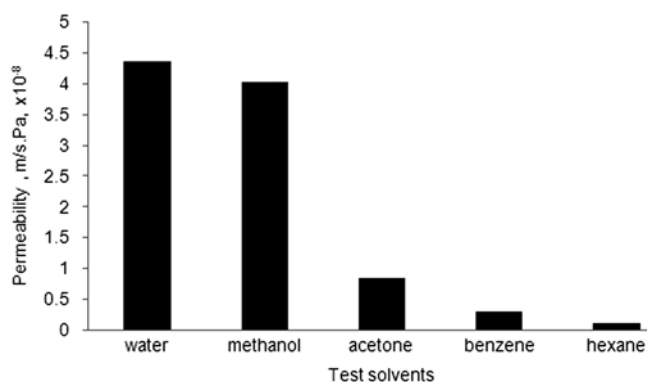Fig. 2 — Shrinkage in sintered membranes



Fig. 3 — Pure solvent permeability test of the synthesised membrane

**SEM and XRD studies**

Figure 4(a) represents morphology of the membrane disc sintered at 1200°C. It is seen that there is uniform pore distribution in these ceramic discs. Fig. 4(b) represents morphology of the membrane discs sintered at 1300°C. They showed surfaces with rough morphological structure, considerably larger pore diameter and a discontinuous distribution of pores. It can thus be stated that the morphology of the membrane depends on the sintering temperature. The pore size and pore structure change with an increase in
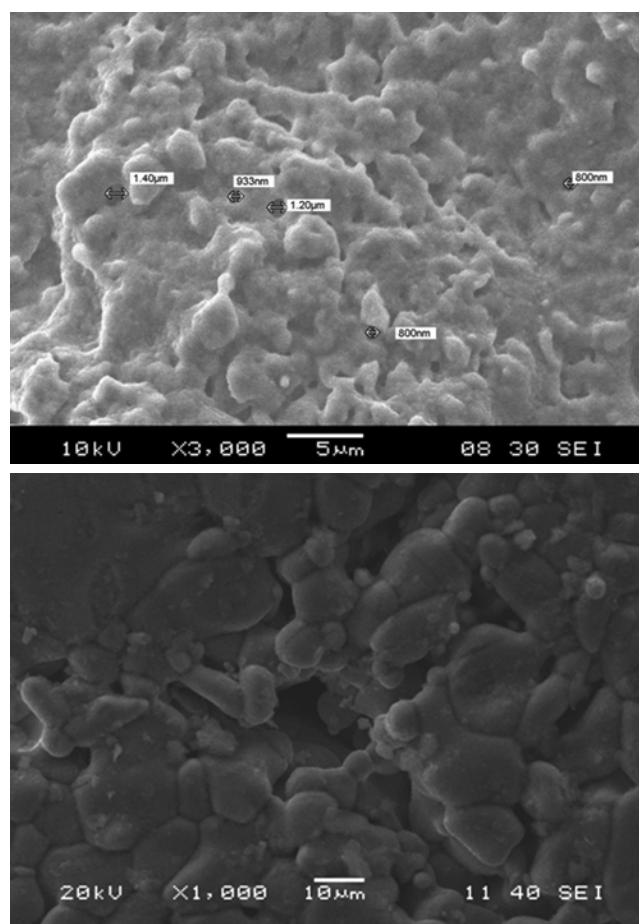


Fig. 4 —(a) SEM image (top view, at 1200°C), (b) SEM image (top view, at 1300°C)

Table 3 — Physical properties of the solvents used for the permeation experiments

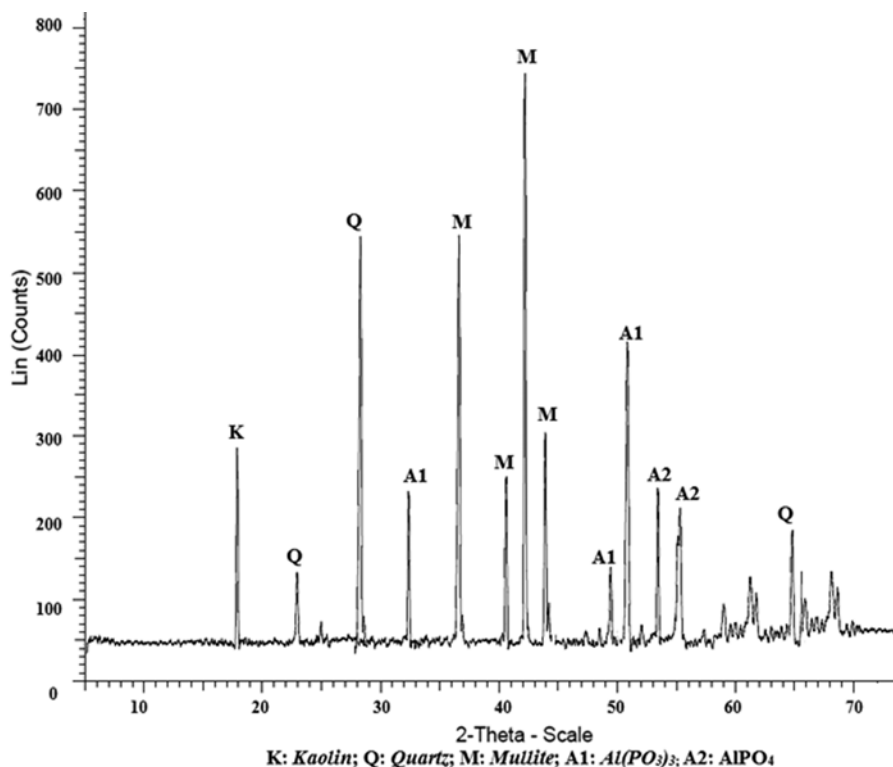| Solvents | MW (g/mol) | Density (g/mL) | Viscosity (cP) | Molar volume, (cm3/mol) | Surface tension, (mN/m) | Dielectric constant |
|---|---|---|---|---|---|---|
| Water | 18 | 1 | 1.02 | 18 | 72 | 80.3 |
| Methanol | 32 | 0.7917 | 0.59 | 40.7 | 22.6 | 32.6 |
| Acetone | 58 | 0.792 | 0.3 | 74 | 23.32 | 20.7 |
| Hexane | 86 | 0.659 | 0.32 | 131.6 | 17.9 | 1.9 |
| Benzene | 78 | 0.876 | 0.603 | 89.05 | 28.9 | 2.28 |

Fig. 5 — X-ray diffraction patterns of membrane supports sintered at 1200°C for 3 h

the sintering temperature. Those sintered at 1200°C showed pore sizes ranging 0.9 to 1.5 μm. The structures were more consolidated. The increase in average pore with an increase in sintering temperature can be attributed to the enhanced growth of grain size at higher temperatures.

The XRD pattern was studied to investigate the phases formed in the sintered ceramics. Figure 5 shows XRD pattern of ceramic membrane sintered at 1200°C. The following phases appear in the sintered membrane: kaolin, quartz, aluminium orthophosphate ($AlPO_4$), aluminium meta-phosphate ($Al(PO_3)_3$), and mullite. The addition of phosphoric acid to (kaolin+alumina) leads to the formation of a new phase – aluminium phosphate. $AlPO_4$ structure is formed below 1200°C where as $Al(PO_3)_3$ is stable at higher temperatures, i.e. ~1200°C and above.

## Conclusion

Microporous kaolin-alumina based ceramics have been prepared by using phosphoric acid as binder and starch as pore former. The porosities of the ceramics sintered at 1200°C varied between 32 to 35% consistently. Average pore size of ceramics sintered at 1200°C ranged between ~0.5–1.5 μm. Hydraulic permeability

was calculated to be ~$1.375 \times 10^{-7}$ $m^3/(m^2.s.kPa)$. These ceramics are stable up to ~450 kPa, beyond which they developed micro cracks. Polar solvents showed higher permeability than non-polar solvents which proved that the ceramic discs are hydrophilic in nature. The results reveal that the discs exhibit reasonably good corrosion resistance in both acidic and basic media. It can therefore be concluded that the ceramics sintered at ~1200°C can be successfully used for hydrophilic permeation experiments up to ~450 kPa operating pressure.

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