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# Overview on industrial membranes

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**Abstract**

In this paper, industrial inorganic membranes are presented. Inorganic membranes are divided into two types: dense and porous membranes, but the last ones correspond to the large majority of the present commercial products. The preparation methods used to manufacture commercial membranes are presented together with their effects on the membrane porous structure. Commercial membranes are briefly described.

## 1. Background

Inorganic membranes were developed in the 40's for nuclear applications, and essentially for the separation of uranium isotopes by the process of gaseous diffusion applied to UF6.

Non-nuclear applications of these membranes started at the beginning of the 80's with MEMBRALOX produced by CERAVER (now SCT), CARBOSEP produced by SFEC (now TECHSEP) and CERAFLO produced by Norton (and now by SCT).

Following these examples several companies introduced inorganic membranes on the market and this number is increasing exponentially. European, American and Japanese companies are now competing.

Inorganic membranes commercially available today are dominated by porous membranes, and particularly by porous ceramic membranes, which are used in cross-flow mode.

In this process, membranes split a feed into a clear filtrate and a retentate which is a concentrated suspension. This comes from the concept of cross-flow filtration. The feed circulates tangentially to the surface of the membrane, with permeation of the liquid phase through the membrane. No cake is formed because the tangential velocity permanently shears the deposit that tends to form on the membrane surface.

## 2. Membrane structure

Inorganic membranes can be divided firstly into dense and porous structures, and for porous membranes into asymmetric and symmetric ones.

Typical dense membranes are made of metals (in general palladium, silver and their alloys) or solid electrolytes (such as zirconia). These membranes are permeable to atomic or ionic forms of hydrogen (Pd layer) or oxygen ($ZrO_2$ layer).

Porous inorganic membranes are made of oxides (such as alumina, titania, zirconia), carbon, glass or metal.

Symmetric and asymmetric membranes are defined by the pore structure. Symmetric membranes exhibit homogeneous pore size throughout

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the membrane (e.g. glass membrane). Asymmetric membranes present a change of structure through the membrane. This change can be gradual with conical pore shape, the membranes are called asymmetric. But in most cases, membranes consist of several layers with a pore size reduction in each layer. The multilayer structure prevents the top-layer precursor from penetrating inside the large pores of the support. In some cases, the top layer can be a dense layer. These membranes are called composite membranes.

## 3. Preparation of porous inorganic membranes

Several methods can be used to prepare porous membranes from inorganic materials, the choice of method depends on the desired material and pore size.

### *3.1. Phase separation and leaching*

Glass membrane with a symmetric structure (isotropic sponge) of interconnected pores can be prepared by phase separation and leaching techniques.

A borosilicate glass ($Na_2O$–$B_2O_3$–$SiO_2$) is heated to 550–800°C, allowing to separate into two phases. One of the phases consists substantially of silicon dioxide which is insoluble in mineral acid. The other phase represents a soluble boric phase rich in alkali. The borate phase is then removed by acid leaching, leaving a porous skeleton of silicon dioxide. This technique can be used to produce either porous glass tubes or hollow glass fibers. The pore size is regulated by the annealing temperature (at constant time and glass composition). Porous glass having a pore size inferior to 2 nm can be produced by this way. But the separation phase is also influenced by the annealing time and/or glass composition, and there are many possibilities for producing glass membranes.

The main disadvantage of a porous glass membrane is the instability of the surface. The pore surface is rather active, mainly because of the presence of silanol groups. These groups can be modified spontaneously by feed or voluntarily by a chemical or physical action, with consequently drastic changes of the membrane characteristics.

### *3.2. Anodic oxidation*

The process of anodic oxidation of aluminum and the resulting structures which were obtained were described 30 years ago. This method is used to produce the commercial ANOPORE membranes.

One side of a thin, high-purity aluminium foil is anodically oxidized in an acid electrolyte, which may contain sulfuric, phosphoric, chromic or oxalic acids. The unoxidised metal remaining on the other side is then removed by dissolution in a strong acid, leaving a regular pattern of pores. The membranes so obtained are not stable under long exposure to water. Their stability can be improved by hydrothermal treatment in water or in a basis. Pore size is determined by the voltage used and by the type of acid. Weak electrolytes produce larger pores than strong electrolytes (under constant current density conditions).

Two types of membrane structure can be obtained:

- symmetric structure with a network of distinctive conical pores perpendicular to the surface of the membrane,
- asymmetric structure with a thick layer of large pores and a thin layer of small pores connected to the large ones (Fig. 1).

The difference in structure is obtained by changing the process parameters during manufacturing.

With anodic oxidation, a very controlled and narrow pore size can be obtained.

### *3.3. Pyrolysis*

Polymers are coated onto porous supports and then degraded by controlled pyrolysis to produce an inorganic membrane.

Fig. 1. Cross view of an alumina membrane obtained by anodic oxidation (courtesy of Whatman).

With this technique, silica membranes are produced from silicone rubber, whereas carbon membranes can be produced from polyacrylonitrile or phenolic resins. This technique is used by Le Carbone Lorraine to produce their carbon membranes. The porous support is formed by carbon fibers obtained by pyrolysis of a 8 mm outer diameter tube (Fig. 2). Depending on the pyrolysis degree, the support can be weakly hydrophilic (low temperature) or more hydrophobic (high temperature). One (or two) layer(s) of specific polymer is deposited onto the support surface. The carbon layer is formed by pyrolysis of the polymeric layer in a controlled environment (inert

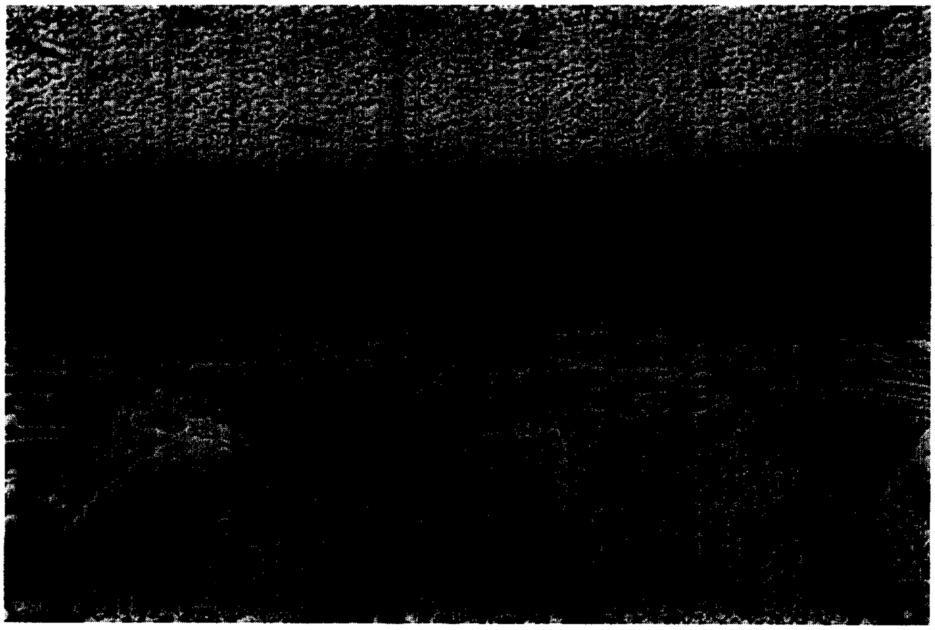

Fig. 2. Cross view of a carbon membrane obtained by pyrolysis (courtesy of Le Carbone Lorraine).

atmosphere ...). For medium size pores (microfiltration), an organic solution of phenolic resin is deposited onto the support, followed by controlled pyrolysis. To produce smaller pores, a polymeric film is produced by in situ polymerization. The degree of carbonisation is controlled by stepped pyrolysis. An inorganic carbon surface is formed and is very stable.

Additives, degree and type of pyrolysis control, the pore size in the range 1 μm down to 2 nm (lab studies).

### 3.4. Particle dispersion and slip casting

Composite ceramic membranes can be prepared by slip casting from particle dispersion. In this method, particles are deposited onto a porous support in one or more layers by dipping or casting (Fig. 3). Particle dispersion can be prepared by mixing, precipitation or crystallisation, and/or sol–gel. The slip containing particles, along with organic binders, surfactants, plasticizers flow into the pores of the dry support by capillary suction. The solvent is removed and the particles are retained to form a layer, which is then stabilized by drying and thermal treatment to form a membrane.

Slip casting is probably the most widely used technique for preparing ceramic membranes.

Pore size is linked to the dispersed particle size. Membranes with small size pores require very small particles and are prepared by the sol–gel technique.

Organic binders allow to increase the strength of the unfired membrane. Plasticizers are added to prevent cracking of the membrane during thermal treatment. Surfactants are used to produce a stable dispersion.

Membrane thickness is controlled by dipping time and slip formulation. Pore size depends on the particle size of the slip and the thermal treatment of the layer.

### 3.5. Sol–gel process

The sol–gel can be divided into two main routes: the colloidal suspension route and the polymeric gel route. In both cases, a precursor is hydrolysed while a condensation or polymerization reaction occurs simultaneously. The precursor is either an inorganic salt or a metal organic compound.

In the colloidal route, a faster hydrolysis rate is obtained by using a water excess. A precipitate of

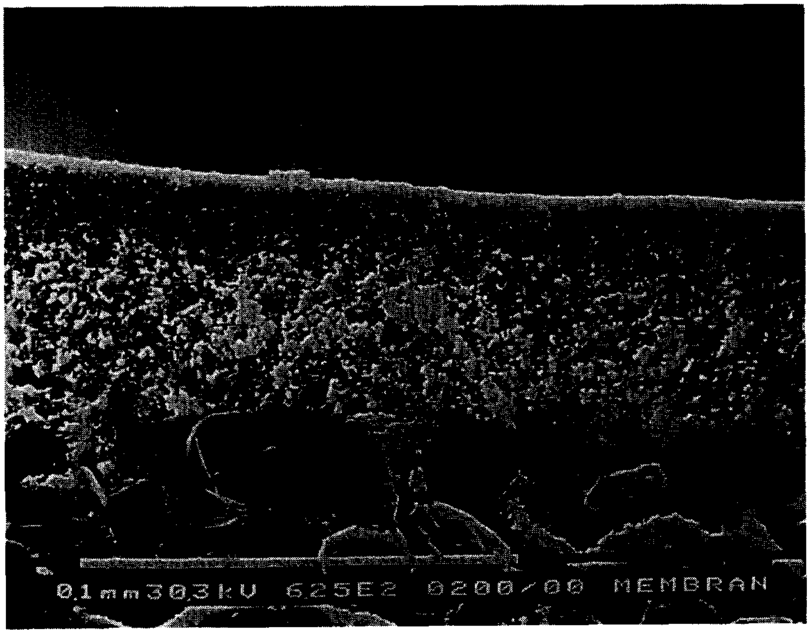

Fig. 3. Cross view of an alumina membrane obtained by particle dispersion (MEMBRALOX).

gelatinous hydroxide (or oxohydroxide) particles is formed and then peptized to give a stable colloidal suspension. By different processes, this suspension is transformed in a gel structure consisting of a network of particles or agglomerate chains.

In the polymeric gel route, the hydrolysis is kept low by using a lack of water. The final stage of the process is a strongly interlinked gel network.

The final structure obtained in both ways is totally different.

## 4. Commercialized inorganic membranes

Today, twenty firms are manufacturing inorganic membranes, most of them were introduced to the market over the last five or ten years (Table 1).

Commercialized inorganic membranes are dominated by porous ceramic membranes. The most prevalent membrane materials are metallic oxides and more precisely alumina and zirconia, but other materials, such as titania, carbon or glass, are available.

Commercialized inorganic membranes exist in three configurations: disks, tubes and multichannels/honeycombs (Fig. 4).

The use of disks has been limited to medical and laboratory applications whereas tubes and monoliths are used in various industrial applications.

Table 1
Commercial porous inorganic membranes

| Manufacturer | Trade name | Material | Pore $\phi$ | Geometry |
|---|---|---|---|---|
| USF/SCT | MEMBRALOX® | $ZrO_2/Al_2O_3$ | 20–100 nm | Monolith |
| | | $Al_2O_3/Al_2O_3$ | 5 nm–12 μm | |
| | CERAFLO® | $Al_2O_3/Al_2O_3$ | 0.2–1.0 μm | Monolith |
| TECH-SEP | CARBOSEP® | $ZrO_2/C$ | 10–300 kD | Tube |
| | | $TiO_2/C$ | 0.14 μm | |
| | KERASEP® | $TiO_2/Al_2O_3+TiO_2$ | 0.1–0.45 μm | |
| | | $ZrO_2/Al_2O_3+TiO_2$ | 15–300 kD | Monolith |
| Le Carbone Lorraine | | C/C | 0.1–1.4 μm | Tube |
| CERASIV | | $Al_2O_3/Al_2O_3$ | 0.1–1.2 μm | Tube/Monolith |
| | | $+TiO_2/ZrO_2/Al_2O_3$ | 5–100 nm | |
| NGK | | $Al_2O_3/Al_2O_3+SiO_2$ | 0.2–5 μm | Tube/Monolith |
| Whatman | ANOPORE® | $Al_2O_3$ | 20 nm–0.2 μm | Disk |
| Gaston County | UCARSEP® | $ZrO_2/C$ | 4 nm | Tube |
| Du Pont/Carré | | $Zr(OH)_4/SS$ | 0.2–0.5 μm | Tube |
| TDK | DYNACERAM® | $ZrO_2/Al_2O_3$ | ≈ 10 nm | Tube |
| | | $Al_2O_3/Al_2O_3$ | 50 nm | |
| ATECH | | SiC/SiC | 0.05–1.0 μm | Tube/monolith |
| | | $Al_2O_3$ | | |
| Asahi Glass | | Glass | 0.1–1.4 μm | Tube |
| Fuji Filters | | Glass | 4–90 nm | Tube |
| | | Glass | 0.25–1.2 μm | |
| Fairey | STRATA-PORE® | Ceramics/Ceramics | 1–10 μm | Tube/Plate |
| | MICROFILTREX® | SS | 0.2–1 μm | Tube/Plate |
| Osmonics | HYTREX® | Ag/None | 0.2–5 μm | Tube/Plate |
| | CERATREX® | Ceramics/Ceramics | 0.1 μm | |
| Ceramem | | Ceramics/Cordierite | 0.05–0.5 μm | Honeycomb |
| Trideltafiltration | | $Al_2O_3/Al_2O_3$ | 0.1–7 μm | Tube/Monolith |
| Hoogovens | | $Al_2O_3/Al_2O_3$ | 0.1–1 μm | Tube |
| Steenecker | | $Al_2O_3$ | 0.4 μm | Tube |
| NOK | | $Al_2O_3/Al_2O_3$ | 0.2–6 μm | Tube |
| TOTO | | $Al_2O_3/Al_2O_3$ | 0.1–0.2 μm | Tube/ |
| | | $ZrO_2/Al_2O_3$ | 5–30 nm | Monolith |
| Carré | | $ZrO_2/SS$ | | Tube |

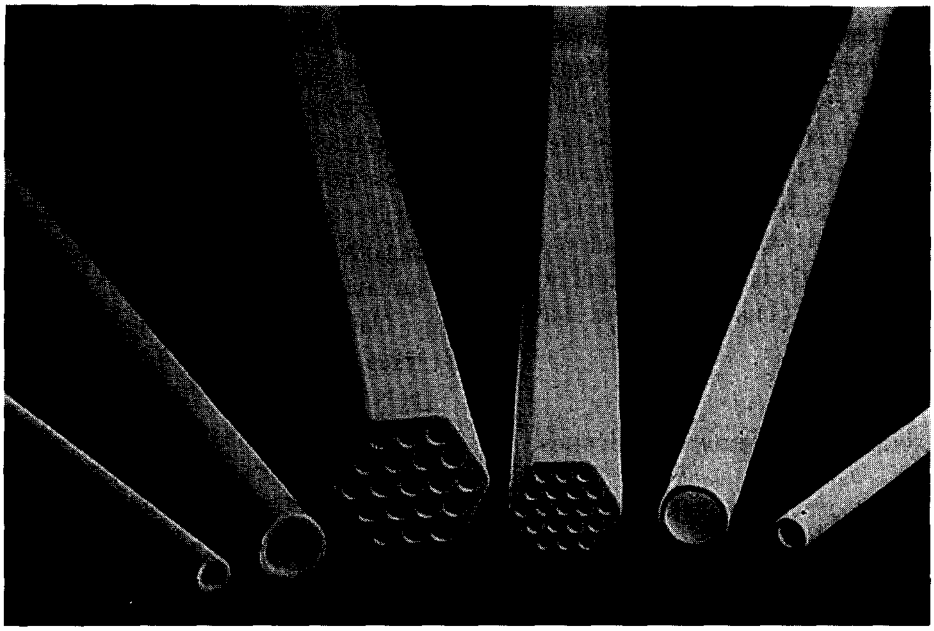

Fig. 4. Inorganic membrane configuration —MEMBRALOX multichannel and tube geometry.

The multichannel/honeycomb configuration represents a technical evolution from single-tube or tube bundle geometry as it potentially offers high-mechanical strength and a higher membrane packing density.

Today, approximately 40000 m$^2$ of inorganic membranes are installed throughout the world. This surface can be estimated as 10% of the total surface of installed membranes operating in cross-flow mode.

The market is dominated by SCT/US Filter with 20000 m$^2$ and TECH-SEP with 15000 m$^2$, which are the oldest manufacturers of inorganic porous membranes.