ABSTRACT

Inorganic mesoporous membranes showed potential for water purification and desalination by nanofiltration. In this work, a composite mesoporous inorganic membrane was synthesized with a two layer structure. The supporting layer was a macroporous $\alpha$-Al$_2$O$_3$ substrate prepared with the colloidal filtration technique. The functional layer was a mesoporous $\gamma$-alumina thin film prepared with the sol-gel method. The synthesis of each layer was systematically studied and carefully optimized to obtain defect-free membranes.

The membrane device was then tested with a homemade water pressurization chamber under various experimental conditions to systematically characterize the water purification performance of the membrane. The experiments determined limiting salt rejection at various testing conditions. The purification behavior was studied for three types of electrolyte aqueous solutions, NaCl, CaCl$_2$ and AlCl$_3$ at a concentration range from 0.001 M to 0.1 M.

A model based on surface charge adsorption and electrokinetic mass transportation was established with commercial FEM modeling software, COMSOL 3.2b, to study the purification mechanism and the performance limitations. Qualitative agreement between the experiment and the modeling results was obtained.
Dedicated to
My parents
ACKNOWLEDGMENTS

I would like to express my deepest gratitude to my advisor, Dr. Henk Verweij, who has given me encouragement, guidance, support and inspiration over the past five years. I also want to thank Dr. Rudy Buchheit and Dr. Patricia Morris for serving on my dissertation committee and providing valuable suggestions.

I am especially grateful to Matthew L. Mottern, Krenar Shqau and Jingyu Shi for the supply of alumina porous supports, many scientific discussions and assistance for the TEM work. I also wish to thank all the members of IMS group, especially Melissa Schillo, and Lanlin Zhang for their sincere help in this dynamic working environment. I can not forget the help and friendship of previous CISM members, especially Chonghoon Lee, Jin Wang, Sehoon Yoo, Santi Chrisanti, Greg Quickel, Nick Szabo, and Vishnu Ravula. Characterization work could not have been accomplished without the help of Hendrik O. Colijn, Cameron Begg and Steven Bright.

Lastly, I wish to thank my parents and my sister for their love, support and encouragement.
VITA

November 15 1978.........................................Born - Xiangtan, P.R.China
2001................................................................B.S, Materials Science and Engineering, Jilin University.
2004................................................................M.S, Materials Science and Engineering, The Ohio State University.

PUBLICATIONS


FIELDS OF STUDY

Major Field: Materials Science and Engineering
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Dedication</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>iv</td>
</tr>
<tr>
<td>Vita</td>
<td>v</td>
</tr>
<tr>
<td>List of Tables</td>
<td>x</td>
</tr>
<tr>
<td>List of figures</td>
<td>xi</td>
</tr>
<tr>
<td>Chapter 1 Inorganic/Organic Reverse Osmosis/Nanofiltration Membranes</td>
<td></td>
</tr>
<tr>
<td>for Water Desalinization Applications</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Organic RO/NF membranes</td>
<td>4</td>
</tr>
<tr>
<td>1.2.1 Asymmetric membranes</td>
<td>4</td>
</tr>
<tr>
<td>1.2.2 Composite membranes</td>
<td>7</td>
</tr>
<tr>
<td>1.2.3 Models for separation process</td>
<td>16</td>
</tr>
<tr>
<td>1.3 Inorganic NF membranes</td>
<td>18</td>
</tr>
<tr>
<td>1.3.1 Synthesis and properties of inorganic NF membranes</td>
<td>18</td>
</tr>
<tr>
<td>1.3.2 Separation mechanism and modeling</td>
<td>26</td>
</tr>
<tr>
<td>1.4 Conclusion and future work in the membrane area</td>
<td>31</td>
</tr>
<tr>
<td>Chapter 2 Synthesis and Optimization of High Surface Quality Alumina</td>
<td></td>
</tr>
<tr>
<td>Compact Membrane Support</td>
<td>33</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>33</td>
</tr>
<tr>
<td>2.2 Experimental procedures</td>
<td>35</td>
</tr>
</tbody>
</table>
5.2.3 Diffusion and convection: Nernst-Planck ...........................................101
5.2.4 Flow: Navier-Stokes ...........................................................................104
5.2.5 Geometry and mesh .......................................................................104
5.3 Results and discussion ...........................................................................105
   5.3.1 Channel length, tortuosity and branching .....................................105
   5.3.2 Concentration profile .....................................................................107
   5.3.3 Model validation ...........................................................................112
5.4 Conclusions and future work .................................................................115

Conclusions ...........................................................................................................117
Bibliography ...........................................................................................................120
Distribution list ....................................................................................................135
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1: γ-Alumina membrane structural properties and performance.</td>
<td>21</td>
</tr>
<tr>
<td>Table 1.2: Titania membrane structure and performance.</td>
<td>22</td>
</tr>
<tr>
<td>Table 1.3: Zirconia membrane structure and performance.</td>
<td>23</td>
</tr>
<tr>
<td>Table 2.1: Direct observation of colloidal filtration compacts, initially stabilized in aqueous HNO₃ at various pH values.</td>
<td>38</td>
</tr>
<tr>
<td>Table 3.1: Volumetric average particle diameter $\bar{\Omega}_s = \frac{3V}{4\pi}$ [nm], using $\bar{V} = \frac{\sum N_i V_i^3}{\sum N_i V_i}$. Here $V_i$ is the median volume (in nm³) of particles for one size interval of 0.5 nm, and $N_i$ is the total number of particles in that size interval.</td>
<td>65</td>
</tr>
<tr>
<td>Table 3.2: Contamination levels (ppm weight) in the sols.</td>
<td>66</td>
</tr>
<tr>
<td>Table 4.1: Water permeability, thickness and resistance of components of a membrane device.</td>
<td>78</td>
</tr>
<tr>
<td>Table 4.2: Pitzer parameters for osmotic coefficient calculation.</td>
<td>89</td>
</tr>
<tr>
<td>Table 5.1: Terminology summary.</td>
<td>103</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure 1.1: Definition of industrial membrane applications in terms of size range and porosity.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.2: Osmotic and RO process.</td>
<td>3</td>
</tr>
<tr>
<td>Figure 1.3: SEM picture of the cross section of an polysulfone asymmetric membrane (10,000x)</td>
<td>5</td>
</tr>
<tr>
<td>Figure 1.4: Cellulose triacetate and the solvent.</td>
<td>6</td>
</tr>
<tr>
<td>Figure 1.5: layer structure of composite membrane</td>
<td>7</td>
</tr>
<tr>
<td>Figure 1.6: polysulfone and solvent</td>
<td>8</td>
</tr>
<tr>
<td>Figure 1.7: Interfacial polymerization</td>
<td>10</td>
</tr>
<tr>
<td>Figure 1.8: NS100 synthesis reaction</td>
<td>11</td>
</tr>
<tr>
<td>Figure 1.9: Synthesis reaction of PA300</td>
<td>12</td>
</tr>
<tr>
<td>Figure 1.10: NS300 synthesis</td>
<td>13</td>
</tr>
<tr>
<td>Figure 1.11: FT30 synthesis.</td>
<td>14</td>
</tr>
<tr>
<td>Figure 1.12: SEM picture of FT30 surface</td>
<td>15</td>
</tr>
<tr>
<td>Figure 1.13: Schematic representation of PSCF model</td>
<td>17</td>
</tr>
<tr>
<td>Figure 1.14: Sol-gel method</td>
<td>19</td>
</tr>
<tr>
<td>Figure 1.15: Schematic of a diffuse electric double layer</td>
<td>27</td>
</tr>
<tr>
<td>Figure 1.16: Concentration and potential profile for positively charged flat surface.</td>
<td>28</td>
</tr>
<tr>
<td>Figure 1.17: Donnan exclusion effect for separation.</td>
<td>30</td>
</tr>
<tr>
<td>Figure 2.1: Apparent density data of AKP15 and AKP30 compacts made by filtration of 20 vol% alpha alumina suspension vs. Aluminon concentration and initial pH, respectively.</td>
<td>39</td>
</tr>
</tbody>
</table>

xi
Figure 2.2: Apparent density data of sintered compacts; AKP30 supports made by filtration of aqueous HNO₃ dispersions at initial pH = 2, and AKP15 supports made by filtration of aqueous Aluminon dispersions at 0.5wt%................................. 40

Figure 2.3: Effect of sintering temperature on the surface of S2.00pH compacts observed by SEM.......................................................................................................................... 41

Figure 2.4: SEM image of cross section of α-Al₂O₃ compacts (S2.00ph) sintered at (a) 1150 C and (b) 1350 C.................................................................................................................. 42

Figure 2.5: Water permeability of AKP15 and AKP30 supports as a function of sintering temperature. ........................................................................................................................................ 43

Figure 2.6: Temperate development of gas (He) permeability for AKP15 and AKP30 supports. ........................................................................................................................................ 44

Figure 2.7: TEM images of FIB cross-sections of sintered S2.00pH compacts coated with zirconia based ceramic taken from [126]................................................................................ 45

Figure 3.1: Funnel setup.......................................................................................................................................................................................... 50

Figure 3.2: 20 nm Anodisc membrane. (a) FIB cross section of the branched top layer (b) top layer surface and (c) surface area with defect...................................................... 51

Figure 3.3: Yield of the filtration process with and without the presence of ultrasonic vibration.................................................................................................................................................................................. 53

Figure 3.4: Standing wave on the surface of an Anodisc filter membrane, demonstrated by decoration with small black particles added for this purpose. ...... 54

Figure 3.5: DLS particle size distribution of the sols.......................................................... 56

Figure 3.6: C-γ spin coated on mica.................................................................................. 57

Figure 3.7: C-γ dip-coated on a silicon wafer. ................................................................. 58

Figure 3.8: Volumetric particle size distributions from AFM image analysis................. 60

Figure 3.9: Data processing for DLS and AFM measurements. ...................................... 61

Figure 3.10: Diameter vs. thickness from AFM analysis. .............................................. 62
Figure 3.11: Differential accumulated volume vs. particle Ø for each sol, using the spherical and the oblate model........................................................................................................... 64

Figure 4.1: Water purification chamber design........................................................... 70
Figure 4.2: Water purification membrane testing setup.............................................. 72
Figure 4.3: Rejection under various stirring conditions for aqueous NaCl solutions. 73
Figure 4.4: Rejection vs flow velocity for aqueous NaCl solutions........................... 75
Figure 4.5: Temperature vs. viscosity for pure H2O.................................................... 80
Figure 4.6: Viscosity vs concentration for aqueous NaCl.......................................... 81
Figure 4.7: Viscosity vs concentration for aqueous CaCl2......................................... 82
Figure 4.8: Rejection vs. flow velocity for aqueous NaCl solutions............................ 75
Figure 4.9: Rejection vs. flow velocity for various concentrations of NaCl............... 83
Figure 4.10: Rejection vs. flowrate for various concentrations of NaCl+1%AlCl3. .................................................................................................................. 85
Figure 4.11: Rejection vs. flowrate for various concentrations of CaCl2+1wt%AlCl3. .................................................................................................................. 86
Figure 4.12: Rejection vs flowrate for various concentrations of AlCl3................... 87
Figure 4.13: The pressure vs. flowrate w/o osmotic effect for NaCl. ......................... 90
Figure 4.14: The pressure vs. flowrate w/o osmotic effect for CaCl2. ....................... 91
Figure 4.15: The pressure vs. flowrate w/o osmotic effect for NaCl+1%AlCl3. ............... 91
Figure 4.16: The pressure vs. flowrate w/o osmotic effect for CaCl2+1%AlCl3. .... 91
Figure 4.17: The pressure vs. flowrate w/o osmotic effect for AlCl3.......................... 92
Figure 5.1: Geometries and renders of modeling results. a...f are various 2D geometries with a color map of the Na\(^+\) concentration. g is the only 3D geometry that has been modeled. c1 is the closeup of the 2D modeling result with a color map of the Na\(^+\) concentration, with blue stream lines of the velocity field; c2 is the
corresponding mesh. g1 is a closeup of the 3D modeling result with colored slices of space charge density, and blue stream lines; g2 shows the 3D mesh.

Figure 5.2: Concentration profile along the channel.
Figure 5.3: Concentration profile at various applied pressures.
Figure 5.4: Normalized mass transport terms. The feed side bulk solution is from \( z = -2.0E-8 \) to \( z = 0 \), the membrane pore channel region is from \( z = 0 \) to \( z = 3.0E-8 \), and the permeate side bulk solution is from \( z = 3.0E-8 \) to \( z = 1.2E-7 \).

Figure 5.5: Comparison of rejection performance for 2D models versus channel length.

Figure 5.6: Comparison of rejection performance for experimental result 1 (solid symbols), experimental result 2 (open symbols) and 3D model results (drawn line)
CHAPTER 1

INORGANIC/ORGANIC REVERSE OSMOSIS/NANOFILTRATION MEMBRANES FOR WATER DESALINIZATION APPLICATIONS

1.1 Introduction

Membrane separation processes are rapidly expanding in many existing and emerging applications, such as chemical engineering [1], petroleum industries [2], environment science [3,6], biotechnology science [4], pharmaceuticals [5], water treatment [1,5-7], dairy/beverage/food industries [5], pulp/paper manufactures, textile industries, metallurgical and electronic industries [7]. In all these industries, various water purification processes are among the most widely used. According to the sizes of the species that the membrane retains, water purification membranes can be classified into 4 categories [7,8]: reverse osmosis (RO) (0.1-1 nm), nanofiltration (NF) (1-2 nm), ultrafiltration (UF) (2-100 nm) and microfiltration membranes (100 nm-10 μm). A comparison between the definition of membrane types and definition of material porosity is provided in figure 1.1
Figure 1.1: Definition of industrial membrane applications in terms of size range and porosity.

As one important subcategory of water purification applications, water desalinization is a process by which the loading of dissolved solids is reduced, especially electrolytes, in various aqueous solutions. Examples include seawater and brackish water desalinization, water softening, waste water recycling/regeneration and industrial ultrapure water supply. Since most dissolved species/electrolytes in aqueous media have relatively small size (<1nm), membrane technologies for water desalinization are normally confined to RO and NF type membranes.

A brief description of the osmotic process is provided below to help visualizing the reverse osmosis process (figure 1.2). Osmosis is a universal phenomenon in which solvent spontaneously passes through a semipermeable (no or very low solute flow) membrane from the side with lower solute concentration (higher solvent chemical potential) to the side with higher solute concentration (lower solvent chemical potential) until the chemical potentials of solvent at both sides are equal. At equilibrium the pressure difference between the two sides of the membrane is equal to the osmotic pressure $\Delta\pi$. An RO membrane acts as such a semipermeable barrier which allows passage of a particular species (solvent) while other species (solute) are retained partially or completely. To reverse the spontaneous flow of the solvent, a pressure difference larger than the osmotic pressure must be applied and, as a result, separation of the solvent from solution is achieved as shown in figure 1.2.
NF membranes may be described as very coarse RO membranes when solutes are macromolecules. However, the mechanisms of ion separation in NF and RO are substantially different. The permselectivity and flux of the RO/NF membranes depend on the membrane material, the preparation procedure and the microstructure of the functional membrane barrier layer [9,10]. When the filtration media is an aqueous system, as in water desalinization, a hydrophilic barrier layer with low solubility towards the solutes is favorable for high flux and high permselectivity.

The materials for RO/NF membranes can be either organic polymers or inorganic ceramics. Organic polymer RO/NF membranes dominate the water desalinization market, be-
cause of their relatively simple synthesis methods and satisfactory performance. However, new NF ceramic membranes have been attracting more and more attention due to many of their merits [18]. Their chemical/thermal stability and mechanical strength enable ceramic membranes to work in harsh/dirty environments and under a wider pressure/temperature/$p_H$ range. Thorough cleaning and regeneration is possible and hence a longer membrane life time can be obtained. Resistance to organic solute and microbial attack reduces the fouling problems associated with traditional organic membranes [18]. The ceramic membranes are also believed to have a higher porosity and permeability when compared with their polymeric counterparts.

This introductory literature review focuses on the RO/NF membrane technologies for water desalinization applications. It summarizes the chemistry, morphology, preparation, performance and separation mechanisms for both organic and inorganic materials. This review is organized as follows. Section 2 focuses on commercially important organic RO/NF membranes; section 3 is dedicated to research progress in inorganic NF membranes and section 4 provides a predictive survey of the future research.

## 1.2 Organic RO/NF membranes

Organic RO/NF membranes have been developed and commercialized for more than 50 years and most of the synthesis research has been carried out by private companies, and not been made available to the public. Therefore, very few academic research papers are found in the RO membrane field, other than application studies and mathematical modeling of membrane performance. Recent examples of review papers include those of Robert J. Petersen 1993, Petersen and Cadotte 1990, Allegrezza 1988 and Cadotte 1985 [11-14].

### 1.2.1 Asymmetric membranes

**Structure & Benefit**

Commercial polymer RO membranes mainly come in two categories, single component asymmetric membranes (or briefly asymmetric membranes) and multiple layer composite membranes (or briefly composite membranes).
Asymmetric RO membranes have an anisotropic structure, consisting of a dense surface skin on a porous sublayer structure (figure 1.3). Both skin and sublayer have the same composition [15, 16]. Normally the asymmetric RO membrane is formed by a single-step phase inversion method, which is relatively simple and cheap. The most important example is cellulose acetate.

![SEM picture of the cross section of a polysulfone asymmetric membrane (10,000x) [17].](image)

**Figure 1.3:** SEM picture of the cross section of an polysulfone asymmetric membrane (10,000x) [17].

### Cellulose acetate

Polymeric cellulose triacetate, see figure 1.4, with segment number, \( n \), between 3000 and 9000 is first dissolved in an organic solvent or solvent mixture to form a casting solution. The casting solution is then applied to the surface of a carrier, which can be a flat support or hollow fiber tube. After that, the carrier is immersed into a non-solvent (normally water) bath, where the coagulation of the polymer occurs to form the membrane morphology. The formed membrane can be post-treated (washed and heated) and collected for
usage. The morphology and performance of the membrane are controlled by various factors, such as polymer concentration, evaporation time, humidity, temperature and the composition of the casting solution [17]. Asymmetric cellulose acetate membranes normally have a flux of $2.8 \times 10^{-3} \ldots 8.5 \times 10^{-3} \text{ m}^3/(\text{m}^2 \cdot \text{s})$, and a rejection rate of 91...97% under the testing conditions of 0.5wt% NaCl, 4.1 MPa and 25°C [11]. Cellulose acetate based membranes are normally very sensitive to thermal, chemical and biological degradation, which limits the application of this type of membrane.

![Figure 1.4](cellulose-triacetate.png)  

**Figure 1.4:** Cellulose triacetate and the solvent.
1.2.2 Composite membranes

Structure & Benefit

The majority of the state-of-the-art commercial polymer RO membranes are composite membranes, which consist of a top layer (barrier layer), a supporting sublayer (support), and sometimes a carrier layer. The chemistry of the barrier layer and support are normally different. Therefore, each layer can be optimized independently. Generally, the support has an asymmetric macro-porous structure, which provides sufficient mechanical strength and permeability. The barrier layer is a dense hydrophilic thin film which provides the major separation function. The membrane is usually carried on a substrate to realize a certain shape, and for further mechanical support (figure 1.5).

![Figure 1.5: layer structure of composite membrane](image)

Composite membranes have some key advantages over asymmetric membranes which make them more successful. A vast variety of chemical compositions can be formed into ultra-thin barrier layers and these thin barrier layers can be tailored with optimized hydrophilic groups and backbone structure, whereas asymmetric membrane formation is limited to linear, soluble polymers.
The composite membranes have the disadvantage of requiring a more expensive method for membrane manufacturing. This requires at least two major steps:

- First, a macro-porous support is synthesized (normally with the immersion precipitation technique).
- Second, the thin barrier layer is synthesized (or synthesized and applied) on the microporous support. Two major routes of barrier layer preparation: interfacial polymerization and dip-coat methods are used most for industrial composite RO membrane manufacturing.

**Macro-porous support**

Many materials that have been investigated include Polyethersulfone, cellulose mixed esters, polyimides, and polyphenylene oxides [11]. The most successful microporous support is polysulfone (figure 1.6), which has remained a mainstay in composite membranes to this day.

Microporous polysulfone is normally prepared by the immersion precipitation technique. The typical procedure is as follows. The Udel P-3500 (polysulfone with MW 30,000) is dissolved in N,N-dimethylformamide to obtain a 15 wt% solution. After degassing treatments, the solution is spread coated on a clean glass plate with a doctor blade and then immersed into a water bath. The liquid solution film is then converted into the microporous membrane by precipitation of the polysulfone.

![Polysulfone](figure1_6.png)

**Figure 1.6**: polysulfone and solvent.
Numerous morphology studies have been carried out with SEM techniques. It has been reported that the shiny surface (corresponding to the original air interface) has a denser layer with pores diameters ranging from 1.9 to 15 nm. The surface area attributed to pores was measured to be 16%. The mean pore size was 7.5 nm. The dull surface (corresponding to the interface contacting the glass plate) contained pores ranging from 0.3 to 2.0 μm [20]. Merin and Cheryan [21] reached a similar conclusion by examining the surface porosity of a commercial polysulfone ultrafiltration membrane with SEM. They found a surface pore concentration of about $4 \times 10^{11}$ pores/cm$^2$, and ranging in size from 1 to 15 nm in diameter. The pores occupied 7…12% of the surface area.

Polysulfone has a much higher $p_H$ tolerance than cellulose acetate, which enables one to use barrier layer formation solutions that are highly acidic or alkaline.

**Barrier layer**

The barrier layers of commercial polymeric RO composite membranes are normally prepared with two methods, interfacial polymerization and dip-coating. In the interfacial polymerization method, a polymerizing reaction occurs between two very reactive monomers (or one pre-polymer) at the interface of two immiscible solvents (figure 1.7). The support layer, which is generally an ultrafiltration or microfiltration membrane (figure 1.7 A), is immersed in an aqueous solution (figure 1.7 B) containing a reactive monomer or a pre-polymer, frequently of the amine-type. The support is then immersed in a second bath containing a solution of water-immiscible solvent and another reactive monomer (figure 1.7 C). The two monomers react with each other at the interface of the two liquid films to form a dense polymeric layer (figure 1.7 D). Heat treatment is often applied to complete the interfacial reaction. The advantage of interfacial polymerization is that the reaction is self-inhibiting, because of limited passage of reactants through the already formed layer, which results in an extremely thin film of thickness within the 50 nm range [17].
As the key component of the polymeric RO membrane, barrier layer materials have been the focus of membrane research for 50 years. Thousands of compositions have been studied and many of them have been commercialized. Some of the most important products are reviewed in the following sections.

**Polyethylenimine and polyepiamine**

**NS-100**

In 1969, Cadotte found that RO membranes could be made with polyethylenimine using an interfacial reaction technique, from which the NS-100 membrane came forth [22]. A water-saturated microporous polysulfone sheet was immersed in an aqueous solution of polyethylenimine (typically 0.67wt% solution in deionized water) and then immersed in a hexane solution containing 0.1wt% toluene diisocyanate. The coated substrate was then heat-cured in an air-circulating oven at about 110°C for 15 minutes. The chemistry of the reaction is illustrated in figure 1.8. This membrane gave >99% salt rejection, with a flux of $5.1 \times 10^{-3} \text{ m}^3/(\text{m}^2 \cdot \text{s})$, when tested at 10.3 MPa and 3.5% synthetic seawater.
SEM of the NS100 membrane showed it to have a smooth, featureless surface [23] with a thickness of roughly 0.6 μm [24]. The appearance of NS100 was deemed as a milestone in membrane technology because NS100 is the first interfacially formed non-cellulose composite membrane and greatly outperforms traditional asymmetric cellulose membranes.

**PA-300**

PA300 was developed and commercialized after NS100, which had a high salt rejection rate and better flux. The first major installation of a composite RO membrane in the world, i.e. the 3.2 million gallon per day seawater desalination plant at Jeddah, Saudi Arabia, utilized the PA300 membrane [25]. PA300 is the interfacial polymerization reaction product of polyepiamine and isophthaloyl chloride (IPC), see figure 1.9, on a porous polysulfone support. This membrane exhibits a flux of $5.7 \times 10^{-3}$ to $7.1 \times 10^{-3}$ m$^3/(m^2 \cdot s)$ and salt rejections of $>99.4\%$ for 3.5% aqueous NaCl solution at 6.9 MPa feed pressure.
Figure 1.9: Synthesis reaction of PA300

**Poly(piperazine)**

NS300

RO membranes based on poly(piperazine) were first studied by Cadotte [26]. The membrane was interfacially synthesized by soaking a microporous polysulfone support with an aqueous amine formulation, which contained 1~2% piperazine, 1% sodium hydroxide as an acid acceptor and 0.5% sodium dodecylsulfate as a surfactant and immersing it in a 1% IPC hexane solution. The formed membrane had a flux of $7.4 \times 10^{-3} \text{ m}^3/(\text{m}^2\cdot\text{s})$ and 98% salt rejection in synthetic seawater at 10.3 MPa.
SEM micrographs of the surface of such membranes showed a very grainy structure; wherein the porosity between grains was likely to be filled only by making the membrane layer thicker. Replacement of a portion of the IPC with a 1,3,5-benzenetricarbonyl chloride (TMC) was used for commercial NS300. The reaction is shown in figure 1.10. SEM studies showed that the surface morphology of the NS300 membrane changed as a function of the TMC content [27]. Structures varied from a grainy surface for the IPC to a swollen-like, rough structure for TMC.

*Aromatic amine polymer*

**FT30**

In 1978, it was discovered that a composite membrane having an excellent combination of high rejection and high flux under seawater test conditions could be made by interfacial polymerizations of monomeric aromatic amines with aromatic acyl halides. Typical recipes for this fully aromatic polyamide membrane consisted of a 2.0% 1,3-benzenediamine solution in water coated onto polysulfone, then interfacially contacted with a
0.1% solution of TMC in hexane [28], see figure 1.11. This discovery was developed at FilmTec Corporation into a new RO membrane product designated FT30.

\[
\begin{align*}
\text{NH}_2 \quad &+ \quad \text{Cl}_2\text{Cl} \quad \text{Cl}\text{C} \\
\text{NH}_2\text{NH}_2 \quad &\rightarrow \quad \text{Cl}\text{C} \quad \text{CO} \\
1,3\text{-benzenediamine} \quad &\rightarrow \quad \text{TMC} \\
\end{align*}
\]

**Figure 1.11:** FT30 synthesis.

SEM photographs of the FT30 surface show a ridge and valley structure [23], see figure 1.12. The average thickness of the barrier layer had been estimated to be 200 nm, which varied from 40 nm (valley) to 260 nm (ridge top). The performance of the membrane is outstanding with a flux of \(1.4 \times 10^{-2} \text{m}^3/(\text{m}^2\cdot\text{s})\) and a >99% salt rejection rate when tested with 0.5% NaCl under 3.4 MPa and 25°C.
The idea of softening groundwater by means of “loose” RO membranes or NF membrane was first applied to Florida municipal well waters with good results [29]. In that application, FilmTec introduced two new composite membranes, NF50 and NF70, which showed great promise for water softening and for simultaneous removal of humic acid. Both of the membranes are fully aromatic crosslinked polyamides. Their NF characteristics can be derived from their modest salt rejection (50% for NaCl), high flux ($7.2 \times 10^{-3} \text{ m}^3/(\text{m}^2 \cdot \text{s})$) and low-pressure operation (0.4MPa) [30]. Great efforts have been dedicated to NF50 performance testing; however, there are little studies of the morphology of the membrane. The actual compositions of NF50 and NF70 membranes have not been disclosed other than that they are aromatic polyamides.

**Figure 1.12:** SEM picture of FT30 surface.
1.2.3 Models for separation process

Separation of RO membranes has long been described by using various theories and models. The central goal of most modeling research is the prediction of the solvent and the solute flux through the membrane. Currently, several models for RO membranes are available. Among them, two categories: non-porous dense membrane structures, and porous membrane structure, are most well developed. Recently, the NF separation mechanism based on the interaction between electrolytes and the charged pore surface has become an active area of research. However, this topic will be discussed in more detail for inorganic membranes in section 1.3.2. The nonporous/porous membrane models will be introduced briefly in the following sections with emphasis on the fundamental physical principles that underlies the models.

Models based on dense membranes

The solution diffusion model was originally developed by Lonsdale, Merten, and Riley in 1965 [31]. This model assumes that both the solute and solvent dissolve in the nonporous and homogenous surface layers of the membrane and then each diffuse across the membrane in an uncoupled manner in response to gradients in their chemical potential. This gradient is the result of concentration and/or pressure differences across the membrane. Many modifications have been made in solution diffusion models to account for non ideal situations. One example is the work of Sherwood, Brian and Fisher [32], which includes pore flow as well as diffusion of the solute and solvent. This model recognizes that imperfections (pores) exist on the membranes surface through which solute and solvent can flow.

Solution diffusion models provide straightforward routines for estimating the performance of RO membranes. However, the models are based on phenomenological experimental data, which will not give us the knowledge of the relationship between the membrane structure and its properties.
Models based on porous membranes

Models based on porous membrane structures normally assume that the mechanism of separation is determined by both surface adsorption phenomena and fluid transport through the pores of the membrane. In contrast to the solution diffusion models, the membrane is assumed to be meso-porous. These models state that the membrane barrier layer has chemical properties such that it has a preferential sorption for the solvent or preferential repulsion for the solutes. As a result, a layer of almost pure solvent is preferentially adsorbed on the surface and in the pores of the membrane. Solvent from this layer is then forced through the pores under pressure (figure 1.13). The first proposed model was called “preferential sorption-capillary flow” (PSCF) model [33] and later a quantitative expression of the PSCF model called “surface force pore flow” (SFPF) model was developed by Sourirajan and Matsuura [34].

![Figure 1.13: Schematic representation of PSCF model.](image)

Figure 1.13: Schematic representation of PSCF model.
Refinement was made by considering the pore radius distribution rather than the average pore size. Sophisticated numerical techniques were used to solve the model and a good agreement with experimental results of FT30 membrane was obtained by Bhattacharyya et al. [35]

1.3 **Inorganic NF membranes**

In the area of RO and NF, research on inorganic membrane materials is still in a relatively early stage of development. Most of the available inorganic membrane materials have pore size distributions in the range of NF rather than RO. This is mainly due to the technical difficulties of synthesizing fine pore sizes for RO membranes (<1 nm). Preparations of metal oxide particles in the size range of less than 10 nm have been realized in many laboratories. Therefore, new inorganic membrane materials with pore sizes ranging from 1 nm to 5 nm have been reported in literatures in the last 15 years. Inorganic NF membranes may have comparable separation performance as organic NF membranes. In addition, numerous potential benefits arising from the inherent properties of inorganic materials have been recognized, such as chemical, mechanical and thermal stabilities, wider pressure/temperature/$p_H$ operation range, compatibility with organic solvent systems and the ability of regeneration.

1.3.1 **Synthesis and properties of inorganic NF membranes**

**Sol-gel method**

The mostly adopted route for the synthesis of inorganic NF membrane is the sol-gel technique (figure 1.14). In this method, a sol is synthesized and applied to a coarse porous support, which results in gel formation on the surface. This is followed by a heat treatment to solidify the gel layer and to convert it into a microporous or mesoporous membrane. Therefore, the sol-gel method includes two major steps: sol preparation and gel formation.

A sol is a suspension of colloidal particles, generally made from a solution of polymerizable metallorganic precursors. A gel refers to the semi-rigid layer formed by the agglomeration of colloidal particles or the polymerization of metallorganic precursors [36].
The sol synthesis normally employs metal alkoxides, $\text{M(OR)}_n$, as the metallorganic precursors. Alkoxides are easily hydrolyzed with water and form macromolecular structures through condensation reactions. A dispersion, consisting of alkoxides, a solvent (such as an alcohol), water and possible other additives, is formulated so that gelation does not occur before deposition. The solution is then coated on the support via dip-coating or slip-casting methods and a subsequent gelation reaction is triggered to form the NF membrane. The formed membranes are usually solidified by heat treatments. The pore size of porous membranes by the sol-gel process can be controlled by colloidal particle diameters and the heat treatment temperature. The majority of the inorganic NF membranes are formed with this method. Summaries of the membranes prepared by the sol-gel method are provided in the following sections.
Many other methods have been investigated for inorganic microporous membrane preparation. Some of them were initially developed for gas separation purposes, but showed potential for producing NF membranes for liquid filtration applications. However, compared with the sol-gel process, none of these preparation methods have been applied widely for NF water purification membranes. This is because of their high cost, narrow applicable materials range, and lack of microstructure control.

**Alumina**

Alumina is the first material that has been used for inorganic membrane preparation, due to its well known colloidal chemistry [37]. Most alumina NF membranes were produced with the sol-gel method, in which a boehmite sol was synthesized by the hydrolysis of aluminum butoxide or aluminum propoxide in hot water (higher than 80ºC), followed by peptization with acids such as nitric acid. The resulting boehmite sol was coated on a macroporous support and formed a layer of boehmite gel. γ-Alumina membranes were obtained after firing the boehmite layer at a suitable temperature. To characterize the microstructure of the membrane, two physical properties were most frequently cited, i.e. the mean pore size and the molecular weight cut-offs (MWCO). MWCO are defined as a molecular weight showing a rejection of 90% when a permselectivity test is done with a solution composed of species of various molecular weights, normally polyethylene glycol (PEG). It was shown that the MWCO increased when membrane was fired at higher temperature because of the growth in particle size and pore size (coarsening effect) [40, 42]. A summarization of properties of alumina membranes is listed in the table 1.1:
<table>
<thead>
<tr>
<th>Ref.</th>
<th>Firing temp.(°C)</th>
<th>MWCO/dₚ(nm)</th>
<th>Thickness (μm)</th>
<th>Separation system</th>
<th>Lp×10¹¹ (m³ m⁻² s⁻¹ Pa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>450</td>
<td>500/1</td>
<td>&lt;1</td>
<td>Acid orange</td>
<td>0.97</td>
</tr>
<tr>
<td>42,45</td>
<td>200-900</td>
<td>2000-20000/2.5-5.4</td>
<td>20</td>
<td>PEG</td>
<td>0.38-3.1</td>
</tr>
<tr>
<td>43</td>
<td>450-650</td>
<td>400-600/1.35-1.7</td>
<td>--</td>
<td>Saccharose, Direct red</td>
<td>0.3-0.6</td>
</tr>
<tr>
<td>41</td>
<td>600</td>
<td>7000/3</td>
<td>3-8</td>
<td>PEG</td>
<td>0.75</td>
</tr>
<tr>
<td>46</td>
<td>--</td>
<td>1000/0.5-0.7</td>
<td>2</td>
<td>PEG</td>
<td>0.68</td>
</tr>
<tr>
<td>39,66</td>
<td>450</td>
<td>460/0.65</td>
<td>0.5-1</td>
<td>Saccharose, organic electrolytes</td>
<td>0.3-0.6</td>
</tr>
<tr>
<td>40</td>
<td>400-900</td>
<td>900-40000/3.4-8.7</td>
<td>~6</td>
<td>PEG</td>
<td>1.3</td>
</tr>
<tr>
<td>44</td>
<td>--</td>
<td>600/0.6-1</td>
<td>1-2</td>
<td>PEG</td>
<td>0.68</td>
</tr>
</tbody>
</table>

PEG = polyethylene glycol.

**Table 1.1:** γ-Alumina membrane structural properties and performance.

Consistent characterizations of the pore size and MWCO are always difficult and the values critically depend on the synthesis conditions, measurement methods and testing environments. Therefore, the relationships between mean pore size and MWCO may have certain deviation for the data obtained in the different laboratories. However, it is agreed that increasing firing temperature results in increasing pore size and MWCO.

**Titania**

Titania membranes show excellent chemical resistance, and can be used in wider pH range than γ-alumina membranes. At present, extensive efforts have focused on the preparation of porous TiO₂ membranes having small pore sizes in the NF range. Membrane with nano-sized TiO₂ particles (3-5 nm) can be prepared with sol-gel methods by carrying out hydrolysis and condensation reactions of titanium alkoxides (such as titanium tert-amyloxide / titanium tetraisopropoxide / tetraethyl orthotitanate) with a certain amount of water in the alcohol media (such as tert-amyl alcohol/ isopropanol)[48,54]. The reaction conditions (temperature, time etc.) are controlled according to individual
recipes. The amount of water and the $p_H$ value are controlled precisely to form a polymeric sol rather than a colloidal particulate sol. Therefore, a smaller particle size resulting in a finer membrane pore size is possible. Table 1.2 shows some recent work on TiO$_2$ membranes.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Firing Temp.(°C)</th>
<th>MWCO/$d_p$(nm)</th>
<th>Thickness ($\mu$m)</th>
<th>Separation system</th>
<th>$L_p \times 10^{11}$ (m$^3$m$^{-2}$s$^{-1}$Pa$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>400-1170</td>
<td>--/3-180</td>
<td>2</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>48,49</td>
<td>200-400</td>
<td>--/1.4-3.2</td>
<td>1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>59</td>
<td>300-400</td>
<td>--/&lt;2-4</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>51</td>
<td>500</td>
<td>--/1.5</td>
<td>--</td>
<td>PEG200(R=0.2-1)</td>
<td>25</td>
</tr>
<tr>
<td>52</td>
<td>500</td>
<td>&lt;1000/1-2</td>
<td>--</td>
<td>Direct Red (MW991)</td>
<td>33.8 pwf</td>
</tr>
<tr>
<td>53</td>
<td>450</td>
<td>480/0.9(cylinder pore)</td>
<td>0.05</td>
<td>PEG</td>
<td>5.6</td>
</tr>
<tr>
<td>54</td>
<td>450</td>
<td>500,600,800/0.8,1.2,&lt;3.5</td>
<td>--</td>
<td>Sugars</td>
<td>0.2,2,3.5</td>
</tr>
<tr>
<td>55</td>
<td>--</td>
<td>1900/2</td>
<td>1.6</td>
<td>PEG</td>
<td>13.75</td>
</tr>
<tr>
<td>56</td>
<td>200-400</td>
<td>&lt;200/1.6-3.4</td>
<td>0.1</td>
<td>PEG</td>
<td>1.11</td>
</tr>
<tr>
<td>57</td>
<td>300</td>
<td>200-800/2</td>
<td>--</td>
<td>PEG</td>
<td>1.11-8.05</td>
</tr>
<tr>
<td>58</td>
<td>300</td>
<td>400/0.9</td>
<td>0.05-0.15</td>
<td>PEG</td>
<td>--</td>
</tr>
</tbody>
</table>

pwf: pure water flux.

Table 1.2: Titania membrane structure and performance.

Normally the sol-gel route results in an amorphous phase TiO$_2$ in the gel dried at room temperature. Phase transition from amorphous to anatase and from anatase to rutile occurs at 300-400°C and 400-600°C, respectively. Therefore, it is important to control firing temperature in order to obtain controlled pore sizes in the membrane structure, because, normally, a phase transformation will result in dramatic increase in pore size.
Zirconia

Zirconia is another promising material for ceramic NF membranes. Zirconium propoxide or butoxide are mainly used as precursors in the generation of zirconia sols. However, these zirconium alkoxides are highly sensitive to water. Violent hydrolysis of the alkoxides always leads to suspension of large particles, which hampers the preparation of nano-sized particle sols. Therefore, only a few reports have appeared on the successful preparation of zirconia NF membranes. A overview of the current research status of ZrO₂ membranes is provided in Table 1.3:

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Firing temp.(ºC)</th>
<th>MWCO/dₚ(nm)</th>
<th>Thickness (µm)</th>
<th>Separation system</th>
<th>Lp×10¹¹ (m³m⁻²s⁻¹Pa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>470-1170</td>
<td>--/3-80</td>
<td>3</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>48</td>
<td>300-400</td>
<td>--/1.4-3.9</td>
<td>1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>69</td>
<td>400</td>
<td>--/1.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>70</td>
<td>450</td>
<td>&gt;10000/4</td>
<td>0.1-0.3</td>
<td>Polysaccharide</td>
<td>0.83 pwf</td>
</tr>
<tr>
<td>71</td>
<td>500</td>
<td>--/3.6</td>
<td>0.15</td>
<td>Soybean oil/hexane</td>
<td>33</td>
</tr>
<tr>
<td>52</td>
<td>500</td>
<td>&lt;1000/1.3</td>
<td>&lt;0.05</td>
<td>Direct Red (MW991)</td>
<td>22.2 pwf</td>
</tr>
</tbody>
</table>

Table 1.3: Zirconia membrane structure and performance.

Zirconia particles undergo a phase transformation at high sintering temperature from the tetragonal to the monoclinic structure. The transformation temperature may vary with different particle sizes. Larbot et al. [47] reported a transformation temperature of 720ºC for their sol-gel prepared zirconia. The phase transformation resulted in an increase in pore diameter.

Composite membranes

Many composite inorganic membranes have been investigated for improved membrane structure and performance. Two methods are employed to prepare composite membranes. One is synthesizing membrane layers of metal oxides that contain more than one
metal element. The other one is producing multiple layers of different compositions. The first method is predominantly applied for composite membrane preparation. Guizard et al. [61, 62] reported the synthesis of electrically conductive RuO$_2$+TiO$_2$ membranes on alumina supports through either colloidal suspension or polymeric gel routes. Precursors were Ti(OPr)$_4$ and RuCl$_3$·3H$_2$O (1/1 molar ratio) dissolved in propanol (2-10%). Organic binder was added to help the formation of the gel layer on the support. It is followed by sintering the membrane at 400-700ºC. Membranes were reported with mean pore diameters of 10-20 nm by using colloidal gels and 5 nm from polymeric gels.

Uhlhorn et al. [63] reported the synthesis of three types of binary membranes γ-Al$_2$O$_3$+TiO$_2$, γ-Al$_2$O$_3$+CeO$_2$ and γ-Al$_2$O$_3$+ZrO$_2$. These membranes were formed by slip-casting the mixed dispersion of two oxides on an α-alumina support or on supported γ-alumina membranes. The sintering temperature ranged from 450-600ºC and the pore diameters were well controlled around 2.4-2.6 nm.

Qunyin Xu et al. [59] reported thermal stability improvements for 20%ZrO$_2$+80%TiO$_2$ or 90%ZrO$_2$+10%TiO$_2$ mixed-oxide membranes. A 1.4 nm mean pore size structure was thermally stable up to 500ºC and 400ºC for 20%ZrO$_2$ and 90%ZrO$_2$ mixed-oxide membranes, respectively. Therefore, an improved mechanical strength was obtained without sacrificing the microporous properties.

A magnesium oxide (13 mol%) stabilized zirconia membrane (ZrO$_2$+MgO) was synthesized and characterized by R. Vacassy et al. [69]. It was believed that the addition of magnesium helped to stabilize zirconia into a cubic crystal structure up to 900ºC. The pore radius and the thickness of the membrane when sintered at 400ºC were 0.43 nm and 50-200 nm, respectively. High water permeability ($3.4 \times 10^{-11}$ m$^3$/m$^2$sPa) and a good salt rejection rate (66.3% for sulfates) were reported for this membrane.

SiO$_2$+ZrO$_2$ composite membranes were fabricated by T. Tsuru et al. [65-68] and T. Yazawa et al. [64] with colloidal sol mixtures (molar ratio Si/Zr 7/3...9/1). According to T. Tsuru, the MWCO of a sugar solution was controlled between 200 and 1000 by regulating the colloidal diameters of sol solutions in the final coating stage. The pore size was from 1.0 to 2.9 nm and the water permeabilities ranged from 0.15 to
1.5×10^{-11} \text{ m}^3/\text{m}^2\text{sPa}, respectively, when membranes were fired at 570°C. The purpose of doping silica with zirconia was to improve the stability of silica in aqueous solutions and it was reported that the membranes were stable in aqueous solution at $p_{H_1} = 5$ and 25°C for periods as long as 100 days.

One case of composite membranes with multiple layers of different compositions was the work done by Y. Elmarraki et al. [60]. They investigated the properties of TiO$_2$-ZnAl$_2$O$_4$ membranes. They prepared a bilayer membrane with a (ZnAl$_2$O$_4$ layer)/(TiO$_2$ layer) structure and also a single layer membrane of a ZnAl$_2$O$_4$+TiO$_2$ mixture. It was speculated that the membrane consisting of two different materials with opposite surface charge increased the electrostatic interactions with the filtered ionic species. The pore sizes of the bilayer membrane and the mixed oxide membrane were 3.5 nm and 6 nm, respectively. It was concluded that the performance of the bilayer membrane was much improved, especially with M$^{2+}$A$^{2-}$ type electrolytes.

Many cases of successful modification/improvement have been demonstrated by various groups, which indicate the great potential of inorganic NF membranes.

**New materials**

Besides the predominant research effort based on Al$_2$O$_3$, TiO$_2$ and ZrO$_2$ as the matrix materials for NF membranes, many other ceramic materials have been investigated by several groups.

Uhlhorn et al. [63] reported the properties of microporous ceria membranes in 1988, and compared them with their work on titania membranes. Sintering of single phase CeO$_2$ membranes at higher temperatures always resulted in denser coatings. The 2 nm mean pore size of 300°C sintered CeO$_2$ membranes became undetectable when the membrane was sintered at 600°C. The overall porosity of CeO$_2$ is much lower than TiO$_2$ membranes.

R. Vacassy et al. [72] synthesized a microporous MgAl$_2$O$_4$ spinel membrane from a stoichiometric mixture of isopropanol solutions of aluminium isopropoxide and magnesium ethoxide. Because of the absence of any phase transition up to 2000°C, MgAl$_2$O$_4$
spinel was considered as a good candidate for inorganic membrane materials. Microporous MgAl₂O₄ spinel membrane sintered at 380–480°C showed a pore size ranging from 0.95–1.03 nm. A membrane of 300 nm thickness was prepared on a mesoporous zirconia substrate.

Hafnia ceramic NF membranes were prepared by J. Palmeri et al. [73, 74]. The reason for considering HfO₂ was its high thermal stability (up to 1850°C without allotropic transformation of the monoclinic form) and high chemical stability. The hafnium alkoxide precursor was synthesized in their laboratory and the sol-gel routine was carried out for nano-pore size membrane preparation. The membranes were sintered in a temperature range of 450…650°C and showed a pore radius of 0.7…2.0 nm. The thickness of the membrane range was 0.1…0.2 μm. The PEG solution testing showed a 420 MWCO at 0.67×10⁻¹¹ m³/m²sPa. The salt rejection behavior of the membrane could be explained by the Donnan exclusion mechanism [74].

L.R.B. Santos et al. [75] reported sol-gel synthesized SnO₂ ultrafiltration membranes. SnO₂ offers higher chemical and thermal resistance compared with the well known materials such as silica, alumina and zirconia etc. The SnO₂ membrane of 0.3 μm layer thickness had a 3.0 nm mean pore size when sintered at 400°C. A high CaCl₂ rejection rate (95%) was reported for this membrane.

Recent research interests of materials for NF membranes focus on new metal oxides that are more stable, controllable and predictable. Development of membrane materials with different ionic adsorption/surface charging properties is also an attractive topic for further exploration. More and more new membrane materials have enriched this research area and broadened the application of inorganic NF membranes.

### 1.3.2 Separation mechanism and modeling

In industrial water desalination applications, NF membranes are normally employed for those processes that require high flux and modest purification capability, such as brackish water softening. When the media to be filtered is an aqueous electrolyte, surface charge phenomena plays an important role in determining the separation behavior based on electrokinetic effects. Ion separation is possible due to the electrostatic interaction between
ions and surface charge, even if the pore size of the membrane is much larger than the ion size [87-91]. Transport mechanisms through charged porous membranes, where electric migration, chemical diffusion and convection occur simultaneously, has been investigated by assuming different geometries for the pore structures of the membranes [90,92,93]. The complicated nature of this problem requires modern computational tools to obtain quantitative predictions for the separation process. The details of each individual model will not be described in this literature review. The focus will be put on the underlying physical concepts.

**Surface charge and double layer**

Most substances acquire a surface electric charge when brought into contact with a polar (e.g. aqueous) medium. It has been proposed in the literature that when a metal oxide surface is contacted with an aqueous solution, complicated surface reactions occur [95]. The resulting net surface charge density is a function of solute concentration and type.

**Double layer model**

*Figure 1.15:* Schematic of a diffuse electric double layer.
Once the surface obtains a net charge, it will influence the distribution of nearby ions. Ions of opposite charge (counter-ions) are attracted towards the surface and ions of like charge (co-ions) are repelled away from the surface. This, together with the randomizing effect of thermal motion, leads to the formation of an electric double layer made up of the charged surface and a neutralizing excess of counter-ions, distributed in a diffuse manner [1.15].

**Potential and concentration distribution**

Quantitative treatment of the electric double layer is a difficult problem. However, with various simplifications and approximations, this problem can be simplified and solved to provide a reasonable level of sophistication and usefulness.

![Figure 1.16: Concentration and potential profile for positively charged flat surface.](image)

The simplest quantitative treatment of the diffuse part of the double layer is based on an infinite extended, uniformly charged flat surface. It is shown that the potential decays exponentially as a function of distance from the surface ($x = 0$) to the bulk solution ($x = +\infty$). The local concentrations of counter-ions and co-ions, which are functions of the local potential, decrease or increase accordingly until the bulk concentration is reached. A qualitative schematic representation of the potential and charge distribution is shown in figure 1.16 for a positively charged surface. Here $1/\kappa$ is called the Debye
length, which is usually considered as the thickness of the double layer as shown in figure 1.16.

**Donnan exclusion and extended Nernst-Planck model**

To simplify the explanation, a capillary model will be taken to represent the pore structure of the membrane. After the membrane is immersed in an aqueous electrolyte solution, a spontaneous preferential adsorption occurs and net surface charge is formed on the pore surface, which results in the presence of a potential and concentration profile. When the pore diameter is small enough ($1/\kappa$ has the magnitude of several tens to several hundreds of nm), the potential profiles overlap significantly and so does the concentration profile. Under such conditions, it is appropriate to consider the pore surface and the solution inside the pores as a spatial region with the same potential, $\Phi_0$. This potential ($\Phi_0$) is higher (or lower) than the bulk solution ($\Phi=0$ at $x>>1/\kappa$) for the case of a positively (or negatively) charged surface (figure 1.17). The potential difference between the feed bulk and the pore liquid is referred to as the Donnan potential [7].
Figure 1.17: Donnan exclusion effect for separation.
It is intuitively clear that the counter ion concentration is higher while the co-ion concentration is lower in the mobile pore phase compared to the bulk phase. It can be seen that the Donnan potential attracts counter ions from bulk phase to the membrane phase and repulses the co-ions from the membrane phase to the bulk phase. Combined with the diffusion movement of the ions, concentration profiles of counter-ions and co-ions, which are similar to those of charged flat surface, will form from the membrane phase to the bulk solution. When a pressure difference is applied across the membrane, the permeating liquid will flow through the pore. Due to the requirement of overall electrical neutrality, the concentration of counter ion and the co-ion in the permeation flux must be equal. However, the co-ion concentration in permeation flux can not be higher than that in its source, which is the membrane phase. Therefore, the counter/co ions concentration in the permeation flux has to be equal to the co-ion concentration in the membrane phase and lower than that in the bulk phase. This is called the Donnan exclusion effect and it underlies the separation mechanism of meso-porous NF membranes.

The models based on the Donnan effect were able to qualitatively predict that the rejection is a function of the feed solution concentration, ionic valences, pH value, and surface adsorption properties [94]. However, this model did not take into account the diffusive and convective fluxes, which are also important for the separation mechanism. For instance, when the potential and concentration profiles at the interface of the permeation side and membrane phase are under consideration, a decaying curve rather than an abrupt drop is more likely to occur. The extended Nernst-Planck model has recently been applied for a quantitative description of the transport phenomena in NF membranes. By taking the diffusion and convection fluxes into account, the extended Nernst-Planck relation is able to predict the separation behavior much more accurately. Calculations of the model always requires advanced computational techniques and normally leads to predictive numerical solution with no adjustable parameters.

1.4 Conclusion and future work in the membrane area

Organic membrane and inorganic membrane have been reviewed and compared in this chapter. Organic membrane is much easier to manufacture and becomes dominantly
commercialized. Inorganic membrane is more stable in extreme operation conditions, such as high or low pH solution and better chloride tolerance. They are also believed to have better resistance against particular and chemical impurities that present in water, and therefore require less restrict pre-treatment for the feed water. Due to the inert nature of inorganic materials, they have longer life time and can be regenerated and reused. However, the properties of inorganic membrane is more sensitive to defects and therefore, the synthesis process of inorganic membrane is much more difficult than organic membranes. This future work section is presented to summarize the review in the chapter and to provide a perspective for future research.

1. The field of commercial organic RO membranes is dominated by two types of polymer compositions, polyamide and cellulose acetates. More than two decades have passed since the development of the NS300 and FT30 polyamide composite membranes, without a major new development in the composition. This field may possibly have reached a maturity in terms of major membrane chemistries. The research opportunities are now more in the areas of solvent-resistant supports, improvements in salt rejections, improved fouling resistance and modeling [11]

2. Inorganic NF membranes hold considerable promise in applications such as water purification, high temperature separation, catalytic membrane structures, and membrane reactors. The related colloidal chemistry and sol-gel processing methods need further investigation. New membrane synthesis methods may be explored.

3. Membranes with new composition and structure should be explored. Application-oriented membrane devices and modules should be designed, developed and optimized.

4. Modeling of membrane separation behavior is becoming an attractive research area. With the development of insights in interfacial chemistry, more capable models will be proposed. Determination of consistent and accurate membrane transport parameters will help improving the reliability of the models.
CHAPTER 2

SYNTHESIS AND OPTIMIZATION OF HIGH SURFACE QUALITY ALUMINA COMPACT MEMBRANE SUPPORT

Filtration casting is used to produce homogeneous porous $\alpha$-$\text{Al}_2\text{O}_3$ disks with a high quality surface, suitable for thin membrane deposition with thickness less than 100 nm. This forming method combines the ability of conditioning a powder into a dilute dispersion of dense particles with a very efficient particle packing process, resulting in very homogeneous compacts with at least one high quality surface. Aqueous slurries of $\alpha$-$\text{Al}_2\text{O}_3$ with solids content of 20 vol% and low viscosity were prepared by using a small amount of dispersion stabilizer and introducing ultrasonic agitation treatment. Relatively high green densities were obtained by vacuum filtration of dispersions with an optimized concentration of stabilizer. The influence of dispersant concentration on surface morphology of compacts is investigated by SEM. In addition mechanical strength, density, water/gas permeability, as well as grain size have been studied to establish the proper sintering temperature for specific membrane support applications.

2.1 Introduction

Inorganic ceramic membranes, based on alumina, mullite, cordierite, zirconia, silica and titania are considered for several applications due to their excellent mechanical strength and resistance to extremely harsh conditions (such as high or low pH, oxidizing conditions and high temperatures). On the availability of such membranes enabled several new developments such as include $\text{H}_2$ [96] and $\text{O}_2$ [97] separation, as well as water purifica-
tion [98]. Usually, inorganic ceramic membranes have an asymmetric multi-layer structure. Their foundation is a macro-porous support sufficiently permeable, strong and also suitable for deposition of successive intermediate and membrane layers [99]. Application of current ceramic membranes is hindered by insufficient flux at acceptable pressure differences. This can be improved by developing thinner quasi-homogeneous membranes with a film thickness down into the 10 nm range.

Because conventional forming methods such as the dry pressing and extrusion may lead to micro-structural inhomogeneity and high surface roughness, the ceramic supports prepared using the above-mentioned technique are inappropriate for application of very thin and perfect membranes.

By insuring the break-down of soft agglomerates as well as removal of hard agglomerated and other impurities in diluted particle dispersions, colloidal processing methods are most suitable for preparing macro-porous defect free supports. Few studies have shown that these methods result in minimizing the occurrence of macro-defects in quasi-homogeneous ceramic particle compact structures [100].

Colloidal processing of $\alpha$-Al$_2$O$_3$ using charge stabilizers was extensively studied as a convenient route to quasi-homogeneous structures [101-104]. The advantage of using charge stabilizers is that they do not affect the viscosity of the dispersion therefore the formation of random dense particle packing structures is promoted.

Recent studies on colloidal processing have focused at different aspects of colloidal compact formation. Many efforts related to $\alpha$-Al$_2$O$_3$ colloidal processing are dedicated to “dilute” state properties such as stability, rheology, and electro-kinetics [105-112]. Other studies describe the sintering process of colloidal filtration compacts and the preparation of fully dense, translucent alumina compacts [113-115]. In addition a few papers pay attention to the “condensed” green or partially sintered compact [112, 116].

In the present study, the method of colloidal filtration is optimized for fine-porous $\alpha$-Al$_2$O$_3$ supports with a very smooth surface and a homogenous pore structure that enables the deposition of uniform ceramic layers with a thickness of less than 100 nm.


### 2.2 Experimental procedures

Studies were carried out with two commercially available high purity $\alpha$-$\text{Al}_2\text{O}_3$ powders, AKP15 and AKP30, (Sumitomo Chemical Co. Ltd, Tokyo Japan) with an average particle size of 600 and 300 nm, respectively. Defect-free compacts could be obtained by colloidal filtration of $\alpha$-$\text{Al}_2\text{O}_3$ dispersion with the optimum dispersant concentration. For the preparation of AKP30 supports, 50 g of $\alpha$-$\text{Al}_2\text{O}_3$ AKP30 powder was mixed with 50 mL of HNO$_3$ solution with concentration of $10^{-2}$ mol L$^{-1}$ (pH=2.0) to have a 1.6 $\mu$mol-HNO$_3$/m$^2$-$\alpha$-$\text{Al}_2\text{O}_3$ powder. Dispersion of as-delivered alpha alumina powder was achieved by ultra-sonic treatment (Model 102C, Branson, USA) for 10 minutes [117] at a power level of 60 W. During this treatment, the temperature of the mixture was kept below 20°C by flowing tap water between the double walls of the glass treatment vessel. For removing large agglomerates and other impurities the dispersions used for compact formation were screened with a 20 $\mu$m aperture Nylon mesh after ultrasonic treatment. In addition to avoid air born contamination the filtration procedure is carried out at Class 100 cleaning room. Disk-shaped $\alpha$-$\text{Al}_2\text{O}_3$ compacts were made by vacuum filtration on an Ø 220 nm pore polysulfone membrane (Millipore, Billerica, MA). The compacts always had a dull (rough) surface at the filtration membrane side, while the opposite (upper) surface of the most homogeneous compacts had a very smooth shiny appearance. This compact surface is further referred to as “top surface”. The AKP15 supports were prepared in the same manner except that the $\alpha$-$\text{Al}_2\text{O}_3$ powder was AKP15 and the dispersion agent was 50 ml aqueous solution of Aluminon at 0.2 wt%, with pH adjusted by ammonia to 9.5.

The compacts encapsulated in alumina trays and cover plates were sintered in air, with a heating/cooling rate of 2°C/minute and the sintering temperature varying between 650 and 1350°C with 10 hrs dwell time.

The compacts’ apparent density was investigated with a commercially available mercury pycnometer (DBA100-1, PMI, Ithaca, NY) that was modified for improved accuracy. In addition the influence of charge stabilizer concentration on compact formation was studied.
The AKP30 compacts are further indicated as S2.00pH750C to indicate the initial pH of the dispersion and the sintering temperature, 2.00 and 750ºC, respectively, in this example.

Water permeation was determined with the dead-end technique. While the compacts were maintained at a constant applied pressure difference, $\Delta p$ of 400 kPa, the accumulated weight of pure water permeate was recorded as a function of time with an electronic balance, and converted into mechanical permeability according to

$$k_p = \frac{j_v \times X \times \eta}{\Delta p}$$

where $j_v$ is the volumetric flux, $X$ the compact thickness in the permeation direction, and $\eta$ the dynamic viscosity, in this case of pure water.

In addition gas permeability was determined in a home-made setup, configured for the non-stationary dead-end mode [118]. The sample mounted in a gas permeation cell was kept at constant temperature inside a drying stove. A constant pressure of testing gas was supplied at feed side. At the start of the measurement, gas passes through the compact into a pre-evacuated reservoir with constant volume, $V_{cell}$. Assuming the ideal gas law to be valid the gas permeability, $k$, is determined for isothermal conditions by non-linear regression from:

$$\ln \left( \frac{P^0_t}{P^0_t - P_v} \right) = k \left( \frac{A}{X} \right) \left( \frac{RT}{V_{cell}} \right) t$$

where $k$ is the gas permeability, $A$ the exposed homogenous support surface, $R$ the gas constant, $T$ the absolute temperature, and $t$ the relative time.

The microstructure of the top surface of the compacts as well as of the cross section perpendicular to the disk surface, made by fracture, grinding and polishing was investigated with scanning electron microscopy (Field-Emission Environmental SEM Philips XL30). To qualitatively analyze the homogeneity of alpha alumina compacts, a very thin slice of compacts was cut by Focused Ion Beam (FIB) (Philips DB235 SEM) milling and imaged with TEM (CM200).
2.3 Results and discussion

It is well known that for the application of membrane supports, high permeability and strong mechanical strength are two desirable properties that are normally contradictory to each other. Therefore, the strategy employed in our synthesis was that one of these two properties was emphasized. For example, AKP30 supports have a low permeability since the particle and pore sizes of such supports were small, therefore, HNO₃ was used as dispersant agent to increase the mechanical strength. On the other hand, Aluminon prepared supports were weaker and therefore, AKP15 was chosen as the particle to have larger pore size and permeability.

The packing density and microstructure of colloidally prepared compacts can be influence by type as well as by the strength of the interaction between the ceramic particles in suspension, described as electrostatic; steric or a combination of those. For AKP30 supports, nitric acid (HNO₃) used in present study provides charge-type colloidal stabilization by preferential proton-sorption. Direct observation of the influence of concentration of charge stabilizer, expressed as $\text{pH} = -\log \{[\text{HNO}_3]\}$, on colloidally compact formation process has been summarized in table 2.1.

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Upper surface appearance</th>
<th>Drying effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>Rough</td>
<td>Little shrinkage; warping; release difficult</td>
</tr>
<tr>
<td>1.5</td>
<td>Smooth</td>
<td>Release difficult</td>
</tr>
<tr>
<td>2.0</td>
<td>Smooth</td>
<td>Some shrinkage; start to release easily</td>
</tr>
<tr>
<td>2.5</td>
<td>Smooth</td>
<td>Significant shrinkage causing cracking</td>
</tr>
<tr>
<td>3.0</td>
<td>Smooth</td>
<td>Significant cracking</td>
</tr>
</tbody>
</table>
Table 2.1: Direct observation of colloidal filtration compacts, initially stabilized in aqueous HNO₃ at various pH values.

In the investigated pH interval (from 1.0 to 3.0) the radial shrinkage was found to increase with the initial $p_{\text{H}}$. According to the data shown in Table 1, optimized alpha alumina compacts could be obtained only with initial nitric acid concentrations equal to $10^{-5}\text{mol g}^{-1}$, based on the dry solid. At nitric acid concentrations, higher than the optimum value, corresponding to pH values lower than 2, excessive warping was observed during drying. Moreover high dispersant concentrations resulted in difficulties to release the compact from the filtration mold after drying. In addition crack formation at very high nitric acid concentrations has been also observed. The supernatant of the $\alpha$-Al₄O₃ suspension stabilized at optimum dispersant concentration was found to contain 1300 ppm Al³⁺ and had a pH ~ 4. HNO₃ tends to be most effective at a pH < 4, where part of the $\alpha$-Al₂O₃ and residual transition alumina structures start to dissolve [119]. While this dissolution may be an advantage in the breakdown of weak agglomerates, it may affect sintering and eventual properties of the compacts [119].

Mercury Pycnometry results for AKP15 and AKP30 compacts obtained by colloidal filtration of aqueous alumina suspension dispersed with Aluminon and HNO₃, respectively, and sintered at 650 C for 10 hrs are shown in figure 2.1. At each concentration, the density was taken from an average of at least five individual samples. Due to the reaction between nitric acid and AKP30 the initial pH was found to change, but details about the time dependence and location could not be obtained. Therefore the density plotted in figure 2.1 is discussed only in terms of initial pH.
Figure 2.1: Apparent density data of AKP15 and AKP30 compacts made by filtration of 20 vol% alpha alumina suspension vs. Aluminon concentration and initial pH, respectively.

The relative density of slightly sintered alumina compacts, obtained with optimum dispersal agent concentration values, were measured with mercury Pycnometry. They were found to be as high as 69% for AKP15 and 66% for AKP30, which is slightly higher than the random packing limit of mono-sized spheres (62-64%) [120, 121]. It is believed that these higher values are not caused by any significant short or long range order; however the slightly oblique shape of $\alpha$-Al$_2$O$_3$ particles and the non-monodisperse particle size distribution could provide an explanation for this observation [122].

The influence of pH on AKP30 compact densities provide in Figure 2.1, shows an asymmetric S-shape curve. The density can be correlated to colloidal stability of the initial dispersion. In order to impart colloidal stability, it is necessary to create repulsion forces between the particles that hinder agglomeration by short range van der Waals attraction [123, 124, 125]. Due to preferential proton sorption, the particles in the dispersion medium acquire a surface charge, leading to an effective surface charge which stabilizes the suspension by an electrostatic mechanism. Initially by addition of nitric acid in the suspension more dispersant can be absorbed on the surface of particle, resulting in an increment of the surface potential. This results in considerable stabilization of the dispersion and a higher compact density. On the other hand if more dispersant (HNO$_3$) is
added, the $\alpha$-Al$_2$O$_3$ partly dissolve [125] which, in turn leads to precipitation and inhomogeneous shrinkage during drying.

The density of $\alpha$-Al$_2$O$_3$ compacts vs. sintering temperature is shown in figure 2.2. From this figure it becomes clear that below 1000 C initial sintering stage takes place with neck formation and overall densification process does not occur. Significant densification was found to occur at temperatures $>$1000ºC. Densification stops at 1250ºC with a relative density of 99.2%.

![Figure 2.2](image)

**Figure 2.2:** Apparent density data of sintered compacts; AKP30 supports made by filtration of aqueous HNO$_3$ dispersions at initial $p_H = 2$, and AKP15 supports made by filtration of aqueous Aluminon dispersions at 0.5wt%.

Microstructural evolution of 8 samples, S2.00ph650…1350C was observed with SEM; representative upper disk surfaces of the compacts are shown in figure 2.3. After heating
at 650ºC the original particles are clearly distinguishable; the compact has significant connected porosity with some neck formation between the particles. The same morphology is found in samples sintered up to 850ºC. In the compacts, sintered at 950 and 1050ºC, the original particles combined to form a smaller number of bigger grains, connected by necks, while the porosity still appears predominantly connected.

![Figure 2.3](image)

**Figure 2.3:** Effect of sintering temperature on the surface of S2.00pH compacts observed by SEM.

After heating at 1150ºC dense regions appear in a matrix of connected grains and porosity. In compacts sintered at 1250ºC the structure is nearly dense while significant coarsening occurred with some isolated porosity between the grains. In the image shown for the sample sintered at 1350ºC further coarsening is observed but no porosity. The latter is accidental for this image since the sample was not fully dense.

Fracture cross-sections of the compacts sintered at two different temperature observed by SEM are shown in figure 2.4. Inspection of these cross-section images confirmed the previous description of the sintering process for which up to 1050 C no densification occurs. At 1150ºC the formation of prismatic fractures was found confirming the occurrence of small regions of high density. The compact sintered at above 1150ºC shows significant transgranular fracture, indicated by the relatively flat regions in the plane of the
picture. Moreover it was clearly visible that at 1350 C the porosity is completely converted into closed and isolated.

**Figure 2.4:** SEM image of cross section of α-Al₂O₃ compacts (S2.00ph) sintered at (a) 1150 C and (b) 1350 C.

The water permeability of S2.00ph750…1150C is shown in figure 2.5. From this figure can be observed that water permeability shows a maximum at a sintering temperature of 950 C. Such behavior could be explained by the occurrence of coarsening in combination with little overall shrinkage. According to the Carman-Kozeny equation, valid for a
packed bed of mono-sized spherical particles, the water permeability scales with porosity, \( \phi_p \), and \( r_p^2 \) where \( r_p \) is a characteristic pore radius.

During sintering up to 950°C, \( \phi_p \) remains constant while \( r_p^2 \) increases because smaller particles “disappear” into bigger particles leading to less flow constrictions. However, if the sintering temperature is further increased (above 1000 C), the overall pore size starts to decrease significantly with decreasing of porosity as shown in Figure 2.4. Above 1250 C the water permeability became effectively zero at which the internal porosity is expected to be closed or no longer connected, in agreement with the micro-structural observations. Moreover, during the water permeability measurements, it was found that compacts show sufficient strength for a pressure drop of 1.5 MPa.

![Water permeability](image)

**Figure 2.5:** Water permeability of AKP15 and AKP30 supports as a function of sintering temperature.
In addition, the He permeability of S2.00ph750…1350C, studied using non-stationary single gas permeation technique is shown in figure 2.6. For interpretation of these measurements it is assumed that permeability can be written as a sum of two terms such as Knudsen and viscous flow. The helium permeability of alumina compacts shows a slight pressure dependence that indicates that helium gas transport occurs primarily by the Knudsen permeability which scales proportional with pore radius [99]. The supports have maximum permeability for a sintering temperature of also 950°C which is in excellent agreement with water permeability results. In addition, above 950°C helium permeability continuously decreases and at ≥1250°C no significant He permeation could be observed. The Knudsen permeability scales as \( r_p \), as opposed to viscous flow permeability scaling as \( r_p^2 \).

![He gas permeability](image)

**Figure 2.6:** Temperate development of gas (He) permeability for AKP15 and AKP30 supports.
α-Al₂O₃ compacts prepared using the above-mentioned optimized colloidal technique posses a very smooth, homogeneous surface roughness that make them excellent candidates for deposition of very thin inorganic film membrane on the order of <100 nm. As an example, a well-defined membrane film with thickness around 50 nm [126] is shown in figure 2.7. From Focused Ion Beam (FIB) cross sections of supported membranes, observed by TEM it can be concluded that the surface roughness of compacts prepared using colloidal filtration technique is estimated to be less than 20 nm. From figure 2.7 it can be also seen that packing of α-Al₂O₃ particles, obtained using nitric acid as a charge stabilizer, is quas-homogeneous over >100 nm length scales.

**Figure 2.7:** TEM images of FIB cross-sections of sintered S2.00pH compacts coated with zirconia based ceramic taken from [126].

The supported membrane structures as shown in figure 2.7 is considered to be a good starting point for high-efficiency nano-filtration membranes and fuel cell structures. In
addition, it offers perspectives on the development of very thin membrane layers for high-flux, high-selectivity gas separation.

2.4 Conclusions

Colloidal filtration of well-dispersed $\alpha$-Al$_2$O$_3$ particles with effective particle size 300 nm (AKP30) and 600 nm (AKP15) was successfully applied to produce defect-free, porous, disk-shaped compacts with a superior quality of the upper disk surface. This surface is suitable for deposition of continues film membranes with thickness of less than 100 nm. Alumina compacts with a well-defined surface quality were obtained with sonification and colloidal filtration of 50 wt% $\alpha$-Al$_2$O$_3$ particles in aqueous solution of HNO$_3$ at pH 2.0 for AKP30 and, aqueous solution of 0.2 wt% Aluminon at pH 9.5 for AKP15. Water and gas permeability, density as well as grain size can be used to establish the proper sintering temperature for specific membrane support application. Both water and gas permeability of optimized compacts show a maximum for a sintering temperature of 950$^\circ$C for AKP30 and AKP15, explained by the occurrence of pore-coarsening, combined with little overall shrinkage. During the water permeability measurements, compacts have shown sufficient strength for a pressure drop of 1.5 MPa for AKP30 and 1.0 MPa for AKP15. The optimized sintering temperatures were found to be 950 $^\circ$C for AKP30 supports and 1050 $^\circ$C for AKP15 supports by taking the permeability and mechanical strength into consideration.
Mesoporous $\gamma$-alumina membranes are been prepared with the well established and documented sol-gel route [140]. To obtain a defect free membrane, it is critical to have a nanoparticle solution available with a narrow particle size distribution and without any other large particle contamination. An innovative ultrasound assisted screening process was developed to purify Boehmite nanoparticle solutions that were used for the sol-gel route of membrane preparation. Systematic studies have been carried out to compare the treated sol quality. The chapter focuses on the ultrasound assisted screen process, which was found to be a potential universal method for nanoparticle solution purification.

3.1 **Introduction**

The realization of unique physical properties of nano scale materials depends critically on the possibility to produce homogeneous micro-structures with characteristic features in the $<100$ nm size range. A viable approach to synthesize such materials consists of colloidal deposition of well-dispersed particles, followed by thermal processing. However, practical syntheses of nanoparticle dispersions often lead to partial agglomeration and a broad size distribution which has an unfavorable effect on the final result. It is therefore interesting to develop size-based methods for efficient removal of agglomerates and large particles. Many existing methods were primarily developed for bio-molecular or organic supra-molecular applications and target dimensions in the 0.5…5 nm range. Recent pro-
gress in the application of these separation techniques to inorganic nanoparticles has extended their capabilities, however, with several limitations. For instance, chromatography [127…129], field flow fractionation [130,131], and capillary electrophoresis [134,135] can only process low particle concentrations or small volumes of liquid. As a result these methods are used, primarily, as characterization techniques rather than as manufacturing/processing methods. The solvent/anti-solvent precipitation method [132,133] is very system-dependent and normally consumes large amounts of solvent. High speed centrifugation has long been used as an initial purification step after nanoparticle synthesis. However, this method also removes part of the smaller particles and therefore inevitably reduces the yield. Another drawback of centrifuge method is that the sediment formed by the particles re-disperses quickly into the supernatant after the centrifuge’s rotation stops, which has a negative effect of the quality of the treated sol.

Traditional screening by filtration has also been widely applied for purification of dispersions. However, the application of this method for polydisperse and agglomerated nanoparticle dispersions gives rise to several technical difficulties, such as clogging of the filter and poor size selectivity [136]. These problems, on the other hand, can be overcome by employing an ultrasound-assisted filtration setup similar to the one described in [137] and a carefully chosen meso-porous straight pore membrane as the filter. For instance, anodic aluminum membranes offer a 20 nm pore size; much larger pore density and hence larger yield than the track etched membrane used in [137].

The purpose of the present paper is to demonstrate the merits of ultrasound-assisted-screening in the purification of nanoparticle suspensions, using anodic alumina membranes with pores sizes, tailored to the primary particle size. A Boehmite sol, prepared by the well-established Yoldas route [138] is used for the purpose of demonstration. Such sols have a relatively wide particle size distribution in the range of 10 nm…1000 nm, and are used, for instance, in the preparation of thin supported γ-alumina membranes with a pore Ø of approximately 4 nm [139]. To prepare homogeneous membranes with a narrow pore size distribution, all particles with a diameter >20 nm need to be removed [139]. In [140] it is shown how removal of larger particles and agglomerates by centrifugation at 59,000g for 3 hours results in major improvement
of membrane quality. This result led us to use this centrifugation treatment as a reference for comparison with the ultra-sound-assisted screening method.

### 3.2 Experimental Section

A concentrated Boehmite nanoparticle sol was prepared by hydrolysis of ATSB, followed by peptization [138]. The screening filter is suspended with its edge clamped to the funnel to allow for maximum transverse vibration in the filter plane. This avoids the formation of a layer of clogged particles to maintain a stable filtrate flux. It is critical that no solid mechanical support is present directly below the filter material so that the ultrasound can propagate unconstrained in the filter/sol interface. Therefore, only a small pressure difference could be applied to promote the filtration flow without disrupting the filter. This pressure difference was maintained at approximately 15 mBar and <30 mBar in any case by using the pressure controller of a Buchi rotovaper system [R-205V, Brinkmann].
A commercially available 20 nm pore Ø anodic aluminum membrane, [47 mm Ø Ano-disc, Whatman], was used as the primary filter with a 0.8 µm pore Ø cellulose nitrate [AAWP04700, Millipore] membrane as a flexible support backing. Anodic alumina membranes were found to be very suitable for such fine particle screening because of their unique straight channel structure and uniform pore size, see figure 3.2. The pore dimension of anodic aluminum membranes can be precisely manipulated and controlled and hence tailored to primary particle sizes in the range of 10…100 nm; a recent review on the state of the art is provided in [141]. It was found that the Anodisc membranes, used in the present study, had an asymmetric structure with a 2 µm thick top layer and a 20 nm pore Ø, on top of a 58 µm thick bulk material with 100 nm pore Ø. Compared to the track etch membrane originally proposed in [137], the two layer structure of the Anodisc membrane results in a high permeability with yet a sufficiently small surface pore.
size. However, it was also found that the membranes had significant surface defects; the total area of which is estimated to be <1% of the overall apparent area.

**Figure 3.2:** 20 nm Anodisc membrane. (a) FIB cross section of the branched top layer (b) top layer surface and (c) surface area with defect.

The funnel setup was placed in an ultrasonic bath [Fisher Scientific] and 80 ml of Boehmite sol was poured into the funnel, followed by ultrasound-assisted screening at a 15 mBar pressure difference for up to 20 hours while maintaining the bath temperature below 10ºC. The particle + agglomerate size distribution of untreated peptized Boehmite
sol (O-γ), centrifuged sol (C-γ), screened sols with (U-γ) and without (F-γ) ultrasound-assistance, were characterized with Atomic Force Microscopy (AFM) [multimode Nanoscope IIIa, Veeco] and Dynamic Light Scattering (DLS) [BI-200SM, Brookhaven]. The as-prepared sols were diluted with aqueous HNO₃ at pH = 3.5 to a concentration of $2 \times 10^{-3}$ g/ml for DLS measurements and further diluted with 18.2 MΩ·cm high purity water [Mili-Q A10 Gradient System, Millipore] to a concentration of $5 \times 10^{-5}$ g/ml for AFM sample preparation. The AFM sample was prepared by spin coating on a 1 cm×1 cm mica surface by application of one droplet of $5 \times 10^{-5}$ g/ml sol at 200 rpm. All sample preparation was carried out at class 100 clean room conditions to avoid airborne particle contamination. The Boehmite content of all sols was obtained by determination of the weight of the gel formed after drying at 70°C for 2 days.

An ion chromatograph [ICS2500 Ion Chromatograph, Dionex] was utilized to test the contamination that is introduced into the sols during the screening process. Before introducing the sol into the ion chromatograph, it was filtered with a 0.1ºµm nitrate-cellulose membrane [VCWP02500, Millipore] to remove most of the particles to minimize the risk of clogging ion the chromatograph column [IonPac AS19 Analytical Column, Dionex].

### 3.3 Results and Discussion

#### 3.3.1 Solid load and filtration rate comparison

Figure 3.3 shows a comparison of the yield of the filtration process with and without ultrasonic agitation. This comparison shows clearly that without ultrasonic vibration, the filter clogs very soon and the filtration process stops. The reproducibility of the filtration yield measurement was not very good due to large variations in the properties of the as-delivered Anodisc membranes. Nevertheless, ultrasound-assisted filtration always exhibited a significantly higher filtration rate which is be explained by a reduction of the clogging effect. During the screening process, a standing wave formed on the surface of the membrane that could be made visible by adding insoluble black particles into the funnel,
as shown in figure 3.4. The formation of this standing wave likely avoids particle clogging and thus results in a sustained, stable and high flow rate for a prolonged period.

**Figure 3.3**: Yield of the filtration process with and without the presence of ultrasonic vibration.
The solid load of original sol was 0.031 g/ml while after centrifuge treatment or filtration with / without ultrasonic excitation, the solid load became 0.012, 0.025 and 0.018 g/ml, respectively. Ultrasonic filtration was found to be capable of retrieving 80% of the particles while simple screening and centrifuge treatment can retain only 58% and 39%, respectively.

3.3.2 Size distributions by Dynamic Light Scattering.

Dynamic Light Scattering has been widely employed for characterization of the size distribution of small particle suspensions for more than four decades, despite several limitations [142]. The DLS method has been thoroughly explored and broadly applied in many different systems by further development of interpretation algorithms and/or combinations with new technologies. To perform a reliable and accurate measurement, the qualitative characteristics of the suspension must be well-known to select a proper type of DLS measurement. For the Boehmite nanoparticle sols of the present study there are two complications:
• The particle shape is non-spherical. From the AFM measurements, discussed in section 3.3, it is concluded that platelets are present with \( \sim 20 \text{ nm}\) \( \Phi \) and a thickness \( \sim 3 \text{ nm} \). This aspect is further discussed at the AFM measurements.

• The particle size distribution is bimodal with the major fraction of particles having a largest dimension of \( \sim 20 \text{ nm} \) and the minor fraction a largest dimension of \( \sim 500 \text{ nm} \).

Detection of a bimodal particle size distributions by multi-angle DLS is described in [143,144]. However, a widely accepted algorithm for solving the multi-angle autocorrelation functions is still under development. On the other hand, combinations of state of art interpretation algorithms, and single angle DLS measurements can result in fairly accurate bimodal distributions, provided two criteria are met:

• The size difference between the two modes must be large: \( \Phi_{\text{big}}/\Phi_{\text{small}} > 2 \).

• The intensity of the light, scattered by the two particle modes must be similar: \( I_{\text{strong}}/I_{\text{weak}} < 20 \) [145].

Fortunately, our Boehmite nanoparticle suspensions were found to meet these requirements and therefore, a single angle measurement at 90° with a conventional CONTIN interpretation algorithm [146] could be used to characterize the particle size distribution of each sol. 5 sets of data were selected for each sol and averaged to produce the results, shown in figure 3.5. This figure indicates that O-\( \gamma \) has a wide, multi-modal particle size distribution in the range of 10…1000 nm. The centrifuge treatment appears to be capable of removing part of the big agglomerates in O-\( \gamma \); however, there is still a substantial amount of coarse particles in the range of 250…400 nm left. This is ascribed to the re-dispersion of sediments shortly after the centrifuge treatment stopped. On the other hand, U-\( \gamma \) showed a much smaller DLS intensity for the same large particle population, while in F-\( \gamma \) that intensity is virtually absent. The larger particles, present in U-\( \gamma \), are likely due to migration of agglomerates through defects in the Anodisc membrane as shown in figure 3.2(c). The absence of larger agglomerates in F-\( \gamma \) is explained by plugging of surface defects in the Anodisc screen in the absence of ultrasonic agitation. It is expected that this plugging occurs due to the initially very high particle flux at the defects. To verify that the occurrence of larger particles was not due to agglomeration over
time, the DLS experiments were repeated 20 days after the first measurement, which revealed no changes in the scattering spectra.

Figure 3.5: DLS particle size distribution of the sols.

3.3.3 Particle size and shape from AFM measurement.

Transmission Electron Microscopy (TEM) is often proposed for a direct observation of nanoparticle size, size distribution and shape in dried sols. However, we encountered considerable difficulties in making such observations. Direct TEM imaging of the ~20 nm Ø particles resulted in blurred shapes overlaid by the micro-structure of the carbon film, used to make the sample conducting. However we found that imaging by application of Atomic Force Microscopy (AFM) provided clear images of the individual particle shape, in addition to perpendicular dimensions. It was found that atomically flat
mica provided a very suitable substrate because the mica surface is hydrophilic and negatively charged at $p_H = 3.5$. This is thought to be beneficial in the formation of an immediate strong adhesion of the positively charged Boehmite particles. It is speculated that the application of the dispersions by spin coating resulted in an instantaneous removal of liquid, such that the particles did not have time to agglomerate during drying. Examples of tapping mode AFM images of C-$\gamma$ on mica and silica are provided in figure 3.6 and figure 3.7, clearly demonstrating the effect of the substrate on agglomeration during deposition.

**Figure 3.6:** C-$\gamma$ spin coated on mica.
Figure 3.7: C-γ dip-coated on a silicon wafer.

A quantitative particle size analysis, using SPIP AFM analysis software [147] was carried out with 3 different 1×1 μm area scans for all 4 sols on mica. A 0.5 nm threshold height was used to remove background noise. 1400…2800 particles were counted for each sol to generate statistically valid histograms of the number vs. diameter and number vs. height. However, the highly localized AFM observation did not reveal visually significant differences between the sols. This is explained by the fact that no large particles (Ø 100…1000 nm) were observed. This, in turn, is ascribed to the low concentration of such large particles as discussed further in this section.
Under the SPIP software platform, a tip characterization command was carried out for each image followed by a tip deconvolution command to compensate for the convolution effect of the finite tip size of 5~10 nm. On average, the tip characterization command, using default settings, reported a tip size of 4…7 nm. A threshold value of 1±0.1 nm was applied for particle size analysis. This threshold value was fine-tuned to isolate closely located particles without introducing too much apparent size reduction for the particle measurement. The collected 3D information of each recognized particle was then sorted and classified according to its diameter. The differential particle volume vs diameter was generated for each sol and the 4 curves obtained in this way are shown in figure 3.8. From this figure it is clear that each sol has similar characteristics in the small size region (<20 nm), while O-γ has significantly more particle volume in the larger size region (30…60 nm). The particles sizes detected by AFM ranged from 2.2 nm to 60 nm and belonged to the group of smaller particles (<100 nm) detected in the DLS measurements. This is explained by the fact that the particle concentration decreases dramatically as the size increases so that many more microscopic images are needed to detect just one such particle, and even more to obtain a statistically correct analysis for larger particles. In practice, it was virtually impossible to obtain relevant population data from AFM for the larger particle group (100…1000 nm) as found in the DLS measurements. A simple estimation shows that, for a well prepared AFM sample, one needs to examine 100 µm² area to find one 100 nm particle and 1 mm² area for one 1000 nm particle. Despite their rarity, the larger particles play a key role in the formation of defects (pinholes) in thin porous films and supported membranes.
3.3.4 DLS and AFM measurement comparison

A comparison of DLS and AFM measurements provides more understanding of pros and cons of both techniques and possibly a quantitative description of the nanoparticle suspension that is closer to the true picture. The DLS measurement was expected to generate a large bias for our sol because the technique does not take the particle shape into account and the state of art CONTIN model fitting assumes a spherical particle shape. Direct determinations of the particle shape factor by DLS use light depolarization techniques [148], which are still under development and not widely available. Therefore, to facilitate a valid comparison between the two methods, we adapted another scheme to use the shape factor obtained from AFM measurement to interpret our DLS measurement data as shown in figure 3.9.

**Figure 3.8:** Volumetric particle size distributions from AFM image analysis.
We assume our sol particles to have a flattened shape, which is confirmed by the AFM measurements. In a first order approximation, the sol particles can be described in terms of an oblate ellipsoid shape with a major axis, $a$, equal to half of the in-plane AFM diameter $\varnothing$, and a minor axis, $b$, equal to half of the AFM thickness $z$. The DLS measurements generate a hydrodynamic Brownian diffusion coefficient, $D^{\text{Br}}$, which is a function of particle size and shape. For spherical particles, the relationship is described with the Stokes-Einstein relation.

$$D^{\text{Br}} = \frac{k_B T}{6\pi\eta(\varnothing_h / 2)} \quad (3.1)$$

in which, $k_B$ is Boltzmann's constant, $T$ the absolute temperature, $\eta$ the viscosity and $\varnothing_h$ the hydrodynamic particle diameter. The Brownian diffusion coefficient for oblate ellipsoids can be obtained from classical hydrodynamic theory. However, this approach results in large discrepancies if the $b/a$ ratio becomes very small [149] as is the case for the
particles studied here. More accurate predictions became available recently from simulations [150]; the results of these predictions can be summarized as

\[
D^{\text{ir}} = X_t \frac{k_BT}{6\pi\eta\sqrt{a^2b}}
\]  

(3.2)

in which the correction factor \(X_t\) depends on \(b/a\) as calculated in the simulation studies. To obtain experimental values for \(b/a\), the AFM data were further analyzed in terms of a particle height (thickness, max \(z\)) vs diameter plot, as shown in figure 3.10.

\[
\text{linear fit of max } z \text{ vs. diameter} \\
z = 0.13 \times \text{diameter} + 0.60
\]

**Figure 3.10:** Diameter vs. thickness from AFM analysis.

Despite the large scatter in the thickness data, the linear fits for the different sols showed very good mutual consistency with \(b/a \approx 0.13\) This value is used in (3.2) to derive the corresponding \(a\) and \(\varnothing\) from the DLS measurement. The DLS intensity needs to be translated into differential volume, as well. In the low concentration limit (no particle-particle
interaction) and using assumptions of a spherical particle shape and a particle size that is small compared to wave length, the intensity of light scattered from one particle, $I_s$, can be expressed as [151]

$$I_s = K \times C_n \times V_i^2$$  \hspace{1cm} (3.3)

in which $K$ is a factor that depends on the incident beam intensity, wave length, scattering angle and other instrument parameters. $C_n$ is the particle concentration and $V_i$ is the volume of one single particle of a particular size $i$. To derive a similar equation for oblate ellipsoids is beyond the scope of this work; therefore, we will just use equation (3.3) to calculate our relative differential volume values. The correction for the oblate particle shape is carried out for particles with $\bar{Ø}_p < 100$ nm only. Any particles larger than that are very likely agglomerations for which a spherical shape can be assumed. Figure 3.11 shows the curves after rescaling, using a particle refractive index of 1.624 for the real part and 0 the imaginary part [152]. It is clearly shown that with the oblate model, the estimated particle diameter ($2 \times a$) is slightly larger than the hydrodynamic diameter. The volumetric average particle volume is used to calculate an average spherical diameter for each sol, as is summarized in table 3.1:
Figure 3.11: Differential accumulated volume vs. particle Ø for each sol, using the spherical and the oblate model.
<table>
<thead>
<tr>
<th></th>
<th>Small particle group (&lt;100 nm)</th>
<th>Large particle group (100…1000 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O-γ</td>
<td>C-γ</td>
</tr>
<tr>
<td>AFM</td>
<td>15.0</td>
<td>9.9</td>
</tr>
<tr>
<td>DLS (oblate model)</td>
<td>11.0</td>
<td>12.0</td>
</tr>
<tr>
<td>DLS (spherical model)</td>
<td>18.2</td>
<td>13.7</td>
</tr>
</tbody>
</table>

**Table 3.1:** Volumetric average particle diameter $\bar{\Omega} = 2\sqrt[3]{\frac{3V}{4\pi}}$ [nm], using $\bar{V} = \frac{\sum N_i V_i^2}{\sum N_i V_i}$.

Here $V_i$ is the median volume (in nm$^3$) of particles for one size interval of 0.5 nm, and $N_i$ is the total number of particles in that size interval.

It is clearly shown in figure 3.11 that the AFM results agree better with the oblate ellipsoid model diameter. Further improvements of the characterizations could involve analyzing more AFM images, and for DSL introducing a better oblate scattering model and taking the immobile hydration layer into consideration. Also in the oblate model, a spherical particle shape is assumed for agglomerates, which results naturally in a very good agreement between the oblate and spherical models for the large size range. However, characterization of the larger particle group with microscopic techniques, such as AFM or TEM, SEM, will always be problematic due to their small concentration and so far, DLS is the only technique that allows us to obtain an estimate for the size distribution in this range.

### 3.3.5 Process contamination

For the tested systems, particular attention was paid to the compatibility of the dispersion medium (aqueous HNO$_3$ solution with $p_H \approx 3.5$) and the anodic alumina screen. The screen material is a quasi-crystalline alumina that has limited long term stability at acidic or basic conditions [153,154]. Depending on the preparation conditions, anions, originally present in the electrolyte solution will become trapped in the alumina screen material. Inspection with SEM/EDAX showed that phosphorous is present in Whatman Ano-
discs, indicating that it is prepared in the presence of H₃PO₄. Therefore, by analyzing the phosphate concentration in each sol, the degree of contamination introduced from dissolved Anodisc material could be estimated. This test was performed for O-γ, C-γ, U-γ and U-γ retentate (U-γ R) as shown in table 3.2. A trace of PO₄³⁻ was detected in U-γ only, which indicates that the dissolution rate of the Anodiscs was less than 2.36×10⁻⁸ g/min. However, a detectable amount of sulfate was found in the sols from an unknown source. C-γ seems to have even less impurities than the original sol which may be due to excessive removal of particles. To improve the stability of the anodic alumina screens, they can be heated to form a more developed polycrystalline structure [154]. Another possibility is to carry out the ultrasound-assisted filtration at lower temperatures: 0…3°C [155], which requires a high capacity cooling system since the ultrasonic treatment generates a significant amount of heat. To reduce other impurities, the ultrasonic funnel material must be carefully selected.

<table>
<thead>
<tr>
<th></th>
<th>Fluoride</th>
<th>Chloride</th>
<th>Sulfate</th>
<th>Phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-γ</td>
<td>0.10</td>
<td>0.57</td>
<td>0.59</td>
<td>0.80</td>
</tr>
<tr>
<td>U-γ R</td>
<td>1.06</td>
<td>1.96</td>
<td>0.31</td>
<td>n/a</td>
</tr>
<tr>
<td>O-γ</td>
<td>0.06</td>
<td>0.40</td>
<td>0.03</td>
<td>n/a</td>
</tr>
<tr>
<td>C-γ</td>
<td>n/a</td>
<td>n/a</td>
<td>&gt;0.01</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 3.2: Contamination levels (ppm weight) in the sols.

3.4 Conclusions

Ultrasound-assisted screening with suspended anodic alumina filters was found to be the best practical method for purification of Boehmite sols prepared by the Yoldas method [138], when considering yield and concentration of unwanted larger particles and contamination. This screening method is suitable for the production of large quantities of dispersion at a fairly high particle concentration. It was found to result in almost com-
plete removal of particles, larger than 100 nm. Screening without ultrasound resulted in a more complete removal of large agglomerates but had a very low yield. To further improve the performance of the screening process, the ultra-sound intensity and frequency might be optimized, or different agitation methods can be considered such as stirring very close to the filter surface. This should lead to a minimization of particle accumulation at the membrane surface while, at the same time, the particles keep plugging the membrane defects. Another approach might involve anodic membranes with straight pores only, instead of the branching structure used in the present studies. Ultra-sonic assisted screening resulted in a small particle (<100 nm) distribution similar to that of purification by ultra-centrifugation, but resulted in less larger particles. This suggests that colloidal deposition of sols, purified by ultra-sonic assisted screening will lead to the formation of higher quality thin films. AFM and DLS measurement can be combined to obtain a detailed analysis of the distribution of particle size and shape. AFM has the advantage of providing detailed information on the particle shape and size distribution, however, lacks the capability of detecting particle size groups that are present at relatively low concentrations. DLS is particularly sensitive in the large size range; however, interpretation of the DLS results can be ambiguous due to fact that unique solution for the autocorrelation functions are not yet available. On the other hand, DLS samples a relatively large dispersion volume, which provides better statistically averaged data than the AFM method.
CHAPTER 4

WATER PURIFICATION WITH INORGANIC

MESOPOROUS MEMBRANE

This chapter describes experimental water purification tests, including instrumentation, design of experiments (DOE) and a systematic summary of the testing results. A dead-end pressurized water chamber was constructed for the testing. During design and construction, special attention had to be paid to the sample holder, the flow rate collection and the electronic monitoring system. Two types of membranes have been used in these tests, mesoporous γ-alumina on top of standard macroporous AKP30 supports (γ/AKP30) and mesoporous γ-alumina on top of standard macroporous AKP15 supports (γ/AKP15). The γ/AKP30 membranes were mainly used to determine the optimized testing conditions for the DOE purpose. Several parameters, including stirring speed, applied pressure, and electrolyte concentration were been investigated and the water purification behavior of the membrane under various conditions was determined. The γ/AKP15 membrane was then utilized for systematic performance testing under the optimized operation conditions. Three different electrolytes were tested at various concentrations and the osmotic pressure was detected during the experiments.
4.1 Introduction

Water purification with several types of inorganic membranes have been reported in [38-59]. However, the testing setup design was normally described very briefly in those studies. Two types of setups were adapted in these tests, cross-flow and dead-end. Cross-flow type testing system is every efficient for hollow fiber membranes and therefore, has become main stream for organic membrane modules. However, it is relatively difficult to make inorganic hollow fiber membrane and for most of the testing of inorganic membranes with disk shape geometry, a dead-end setup was utilized [95].

Normally at the initial stage of the development of a new type of membrane, the molecular weight cut-off (MWCO) was measured to determine the pore diameter of the mesoporous membrane and therefore, the optimized preparation procedure parameters such as sintering temperature. After the preparation process was thoroughly established, the ionic selectivity performance would be characterized to determine the optimized operation condition of the membrane. For this work, we employed a well established γ-alumina system so that we could focus more on the optimization of microstructure and operational conditions, and find out the maximum performance of such membranes.

With the fully optimized membrane structure and carefully chosen operation conditions, we were able to detect the osmotic effect during water purification testing, which has never been observed under dynamic operation conditions [95, 157, 158].

4.2 Experimental Setup

A stainless steel water chamber was designed and constructed for permeability and perm-selectivity testing of the water purification membranes. The assembly design was shown in figure 4.1.
The chamber was pressurized with a nitrogen gas tank up to 1.5 MPa. An autoclave stirrer was installed to introduce sufficient agitation under pressurized conditions. This mechanical stirring was inevitable for a dead-end setup because, during operation, the accumulated ions at the feed side of the membrane must be mixed back in the bulk of the feed to reduce external mass transfer limitations effect. The membrane holder was designed to have two outlets, for center flow and edge leak flow. The center flow collected purified water that passed through the membrane layer and support perpendicularly. The edge flow collected possible water leakage through the membrane sealing and the rough sur-
face region and avoided internal pressure build up. This configuration prevented mixing of the edge leakage stream to the center flow and thus, avoided contamination of the center flow. The collected water in the center flow was then directed to a container that was continuously weighted with a digital analytic balance. The reading of the balance was simultaneously transferred to a computer. Additional data that were automatically collected consisted of:

- the pressure of the chamber, measured with a digital pressure gauge,
- the temperature of the feed solution, measured with a thermocouple probe,
- the rotation speed of the stirrer measured with a tachometer installed in the stirrer axial.

All the data was monitored and recorded with National Instruments Labview™ software. After one round of experiments was done, the collected sample was tested with ion chromatography for to obtain ion concentrations in the feed. The entire water purification membrane testing setup is shown in figure 4.2.
4.3 **Operational Condition Determination**

The membrane utilized for the optimized operation testing condition was mesoporous $\gamma$-alumina on top of standard macroporous AKP30 supports ($\gamma$/AKP30), due to the availability of such membrane at the early stage of the experiments. NaCl aqueous solutions of various concentrations at pH 4.6 were used as the testing electrolyte. The applied pressure was 0.7…17 MPa (10…250 PSI). Membrane performance was characterized with two parameters; permeability and permselectivity. The permeability is defined as:

$$k_p = \frac{\eta X}{A} \frac{dV}{d\Delta p} \frac{dt}{dt}$$  \hspace{1cm} (4.1)$$

where, $\eta$ is the viscosity of the solution, $X$ is the thickness of the membrane, $A$ is the apparent surface of the membrane, $\Delta p$ is the pressure difference between the feed side and
the permeate side, and \( \frac{dV}{dt} \) is the flow rate. Permeability is a characteristic property of a specific membrane, which is independent of the testing conditions. To characterize the permselectivity, the rejection was used, defined as follows:

\[
R = 1 - \frac{c_f}{c_p}
\]  

(4.2)

where, \( c_f \) is the feed side electrolyte concentration and \( c_p \) the permeate side concentration. By studying the \( R \) value under various operation conditions, one can determine the water purification behavior of the membrane. The first investigated operation condition is the stirring rate as shown in the figure 4.3.

![Aqueous NaCl@pH 4.6, Δp=1.38 MPa](image)

**Figure 4.3:** Rejection under various stirring conditions for aqueous NaCl solutions.
It is easily understood that a larger stirring speed causes a better mixing and less external mass transfer limitations at the feed side of the membrane and therefore, generated better rejection until the stirring effect reaches a saturation plateau region. For dilute electrolyte solutions, the plateau region was reached at a lower stirring speed. In order to be consistent, a 2000 rpm stirring speed was chosen for the later systematic studies to guarantee sufficient mixing for all experiments.

A similar plateau type rejection vs. flow velocity behavior was found for the membrane data shown in figure 4.4. This type of purification behavior was found for many membranes and electrolyte systems. As the pressure increased, the flow velocity and rejection increased until it reached a plateau value. This phenomenon was used as a guideline to determine the maximum rejection. More comprehensive results will be presented in the next section when multiple electrolytes are compared.
To achieve the best performance, the applied pressure should be as high as possible to obtain a high rejection and flowrate. This implies that mechanical strength of the membrane becomes the limiting factor if the cost of generating high pressure is not taken into account.

### 4.4 Membrane Performance Summary

Once the optimized operational conditions were determined for mesoporous $\gamma$-alumina membranes, systematic water purification tests were carried out for the routinely prepared one layer $\gamma$-alumina/AKP15 support membrane structure. It was noticed that the chemical stability of such a membrane is not sufficient for prolonged operation under standard water purification conditions, i.e. an electrolyte solution at $p_H = 4.6$. Tested electrolytes
included CaCl₂ and AlCl₃. Only with AlCl₃ solutions, the membrane showed a completely stable performance because in that case the process of γ-alumina dissolution is fully suppressed. Therefore, a new series of electrolyte tests was carried out with the addition of a small amount of AlCl₃.

4.4.1 Permeability comparison

The permeability value for each layer of the membrane was calculated and compared. The permeability of the supports could be determined directly with stand-alone supports, while the permeability of the γ-alumina layer could be determined with a series resistor model described as follows. In case one or more support (u) layers are present, in addition to a functional membrane (m) at the feed side, the permeability of each layer and the total permeability are related by:

\[
j_i = k_{i,\text{tot}} \frac{P_f - P_p}{X_{\text{tot}}} = k_{i,m} \frac{P_f - P_{m/u_1}}{X_m} = k_{i,u_1} \frac{P_{m/u_1} - P_{u_1/u_2}}{X_{u_1}} = \cdots = k_{i,u_{\text{max}}} \frac{P_{u_{\text{max}}/u_{\text{max}}} - P_p}{X_{u_{\text{max}}}} \tag{4.3}
\]

where, \( j \) is the flux; \( c, k_{i,m}, k_{i,u_1}, \) and \( k_{i,u_{\text{max}}} \) are the permeability of the entire membrane device including every layer, the top membrane layer, the layer \( u_1 \), and the layer \( u_{\text{max}} \), respectively; \( P_f, P_p, P_{m/u_1}, \) and \( P_{u_1/u_2} \) etc. are the pressure at the feed side, permeate side, interface between membrane layer and the \( u_1 \) layer, and interface between \( u_1 \) layer and \( u_2 \) layer etc., respectively; \( X_{\text{tot}}, X_m, X_{u_1}, \) and \( X_{u_{\text{max}}} \) are the thickness of the entire membrane device including every layer, the membrane top layer, the \( u_1 \) layer and the \( u_{\text{max}} \) layer, respectively. Determination of \( k_i \) for one layer from \( k_{i,\text{tot}} \), requires knowledge of the thickness of all layers, and the \( k_i \) of all other layers. The latter should be obtained from other experiments with identical quasi-homogeneous layers in simpler structures. As an example we show the calculation of \( k_{i,\gamma} \) of 1 γ-alumina membrane (γ) layer on 1 α-Al₂O₃ support (α) layer with known permeability \( k_{i,\alpha} \).
\[ j = k_{i}^{\text{tot}} \frac{P_{t} - P_{p}}{X_{\text{tot}}} = k_{i,\gamma} \frac{P_{t} - P_{\alpha/\gamma}}{X_{\gamma}} = k_{\alpha,\alpha} \frac{P_{\alpha/\gamma} - P_{p}}{X_{\alpha}} \]  

\[ \frac{X_{\text{tot}}}{k_{i}^{\text{tot}}} = \frac{X_{\gamma}}{k_{i,\gamma}} + \frac{X_{\alpha}}{k_{i,\alpha}} \rightarrow k_{i,\gamma} = \frac{X_{i}k_{i}^{\text{tot}}k_{i,\alpha}}{X_{\text{tot}}k_{i,\alpha} - X_{\alpha}k_{i}^{\text{tot}}} \]  

In an initial experiment, \( X_{\text{tot}} = 2.0225 \times 10^{-3} \) m, \( k_{i}^{\text{tot}} = 2.7125 \times 10^{-17} \) m², \( X_{\alpha} \approx X_{\text{tot}} = 2.0225 \times 10^{-3} \) m, \( k_{i,\alpha} = 3.1499 \times 10^{-17} \) m², \( X_{\gamma} \approx 0.8 \times 10^{-6} \) m. Substitution of these values in (4.5) leads to \( k_{\gamma} = 7.7267 \times 10^{-20} \) m². The same permeation experiments have been carried out at different pressures for the supports. The permeability is found to be independent from the applied pressure as expected.

From the perspective of membrane technology, it would be valuable to find the resistance from each layer of the membrane device. The resistance of a layer was defined as:

\[ R_{i} = \frac{\Delta p}{j_{i} \eta_{i}} = \frac{X}{k_{p}A} \]  

Even though the \( \gamma \)-alumina layer had very low permeability, because it was significantly thinner than the support, it only contributed to \( \frac{1}{2} \) to \( \frac{1}{3} \) of the total resistance of the membrane. This can be further reduced to approximately half of the current value if a thinner layer was made. The results are summarized in table 4.1. Any given membrane device would be a combination of \( \gamma \)-alumina and AKP30 or \( \gamma \)-alumina and AKP15.
### Table 4.1: Water permeability, thickness and resistance of components of a membrane device.

<table>
<thead>
<tr>
<th></th>
<th>Permeability</th>
<th>Thickness</th>
<th>Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>AKP30</td>
<td>3.7E-17 m$^2$</td>
<td>2 mm</td>
<td>7.9E16 m$^{-3}$</td>
</tr>
<tr>
<td>AKP15</td>
<td>7.3E-17 m$^2$</td>
<td>2 mm</td>
<td>4.1E16 m$^{-3}$</td>
</tr>
<tr>
<td>$\gamma$-alumina</td>
<td>7.7E-20 m$^2$</td>
<td>2 µm</td>
<td>3.8E16 m$^{-3}$</td>
</tr>
</tbody>
</table>

### 4.4.2 Viscosity correction for flowrate data

Because flow rate is affected by the viscosity which, in turn, is a function of temperature and electrolyte concentration; a correction is applied to the water viscosity for these effects. For the systems under study, this results in a correction of 1…10%, which is significant in the consideration of (small) osmotic effects. The viscosity correction is carried out as follows. The viscosity dependence on temperature is obtained with the Andrade equation [159,160].

$$\eta = \eta_{H_2O}^0 \exp\left(\frac{U_{H_2O}^n}{T}\right)$$  \hspace{1cm} (4.7)

where, $\eta$ is the dynamic viscosity in Pa s, $\eta_{H_2O}^0$ is a constant, $U_{H_2O}^n$ is the flow activation energy and $T$ is absolute temperature in K.

To predict the viscosity dependence on electrolyte concentration, various empirical formulas or models have been introduced by many authors. These formulas are generally an extension of the Andrade equation with a similar exponential relationship and extra terms that are designated to cover wider and higher ranges of electrolyte concentration. A brief review of these works can be found in [161]. Jones and Dole [162] introduced an empirical equation, which is widely accepted for strong electrolyte aqueous solutions:
\[
\frac{\eta}{\eta_{\text{H}_2\text{O}}} = 1 + C_2 \sqrt{c} + C_3 c
\]  

(4.8)

where \( \eta_{\text{H}_2\text{O}} \) is the viscosity of pure water, \( C_2 \) and \( C_3 \) are constants specific for the type of electrolyte and \( c \) is the molarity (concentration). This formula is usable for a fairly wide range of electrolyte concentrations and therefore, it is employed to obtain the viscosity of various electrolytes at different concentrations and temperatures. The constants \( C_2 \) and \( C_3 \) are first extrapolated from known electrolyte data [163]. Then, the viscosity of the electrolyte at 25ºC is calculated and the flowrate is corrected for a 25ºC measurement condition. The known \( \ln(\eta) \) vs \( \frac{1}{T} \) relation for pure water is shown in figure 4.5 and used to obtain the parameters for the Andrade equation. \( (\frac{\eta}{\eta_{\text{H}_2\text{O}}} - 1) \) vs. \( \sqrt{c} \) curves are shown in figure 4.6 and figure 4.7. It is generally noticed that under the current experimental conditions, the viscosity correction consist primarily of the temperature effect (up to 30%), with only a minor concentration effect (5%). Due to lack of experimental data, a concentration correction for the AlCl\(_3\) solutions was not applied. However this correction is also expected to be minimal as compared to the temperature correction.
**H$_2$O viscosity vs. temperature relationship**

\[
\ln(\eta) = 1.956.7 \times \frac{1}{T} - 6.6801
\]

**Figure 4.5:** Temperature vs. viscosity for pure H$_2$O.
Figure 4.6: Viscosity vs concentration for aqueous NaCl.

\[ \frac{\eta}{\eta_{H_2O}} - 1 = 0.0056\sqrt{c} + 0.0889c \]
4.4.3 Purification results

The purification experiments were performed as described previously in this chapter. The rejection vs. flowrate, corrected for temperature and concentration, is shown in figure 4.8-4.12. The observed trends in the purification behavior of $\gamma$-alumina membranes are summarized as follows:

- For the same feed concentration, electrolytes with higher charged cations have a higher rejection.
- For the same feed concentration, a higher flowrate results in higher rejection until it reaches a limiting value.

Figure 4.7: Viscosity vs concentration for aqueous CaCl$_2$. 

\[
\frac{\eta}{\eta_{\text{H}_2\text{O}}} - 1 = 0.0157\sqrt{c} + 0.2261c
\]
Electrolyte solutions of higher concentrations of the same electrolyte, have a lower limiting rejection value and require a higher flowrate to reach this limiting rejection.

Pure water, NaCl and CaCl₂ solutions at \( p_H = 4.6 \) caused a gradual dissolution of membrane material, which was concluded from the permeability changing with a typical time constant of 1 day. The addition of small amounts of AlCl₃ fully stabilized the permeability and resulted in a much consistency of the results.

**Figure 4.8:** Rejection vs. flowrate for various concentrations of NaCl.
Figure 4.9: Rejection vs. flowrate for various concentrations of CaCl$_2$. 
Figure 4.10: Rejection vs. flowrate for various concentrations of NaCl+1wt%AlCl₃.
Figure 4.11: Rejection vs. flowrate for various concentrations of CaCl₂+1wt%AlCl₃.
4.4.4 Osmotic effect

An osmotic pressure difference develops between solutions, separated by a semi-permeable membrane. It is caused by differences of the pressure-independent chemical potential of the solvent at both sides of the membrane. In most cases the solvent chemical potential of solution molecules in the solution with the lower solute concentration is higher than that of the solution with the higher concentration. Therefore, solvent molecules tend to transfer from the lower concentration solution to the higher concentration solution. To overcome this tendency, an additional osmotic pressure, \( \Delta p_{\rho'_{\rho}} \), is needed at the high concentration side of the solution. The simplest quantitative expression for the osmotic pressure, \( \Delta p_{\rho'_{\rho}} \), is the van’t Hoff equation, which is only applicable for dilute solutions:
Here $M$, $R$, and $T$ are the molarity concentration of the solutions, gas constant (8.314472 J K$^{-1}$ mol$^{-1}$), and absolute temperature (K), respectively. However, the van’t Hoff equation is not applicable at higher concentrations because in that case the free energy of solvent starts to deviate from linear dependence on concentration. Therefore, to accurately predict the osmotic effect, the thermodynamic properties of the solution system must be thoroughly understood. Such studies for aqueous systems have been extensively investigated both experimentally and theoretically. Regardless of the recent progress in this area, Pitzer and Mayorga’s work [164-166] in the 1970s remains the most concise and accurate method for describing low to intermediate concentration (<6M) electrolyte solutions which are used in this study. The formulation is introduced below for a pure electrolyte $M_{v_M}X_{v_X}$ with tabulated parameters for NaCl, CaCl$_2$, and AlCl$_3$.

$$\Delta P_{\varphi}^{eq} = \varphi cRT$$  \hspace{1cm} (4.9)
Table 4.2: Pitzer parameters for osmotic coefficient calculation.

<table>
<thead>
<tr>
<th></th>
<th>$\beta_{MX}^{(0)}$</th>
<th>$\beta_{MX}^{(1)}$</th>
<th>$C_{MX}^\varphi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl [168]</td>
<td>0.0738</td>
<td>0.2712</td>
<td>0.00167</td>
</tr>
<tr>
<td>CaCl$_2$ [168]</td>
<td>0.3076</td>
<td>1.6432</td>
<td>0.00169</td>
</tr>
<tr>
<td>AlCl$_3$ [169]</td>
<td>0.6993</td>
<td>5.84467</td>
<td>0.00273</td>
</tr>
</tbody>
</table>

where, $A_\varphi$ is the Debye-Huckel coefficient, $N_A$ Avogadro’s number, $\rho_w$ the density of the solvent (normally water), $q_{el}$ the elementary charge, $\varepsilon$ the dielectric constant of the solvent, $k_B$ Boltzmann’s constant, $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$ second viral coefficients indicated in the table 4.2, $\alpha$ a fitting constant found to be satisfactory for all solutes considered in [165] when it is 2.0, $I$ the ionic strength $1/2\sum m_i z_i^2$, $b$ another fitting constant obtained as 1.2 in [164], $z_M$ and $z_X$ the respective numbers of elementary charges of $M$ and $X$, $m$ the modality of the solution, $\nu = \nu_M + \nu_X$ is the number of ions in the electrolyte formula, and $C_{MX}^\varphi$ is another coefficient provided for each electrolyte in table 4.2. The quantity $\varphi$ is known as the “osmotic coefficient”. Because the dielectric constant of water is very sensitive to temperature; $A_\varphi$ also becomes strongly temperature dependent. Pitzer [167] introduced a data array for fitting the relative dielectric constant of water at various temperatures. A single parameter equation [170] is used to simplify that expression with:

$$\varepsilon = 305.7 \times \exp(-12.741 + 0.01875 \times (T - 273.15)) - (T - 273.15)/219.)$$ (4.15)

This equation is adapted in this work to determine $A_\varphi$ at various temperatures. Once the osmotic pressure difference was found for each tested solution, corrected flow rate data
were plotted against the applied pressure difference, Δp, and Δp - Δp_{eq}^{\text{eq}} / Δp_{AA}^{\text{eq}} \text{, as shown in figure 4.13-4.17.}

\textbf{Figure 4.13:} The pressure vs. flowrate w/o osmotic effect for NaCl.
Figure 4.14: The pressure vs. flowrate w/o osmotic effect for CaCl$_2$.

Figure 4.15: The pressure vs. flowrate w/o osmotic effect for NaCl+1%AlCl$_3$. 

91
Figure 4.16: The pressure vs. flowrate w/o osmotic effect for CaCl$_2$+1%AlCl$_3$.

Figure 4.17: The pressure vs. flowrate w/o osmotic effect for AlCl$_3$. 

The subtraction of the osmotic effect at higher concentrations results in a linear relation between the flow rate and (corrected) applied pressure. This indicates that the osmotic effect provides an internal pressure difference that counteracts the applied pressure. For this effect to be readily noticed, however, several criteria must be satisfied.

- The concentration of the tested solution must be high enough and the rejection must be sufficient to generate enough concentration difference so that the resulting osmotic pressure is more than 5...10% of the applied pressure.
- The membrane must be chemically stable to obtain a reproducible flow rate.

The osmotic effect is most convincingly demonstrated with moderately concentrated electrolyte solutions with \( z_M > 1 \), which show a saturated region in their rejection vs. flow rate curve. At a relatively high differential pressure, the rejection reaches a maximum value and a constant concentration difference is maintained between the feed and permeate side so that a constant osmotic pressure difference can be derived from the flow rate vs applied pressure curve. When a lower \( \Delta p \) is applied, the rejection decreases to zero and as does the osmotic pressure. Therefore, for relatively low \( \Delta p \), the flow rate vs \( \Delta p \) curve starts to approach the flow rate vs \( (p-\Delta p_{eq}^\epsilon + \sigma \Delta \lambda) \) curve. The resulting nonlinear behavior can be only explained by the osmotic effect since pure viscous flow results in linear behavior, and all possible corrections, including the effects of temperature and electrolyte concentration, on and viscosity have been applied.

### 4.5 Conclusion

With a carefully designed and constructed water purification setup and a thoroughly planned experimental procedure, consistent water purification results were obtained with a \( \gamma \)-alumina membrane.

For the first time, the osmotic effect was clearly detected during the testing; provided the electrolyte system was properly chosen, and any membrane degrading situations, such as clogging and dissolving had been kept at their minimum level.
Our observation and calculation indicate that, under current experimental conditions, temperature and electrolyte concentration have a small effect on the value of the solution’s dynamic viscosity, in the order of 1…3%.

The Pitzer and Mayorga's model for the thermodynamic properties of electrolyte solutions is sufficiently accurate for using in the analysis of current water purification experiments.
CHAPTER 5

MESOPOROUS MEMBRANE NANOFILTRATION MODELING

WITH COMSOL MULTIPHYSICS

Nanofiltration with meso-porous membranes can be used in water desalination, water softening and purification applications. The purification mechanism rests upon an electrostatic field effect, induced by charged groups adsorbed or imbedded on the membrane surface. When immersed in aqueous electrolyte solution, the charged surface will spontaneously develop a diffuse layer of excess countercharge in the solution. This will cause a deviation of ion concentration distribution within the pore phase from the original solution values. This effect will have the result that, under pressure-driven operation, the solution at the membrane permeate side has an ionic concentration that is less than that at the feed side. Since the concentrations of positive and negative charges do not exactly cancel out in the pore phase, a strong electrical field will form at the exit of the pore and promote a strong migration of ionic species, which will counteract the normal diffusive and convective transport. This process can be described by modeling three phenomena that occur simultaneously in the system: incompressible fluid flow; chemical diffusion, field-driven migration and convection of ionic species; and electrostatic interaction. To obtain a quantitatively valid model, several corrections; such as non-ideal solution thermodynamics, dependence of the diffusion coefficient on ion concentration, variations in local water permittivity, have been taken into account in this model. The simulation results demonstrated correctly the experimental trends, and predicted limiting performance at extreme conditions.
5.1 Introduction

Modeling of the nanofiltration process of mesoporous (pore diameter $\Omega_p = 2\ldots50$ nm) membranes involves a thorough investigation at the intersection of four major fields: surface chemistry, electrostatic interactions, mass transportation and fluid dynamics. The purpose of the modeling is to understand the species’ transportation process and to predict purification performance under defined operation conditions.

Many authors have taken up this challenge task with various approaches [171-188]. The majority of these studies are based on a one-dimensional FEA approach, which considers transportation phenomena along the membrane thickness direction, and using the simplification of averaging physical phenomena and membrane properties in the other two perpendicular directions. Such simplifications reduce computational expenses, but sometimes generate relatively crude results such as a discontinuity in the ion concentration profile. In addition they result in intuitively inaccurate assumptions such as uniform potential and electrical neutrality for each slice, perpendicular in the pore direction. As more advanced and powerful modeling tools become available, these simplified models can be revised and rebuilt by using a more consistent physical framework and a larger degree of detail. This work focuses on establishing a 3D transportation model that incorporates detailed electrokinetic interactions and ionic charge distributions. For instance, one of the major differences between this work and previous studies is that in this work, the electrical double layer inside the membrane pore phase was modeled with the FEM method to obtain a detailed axial distribution profile; while in previous work, the potential was assumed axially uniform and the charge concentration was directly calculated from the Boltzmann relation.

Similar FEM approaches have been taken recently by the microfluidics community. A typical microfluidics model investigates the fluid flow confined in micrometer scale channels, and the effect of various physical-chemical phenomena such as thermal effects [189], electrokinetics [190], diffusion, and surface reactions [191]. In state-of-the-art nanofiltration membranes, the membrane pores have a much smaller channel cross section and a more tortuous geometry than what is normally considered in micro-fluidics.
The practical membrane pore geometry, as it turns out, can be simplified with to a straight channel with a minimal effect on the purification results. However, the complications raised by nanoscale pore dimension need to be thoroughly analyzed and modeled, which is the subject of this work.

5.2 Theory

5.2.1 Surface charge density

The water purification mechanism of the inorganic nanofiltration membrane rests upon the spontaneous chemi-sorption of charged species of one sign, resulting in the development of an electrical double layer (EDL). This occurs when the membrane material is brought into contact with an aqueous solution. This work considers, the case of a mesoporous γ-alumina membrane immersed in NaCl solutions at pH = 4.6. Several surface reactions take place and four of them are considered here, following a widely adapted 2-pK charge-regulation model [188, 192-197]

\[
\begin{align*}
-\text{OH}_2^+ & \xrightleftharpoons{K_1} -\text{OH} + \text{H}^+ (s) \\
-\text{OH} & \xrightleftharpoons{K_2} -\text{O}^- + \text{H}^+ (s) \\
-\text{O}^- \text{C}^{n+} & \xrightleftharpoons{K_c} -\text{O}^- + \text{C}^{n+} (s) \\
-\text{OH}_2^+ \text{A}^{m-} & \xrightleftharpoons{K_d} -\text{OH}_2^+ + \text{A}^{m-} (s)
\end{align*}
\]

(5.1)

Here, −OH is a hydroxyl group on the surface of γ-alumina membrane, −OH$_2^+$ and −O$^-$ result from ionization of this group by either adsorption or desorption of a proton. Such charged groups can further adsorb cations C$^{n+}$ or anions A$^{m-}$ to form, respectively, −O$^-\text{C}^{n+}$ or, −OH$_2^+\text{A}^{m-}$ surface groups. The equilibrium constants $K_1$, $K_2$, $K_c$, and $K_d$ are obtained from the literature [188]. A net surface charge, $\sigma$, results from the summation of all the chemisorbed, charged groups on the surface. It can be further expressed as a function of the concentration of the mobile ions close to the surface, $c_{\text{H}^+ (s)}$, $c_{\text{C}^{n+} (s)}$, and $c_{\text{A}^{m-} (s)}$ as:
\[ \sigma = F \cdot c_{\text{tot}}^+ \left( \frac{c_{H^+(s)}}{K^+ c_{H^+(s)} + (c_{H^+(s)})^2 - K^+ K^-} \right) \]  

(5.2)

where \( F \) is the Faraday constant. The total surface site concentration, \( c_{\text{tot}}^+ \), can be obtained from the literature [188]. The surface ion concentrations, \( c_{H^+(s)}, c_{C^{n+}(s)}, \) and \( c_{A^{m-}(s)} \), are related to the bulk concentrations, \( c_{H^+(b)}, c_{C^{n+}(b)}, \) and \( c_{A^{m-}(b)} \), through the Boltzmann relationship,

\[ c_{i(s)} = \gamma_i c_{i(b)} \exp \left( \frac{-z_i F (\Delta \Phi)}{RT} \right) \]  

(5.3)

Where \( x \) can be \( H^+, C^{n+}, \) or \( A^{m-}; \gamma_i \) is the activity of the corresponding species \( i \), which can be obtained as a function of \( c \) by using a widely accepted empirical expression by Davies [198] as

\[ -\log(\gamma_i) = 0.51 z_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 I \right) \]

\( z_i \) is the charge carried by \( i; R, T \) are the ideal gas constant and temperature respectively; \( \Delta \Phi \) is the potential difference between the bulk and the surface and the only dependent variable. This potential difference is connected to the surface charge density \( \sigma \) through the experimental data of double layer capacitance, \( \mathbb{C} \), as

\[ \sigma = \mathbb{C} \cdot \Delta \Phi \]  

(5.4)

Therefore, the surface charge model contains a set of self-confined equations that can be solved numerically to determine the value of the surface charge density \( \sigma \) at any given bulk solution composition.

Once the surface charge density is determined for one type of feed solution, it is applied to the entire membrane pore channel and the electrical double layer modeling uses this value. This assumption can be justified by considering the “gate effect” at the interface between bulk solution and the membrane phase. Once the electrolyte solution passes the “gate region” (EDL at the interface) and enters the pore, the ion concentration will not vary significantly within the pore channel and therefore, the surface charge density will be approximately a constant.
5.2.2 Electrostatics: electrical double layer (EDL)

The occurrence of an electrical double layer (EDL) plays an essential role in the purification mechanism of nanofiltration with mesoporous membranes. The key problem, addressed in double layer studies is to reveal the relationship between the potential difference across the interface and the spatial distribution of the species within the interfacial region. Even to this day the EDL is not completely understood, while it has been studied extensively for 150 years when the first capacitor model was introduced by Helmholtz [200]. A more realistic EDL model with a diffusive distribution of ions, rather than a single plane, in the electrolyte was first proposed by Gouy [201] and Chapman [202] and became the basis of modern EDL descriptions. In the 1980s, a group of new models identified as restricted primitive models (RPM) were proposed for describing EDLs at high concentrations and high surface charge densities [203]. A common feature of these models is that the electrolyte is represented by a fluid of charged hard spheres of finite diameter and the solvent by a continuum with an isotropic dielectric constant. Another promising approach was based on density-functional theories [204]. This approach describes the Helmholtz free energy as a function of the particle density, and minimizes that free energy to obtain a solution for the equilibrium distribution. These refined models were able to predict the behavior of the EDL at high surface charge densities and concentrations, such as oscillations in the concentration profile, and charge inversion phenomena. As modern computation tools became available, investigators started modeling the EDL by calculating the interaction between large amounts of individual molecules. In these efforts, one of two techniques was generally used to perform the simulations [205]: molecular dynamics (MD), in which the equations of motion are solved simultaneously for each molecule, and the Monte Carlo method (MC), in which an equilibrium ensemble is generated from a random walk algorithm. In case the intermolecular potential is known with sufficient detail, the properties and structure of the EDL can be computed for systems consisting of a few hundred to a few thousand particles. Without further experimental evidence being currently available, computational simulation provides a shortcut to the reality of the EDL structure and may be the only way to address problems as in the current paper. However, the scale of current MD or MC simulation is still far
from sufficient to model a macro scale phenomena such as the nanofiltration process. Therefore, continuum finite element methods are still employed and will be still on the stage for a while for this type of modeling work.

In this work, we determined the concentration profile of the EDL numerically instead of analytically to bypass two complications:

- The confined membrane pore size is of the same order of magnitude as the EDL thickness.
- Interactions with other phenomena such as convection.

We applied the classic Gouy-Chapman approach instead of the newly (in 80s) developed EDL models by assuming point charges and a continuum dielectric medium. The new EDL theories are not considered here for two reasons:

- The systems studied are relatively dilute with a modest surface charge density, which can be modeled with sufficient accuracy by the Gouy-Chapman theory.
- Advanced models, generally not based on simple partial differential equations, are difficult to implement in the COMSOL platform.

While it is well-known that FEM is not suitable for very small length scales where sizes of individual molecules start to play a significant roles, our system turns out to be still marginally solvable with the FEM method.

A combination of Poisson’s equation combined with diffusion theory is employed to determine the development of the EDL in the pore entrance and along the channel. We write Poisson’s equation as:

$$-\nabla \cdot \varepsilon \varepsilon_r \nabla \Phi = \rho_e$$

(5.5)

It has been noticed by many researchers that the dielectric constant of aqueous electrolyte solutions is no longer a constant, close to a solid liquid interface. This deviation was believed to result from two phenomena:

- Preferred orientation of water dipoles around charged species.
- Restrictions in the free movement of water molecules in a confined space of nm dimensions. In our system, both effects may present simultaneously.
For the first, a widely accepted empirical formula proposed by Podgornik [206] is used

\[ \varepsilon_r(y) = \frac{\varepsilon_{\text{max}}}{1 + (\varepsilon_{\text{max}}/\varepsilon_{\text{min}} - 1) \exp(-2y/\lambda)} \]  

(5.6)

where the dielectric constant \( \varepsilon_r(y) \) is a function of the distance, \( y \), away from the interface. \( \lambda \) is the Debye length of the electrolyte under consideration [206]. \( \varepsilon_{\text{max}} \) is the bulk dielectric constant of the media, which is 78.5 for water. \( \varepsilon_{\text{min}} \) is the surface dielectric constant of the media, which is 4 for water at a charged mica surface according to Teschke [207].

We use a similar equation for the external \( \gamma \)-alumina membrane water interface, since for most of operation conditions, the \( \gamma \)-alumina surface is strongly charged. Therefore a maximum water molecule rearrangement at the interface, and hence a minimum dielectric constant was anticipated. On the other hand, no correction was applied to \( \varepsilon_r \) inside the pore channel because due to symmetry, the electrical fields from the walls of the pore channel partly canceled each other out so that little water molecule re-orientation occurs. Another effect that will reduce \( \varepsilon_r \) of water is a confinement effect in pores of <10 nm dimensions. Molecular dynamics simulations indicated a 10% reduction of \( \varepsilon_r \) in a spherical cavity of about 4.8 nm in diameter [208, 209]. However, due to lack of modeling data for the present case, and the fact that the predicted reduction is limited, this effect is not included in current modeling work. However, this refinement can be easily added to the model if these data are available.

5.2.3 Diffusion and convection: Nernst-Planck

A modified Nernst-Planck equation was applied to describe the ionic species transportation phenomena, as described by the equation below:

\[ \mathbf{j}_i = -D_i c_i \nabla \ln(\gamma_i c_i) - D_i \frac{F}{R T} c_i z_i \nabla \Phi - c_i \mathbf{v} - \frac{V_i}{R T} c_i \nabla p \]  

(5.7)

In the simplest purification test, for example, with an NaCl solution at pH = 4.6, 3 species, concentrations of H\(^+\), Na\(^+\), and Cl\(^-\) are obtained from the model and the concentration of OH\(^-\) is calculated on the assumption that the water autoprotolysis reaction equilibrates everywhere. For each given charged species in the electrolyte solution, the total flux of this species, \( \mathbf{j}_i \), equals to the summation of the four terms. The right side the first
term is the chemical-diffusion that takes place under the influence of a chemical potential gradient, exclusive of the electrostatic contribution. \( D_i \) is the component diffusion coefficient of species \( i \), \( c_i \) is the concentration of \( i \), and \( \gamma_i \) is the activity coefficient of \( i \). The second term represents the migration term, which is driven by the electrical potential gradient (field). The third term is the (fluid-flow-caused transportation term) convection term, where \( v \) is convection flow velocity of the solvent, water. The fourth term is another migration term, which takes the effect of solute on the liquid volume into account [188], however, it is noticed in the model that this term is generally significantly smaller than the other terms. The terminology is summarized in table 5.1. At current stage, the model does not calculate the osmotic effects because related diffusion coefficient is not available and therefore the diffusion term of water due to \( v \mu_{H_2O} \), is ignored.
<table>
<thead>
<tr>
<th>Terms (abbreviation)</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion (diff.)</td>
<td>$\int \nabla^{\text{channel}} \gamma_i \ln(\gamma_i c_i)$</td>
</tr>
<tr>
<td>Migration (mig.)</td>
<td>$\int -\frac{F}{RT} c_i z_i \nabla \Phi^{\text{channel}}$</td>
</tr>
<tr>
<td>Convection (conv.)</td>
<td>$\int c_i v^{\text{channel}}$</td>
</tr>
<tr>
<td>Water flow (w. flow)</td>
<td>$\int v^{\text{channel}}$</td>
</tr>
<tr>
<td>Normalized Diffusion (norml. diff.)</td>
<td>Diffusion/Water flow</td>
</tr>
<tr>
<td>Normalized Migration (norml. mig.)</td>
<td>Migration/Water flow</td>
</tr>
<tr>
<td>Normalized Convection (norml. conv.)</td>
<td>Convection/Water flow</td>
</tr>
</tbody>
</table>

**Table 5.1:** Terminology summary.

The diffusion coefficients have a lower value in the membrane pore than in the ideal bulk solution due to a more constrained movement of water molecules and ions in the <10 nm size channel [211]. The values used here are adapted directly from literature [188, 210], and not corrected for that effect.
5.2.4 Flow: Navier-Stokes

The incompressible Navier-Stokes equation can be expressed as

\[ \frac{\partial \mathbf{v}}{\partial t} + \rho_e (\mathbf{v} \cdot \nabla) \mathbf{v} = -\nabla p + \mathbf{F} + \eta \nabla^2 \mathbf{v} \]  
(5.8)

Here, \( \rho_e \) is the density of the liquid, \( \mathbf{v} \) the velocity, \( t \) time, \( p \) pressure, \( \mathbf{F} \) the external body force and \( \eta \) the viscosity of the liquid. For the steady state analysis that we conduct here, the first term vanishes. In this simulation, the force term represents the electrokinetic effect [212] and can be expressed by the equation below [190]:

\[ \mathbf{F} = -\rho_e \nabla \Phi \]  
(5.9)

The electrokinetic term generally does not affect the linearity of the flowrate vs. pressure relationship. It was noticed in this model that at the interface between the bulk solution and the membrane surface the fluid sensed an attraction force, which promoted the entrance and resisted the exit of the fluid. These two trends cancelled each other out so that the total flow was then not significantly affected by the electrokinetic force.

Another effect associated with the nanoscale dimensions is that at the solid liquid interface, the liquid molecules interact with the channel wall and classic Navier-Stokes on-slip boundary condition does not apply. For this reason, a “slip contact” boundary condition or modified hydrodynamic model was developed for nanoscale fluids [213]. However, these studies are still under development and, therefore, are not considered for the present case.

5.2.5 Geometry and mesh

The model was applied to both 2D and 3D channels. The model geometry contains 3 sections: a bulk solution at the feed side, a membrane pore channel, and a bulk solution at the permeate side. At the feed side, convection worked against the diffusion of ion species and compressed the EDL; while at the permeate side, convection and diffusion worked together to elongate the EDL. Therefore, the feed side geometry was taken shorter than the permeate side geometry. The lengths of the bulk solution were determined by trial and error. The criterion is that the concentration profile gradient at the entrance and exit boundaries of the modeled geometry must be less than 1E-6 M/m. The
membrane pore channel diameter was set to 4 nm, which was based on numerous experimental observations [214]. The length of the channel varied from 30~120 nm for the 2D model and was 30 nm for the 3D model, because computational resource limitations (8Gb of memory) did not allow for larger lengths. The effects of the channel tortuosity and channel splitting and joining were investigated with the 2D model only. For the 3D model, solutions for such complicated geometries were not feasible for the same reason. The mesh was rough in the bulk solution sides and very fine in the interface and channel region. As a rule of thumb, the cross section of the channel region should have at least 10 grid points to generate a reasonable concentration profile gradient. To do so, the “maximum element size” and “element growth rate” of the interface boundaries at the mesh parameter dialog window were set to “4E-9/20” and “1.05” for the 2D model and “4E-9/12” and “1.05” for the 3D model. The degree of freedom (DOF) of the model was 96…390K for the 2D model and 255K for the 3D model.

5.3  Results and discussion

5.3.1  Channel length, tortuosity and branching

Several channel types with different lengths and shapes were used, as summarized in figure 5.1. Geometries a, b, and c were used to examine the effect of channel length (30, 60, 120 nm respectively) on rejection performance, d for the tortuosity effect, and e, f for the splitting and mixing effect. Rejection is defined as $1 - \frac{c_f}{c_p}$, where $c_f$ is the feed side electrolyte concentration and $c_p$ the permeate side electrolyte concentration. The optimized flow velocity is defined as the flow velocity at which the rejection had a maximum value. Since it was shown, with the 2D models, that the channel length, tortuosity and branching did not affect the maximum (limiting) rejection significantly, the 3D model was used only with the straight channel geometry only to keep it simple, and to evade computational resource limitations.
For an aqueous 0.01M NaCl solution with pH = 4.6, the maximum rejection found for 2D geometries a, b, c, d, e, and f, was 0.280, 0.295, 0.303, 0.309, 0.302, and 0.292, respectively; while for 3D geometry g, it was 0.541. The channel length must have a minimum
value (approximately 30 nm) below which the concentration profile would not have enough space to fully develop and hence result in less rejection. If the channel length is longer than that optimized value, no more improvements in rejection are observed. Current practical membrane thicknesses are much larger than the minimum channel length to minimize the occurrence of pinhole defects. Tortuosity and branching had a slight effect on the internal mixing, which disturbed the unbalanced concentration distribution and therefore, degraded rejection slightly.

5.3.2 Concentration profile

To visualize the purification process, the concentration distribution profile is shown in figure 5.2 for the 3D channel geometry along the symmetry axial from point (0, 0, -1.2e-7) to point (0, 0, 2.0e-8). The convection flow was along the z direction. The position of the feed side bulk solution is from \( z = -2.0e-8 \) to \( z = 0 \) and has the same concentration for \( \text{Na}^+ \) and \( \text{Cl}^- \) of 10 mol/m\(^3\). The channel region is from \( z = 0 \) to \( z = 3.0e-8 \), for which the concentration profile clearly shows the EDL developed at the membrane pore/liquid interface, and resulting in a large unbalance between positive and negative charge density within the pore channel. The permeate side bulk solution is from \( z = 3.0e-8 \) to \( z = 1.2e-7 \) and showed a re-balanced zero net charge and a lower overall NaCl concentration than at the feed side. The model revealed a rejection of 0.541 for this case.
Figure 5.2: Concentration profile along the channel.
It was experimentally observed that the rejection of the nanofiltration membrane increased until it reached certain plateau value with increasing applied pressure. This phenomenon was also found in the model as shown in figure 5.3, which can be considered as a validation of the simulation. In our model, the rejection increases significantly with velocity until it reaches a certain peak value and then decreases slightly. To understand this phenomenon, it is helpful to investigate the different components of the mass transport at every location, and for each applied pressure. This was done by integrating the diffusion, migration, and convection terms at a series of z positions and plotting them on one figure for comparison as shown in figure 5.4. To avoid too much overlap, the data of only two different pressures were chosen for this figure. It was generally observed that at the interface, the magnitudes of the diffusion and migration terms were comparable to
each other and much larger than the convection term; while in the bulk solution, they were almost zero. This is understandable because the concentration profile remained constant in the bulk region and changed only significantly at the EDL region, close to the interface of the pore and bulk solution. A close look at the diffusion, migration and convection terms provides a good insight into the purification mechanism. As the applied pressure increases, every transport component increases. However, the pressure-driven viscous flow increases even more. Therefore, it makes more sense to compare normalized transport terms, obtained by dividing each term by the pressure-driven water flux, and excluding the pressure-driven flow. It was then noticed that, as the applied pressure increases, the normalized transport terms decrease, which means that each term contributes less to the ion concentration profile. After normalization, the migration and diffusion term were still large compared to the convection term. However, these two large terms always had opposite signs and mainly canceled each other. As a net result, the summation of normalized diffusion and migration became comparable to the convection term and generally worked against that term, reducing the overall total transport of ionic species. A closer look at the entrance of the pore makes this clear. For the co-ion Na\(^+\), the normalized migration term was larger than the diffusion term. When the applied pressure increases, both normalized terms decrease but the normalized migration term changes not as fast as the diffusion term. Therefore, the net result is that the diffusion+migration term becomes larger and holds back more Na\(^+\) ions at higher applied pressure. On the other hand, for the case of the counter ion Cl\(^-\), the magnitude of the diffusion term is larger than the migration term and the summation of diffusion+migration was still against the convection term. At a higher applied pressure this effect also becomes stronger and holds back more Cl\(^-\) ions as well. The large oscillation of the diffusion+migration term of Cl\(^-\) at the interface might be caused by an insufficiently fine mesh and numerical noise. With the availability of more computer memory, a finer mesh might improve this issue.
Figure 5.4: Normalized mass transport terms. The feed side bulk solution is from $z = -2.0E-8$ to $z = 0$, the membrane pore channel region is from $z = 0$ to $z = 3.0E-8$, and the permeate side bulk solution is from $z = 3.0E-8$ to $z = 1.2E-7$.

When the applied pressure exceeds the optimum value, for this case 1.1 MPa, the rejection starts to degrade slowly. This can be explained by close examination of the concentration profile within the pore channel for these pressure values. The Na$^+$ and Cl$^-$ concentration profiles both shift significantly towards a higher value, which results in a higher permeate side concentration. At this point, it is not possible to conclude that such an increasing and then decreasing rejection behavior is a universal phenomenon or a case sen-
sitive special situation. No experimental results are yet available to validate the decreasing rejection after the maximum value.

### 5.3.3 Model validation

The 3D modeled results were compared with experimental membrane results. In the model, it was noticed that the longer the membrane pore channel, the lower the optimum flow velocity. Such behavior was indeed observed with the 2D model for various channel lengths as shown in figure 5.5. It was further estimated that the optimized flow velocity was proportional to 1/channel length. Such a relationship was also assumed for the 3D model and will be tested if appropriate computational resources become available. In direct comparisons with experimental results, we noticed a discrepancy that could be removed by scaling down the model velocity with a flow velocity scale factor of 50, see figure 5.6. To understand this scale factor, one needs to consider the actual experimental membrane pore length, which is equal to the membrane thickness, 500 nm for a single coated membrane, times the tortuosity, \( \tau = 3 \ldots 4 \) for a \( \gamma \)-alumina membrane [214]. The total length of a realistic membrane pore was then found to be 1500\ldots2000 nm, which was 50\ldots67 times longer than the modeled 30 nm channel length. This is in very good agreement with our scaling factor.

Another possible factor that might affect the flow velocity scale factor estimation rose from the effective membrane area. However, this effect had already been taken into account when the geometry of the membrane channel was constructed. The effective membrane area can be characterized with a quantity, \( \phi_p \), which is the ratio between total open area of the pore and membrane cross section area. For close packed sphere, \( \phi_p \) is \( \frac{2\sqrt{3} - \pi}{2\sqrt{3}} \), which is approximately 0.1. Unfortunately, no data of this quantity was available yet for our mesoporous \( \gamma \)-alumina membrane. Therefore, when the geometry of the model was constructed, the ratio between the cross section area of the bulk feed solution and the membrane pore channel was chosen to be 0.35, to compensate this effect without making the channel geometry become unfavorable for mesh generation. The results were not further modified thereafter.
The qualitative agreement between the computational and experimental results was very good if the flow velocity scale factor was taken into account as shown in figure 5.6.

![Graph showing rejection performance for 2D models versus channel length.](image)

**Figure 5.5:** Comparison of rejection performance for 2D models versus channel length.
However, the rejection of the 3D model was more dramatically affected by the feed solution concentration than in the experiments. The reason of this discrepancy might be that the FEM continuum approach starts to break down at higher concentrations where the EDL becomes very thin, of atomic dimensions. Also the Davies thermodynamics correction may be an oversimplification for the higher concentrations. However, more advanced thermodynamic equations, such as Pitzer-Mayorga’s method [165], could not be applied because our current implementation could not handle that level of complexity. It was observed that tortuosity and branching effects did not change the maximum rejection value significantly, but tended to stabilize the rejection value after the flow velocity became larger than the optimized value. Explanations for these experimental and computational observations still need to be explored. The model predicts a decrease of rejection...
with flow velocity at very high values. This could not be found in the experiments since the state-of-the-art membranes can not sustain the required high levels of applied pressure. Instead, only a very blurred trend of rejection diminishing could be observed for NaCl solution at very dilute concentration (1mol/m³). However, as the technology evolves, and more permeable, stronger supported membranes become available, the effect of diminishing rejections at high pressures may become observable.

5.4 Conclusions and future work

The process of nanofiltration of mesoporous membranes can be qualitatively modeled with FEM methods, provided sufficient computational resources are available to handle this calculation-intensive task. The present implementation coupled three major physics processes, mass transport, fluid dynamics and electrostatic interaction, and successfully revealed the purification mechanism. The effect of the pore morphology, including the channel length, the tortuosity, and the branching effect, was studied with 2D models. It was found that channel length, tortuosity and branching did not affect the maximum rejection value significantly, while the channel length scaled reciprocally with the optimized flow velocity. This observation was used to correct the 3D model results and a good agreement was found between the model and experimental value.

To obtain a model that is more accurate and reliable for the nanofiltration process, several refinements should be considered in the future. The most important factor is to develop an algorithm to connect the discrete phenomenon at the nanoscale to a continuum approach that is compatible with finite element methods so that more accurate EDL modeling can be realized. The second significant improvement may be the construction of a more realistic channel that includes the channel morphology, such as tortuosity and channel branching. Conventional 1D models tend to simplify this aspect by averaging membrane properties and introducing experimental fitting parameters into the models. This work did not consider fitting parameters to obtain a model that is more independent of the experimental results, and relies more on the physical membrane structure itself. A third improvement would be to obtain more accurate surface charge calculation algorithms, preferably implanted into the frame work of the FEM model, and real-time calculation of
the surface charge from local concentrations within the channel. However, this effort requires a substantial rebuild of the surface charge modeling algorithm. The surface reaction data necessary for such a model may not be readily available since the large charge unbalance in the membrane pore channel is difficult to establish in conventional surface charging experiments. A fourth aspect that can be further fine tuned are the effects caused by the nanoscale dimensions, such as the dielectric constant changing at the surface and nanofluidic dynamics. Many of these related topics are still active research areas, and a widely accepted methodology and algorithm is yet to be developed.

A FEM membrane nanofiltration model as presented will enable further membrane device design and optimization, by considering the supported layer and materials morphology. In addition the model may provide a starting point for the investigation of the effect of an externally applied electric field [216].
CONCLUSIONS

Inorganic mesoporous membrane can be used for nanofiltration processes. They show great potential in water purification applications such as seawater desalinization, brackish water softening, waste water recycling/regeneration and industrial ultrapure water supply. This concept was verified with a membrane consisting of a mesoporous γ-alumina layer on top of a macroporous α-Al₂O₃ support.

The colloidal filtration casting technique was adapted and fully optimized to produce homogeneous porous α-Al₂O₃ disks with a high quality surface, suitable for thin membrane deposition. The colloidal filtration of well-dispersed α-Al₂O₃ particles with effective particle size 300 nm (AKP30) and 600 nm (AKP15) was successfully applied to produce defect free porous disk shape compacts with a superior quality of the upper disk surface. Alumina compacts with well defined surface smoothness were obtained with sonification and colloidal filtration of 50 wt% α-Al₂O₃ particles in aqueous solution of HNO₃ at pH 2.0 for AKP30 and, aqueous solution of 0.2 wt% Aluminon at pH 9.5 for AKP15. Observation of water and gas permeability, density as well as grain size can be used to establish the proper sintering temperature for specific membrane support application. Both water and gas permeability of optimized compacts show a maximum for a sintering temperature of 950°C for AKP30 and AKP15, explained by the occurrence of pore coarsening combined with little overall shrinkage. The optimized sintering temperatures were found to be 950 C for AKP30 supports and 1050 C for AKP15 supports.

Mesoporous γ-alumina membranes were prepared with the well established and documented sol-gel routine. An innovative ultrasound assisted screen process was developed to purify the Boehmite nanoparticle dispersion that was used for the sol-gel route of membrane preparation. Systematic studies with AFM and DLS methods have been carried out to compare the treated sol quality. It is found that this screening method is suit-
able for the production of large quantities of dispersion at a fairly high particle concentration. It results in almost complete removal of particles, larger than 100 nm. Screening without ultrasound resulted in a more complete removal of large agglomerates but had a very low yield. The colloidal deposition of sols, purified by ultra-sonic assisted screening will lead to the formation of higher quality thin films.

A dead-end pressurized water chamber was constructed to perform an accurate, comprehensive and reproducible testing of the water purification membrane. The testing first determined the optimized testing conditions, with several parameters, including stirring speed, applied pressure, and electrolyte concentration. The membrane was then tested systematically under the optimized operation conditions. Three different electrolytes were tested at various concentrations and the osmotic pressure was detected during the experiments. It is noticed that environmental effects such as temperature and electrolyte concentration only slightly affected the flowrate measurement to the extent of 1–3% for most of the cases. For the first time, the osmotic effect was clearly detected during the testing and quantitatively characterized with the thermodynamic model of Pitzer and Mayorga. Sufficient accuracy for the osmotic effect correction was obtained.

The water purification mechanism of the inorganic mesoporous membrane rests upon an electrostatic field effect, induced by charged groups adsorbed on the surface of the membrane. The nanofiltration process was described with a FEM scheme by modeling three phenomena that occur simultaneously in the system: incompressible fluid flow; chemical diffusion and field-driven migration, and convection of ionic species; and electrostatic interaction. Several corrections; such as non-ideal solution thermodynamics, dependence of the diffusion coefficient on location, variations in local water permittivity; were taken into account in this model to obtain quantitatively valid results. The effect of the pore morphology, including the channel length, the tortuosity, and the branching effect, was studied with 2D models. It was found that channel length, tortuosity and branching did not affect the maximum rejection value significantly, while the channel length scaled reciprocally with the optimized flow velocity. The simulation results demonstrated correctly the experimental trends, and predicted limiting performance at extreme conditions.
The current study covered a full spectrum of research activities from support preparation, membrane synthesis, water purification testing to mechanistic modeling. Within each of these areas, our principle goals were reached and in-depth knowledge was obtained. Based on the thorough understanding of these subjects, topics worth of further investigation are summarized as follows:

- The membrane support must be more permeable. New materials and new preparation methods can be studied. One promising candidate is anodic alumina prepared with electrochemical oxidation of aluminum. The preparation process must be customized and fine-tuned to obtain an anodic alumina membrane with balanced properties of permeability, mechanical strength, thermal/chemical stability and surface smoothness.

- New membrane materials should be studied further. Meso-porous γ-alumina membranes are very suitable for fundamental studies because of their strong tendency towards surface adsorption that amplifies the purification effect. However they are not very stable in extreme (high or low pH) and even mild operation conditions. New materials should be studied, such as meso/micro porous titania or tin oxide membranes, which are known to be more stable in extreme conditions.

- New membrane operation configurations and conditions can be studied. It should be possible to utilize a semi-conductive membrane, such as SnO₂, and apply an external potential to alter the surface charge density of the membrane. This is expected to make the performance of the membrane more controllable and less dependent on the electrolyte properties, such as solution pH, electrolyte type and concentration. However, the manner of attaching the electrode can be critical for such application, and therefore, should be carefully considered and studied, possibly combined with the modeling approach shown.

- In the area of modeling, some aspects of the current model can be refined, such as the implementation of an osmotic effect, real time surface charge density calculation and better algorithms for electrical double layer modeling. To expand the model to other electrolytes, mixed electrolytes and other membrane materials, one must obtain more experimental data for surface reactions, diffusion coefficients and material properties.


129


159. E. N. da C. Andrade, Phil. Mag. 17, 698 (1934).


163. Handbook of Chemistry and Physics, CRC Press; 81st edition (June 6, 2000)


189. Gongyue Tang, Deguang Yan, Chun Yang, Haiqing Gong, John Chee Chai, Yee Cheong Lam, Electrophoresis 2006, 27, 628–639


213. Zhaoli Guo, T. S. Zhao and Yong Shi Generalized hydrodynamic model for fluid flows: From nanoscale to macroscale PHYSICS OF FLUIDS 18, 067107 (2006)


DISTRIBUTION LIST

Dr. Henk Verweij
Dr. Rudy Buchheit
Dr. Patricia Morris
Graduate School
The Ohio State University