Chemical Stability of Ceramic Membrane

ADDITIONAL THESIS

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Introduction

The treatment of wastewater into drinking water is gaining more and more attention due to the water scarcity and increasing water quality requirement. Limited clean water sources will lead to rises in water price, which can significantly increase the treatment costs of wastewater. Furthermore, regulations on the quality of drinking ground, surface and wastewater qualities are becoming stringent, and therefore the calling for higher effective water treatment technologies is of paramount high (Lee *et al.*, 2015a). Among those treatment processes available in industry, membrane filtration is a technology that has been practised successfully for many decades since its emergence in the 1960s (Lee *et al.*, 2015b; Van der Bruggen and Vandecasteele, 2002). Membrane technology has been proved to be highly feasible to produce water with elevated quality from various water sources, such as surface water, well water, brackish water and so on (Ashaghi *et al.*, 2007). Pressure-driven membrane processes include microfiltration(MF), ultrafiltration (UF), nanofiltration(NF) and reverse osmosis(RO). MF and UF often serve to remove large organic molecules, large colloidal particles, and also part of bacteria and viruses (Lens *et al.*, 2001; Ashaghi *et al.*, 2007). With a narrower pore size than MF and UF membranes, NF and RO membranes can even remove much lower molar mass species, such as salt ions and organics. As a result of higher rejection performance, they usually require a higher pressure. However, severe fouling phenomenon and relatively high replacement costs of polymeric membrane which is dominant commercial membranes in market are still big issues concerning widening the application of this method.

Fouling is a phenomenon that the feed solution compounds retain onto the membrane surface, leading to a decrease of flux during filtration process. There are several ways to reduce fouling formation, among which chemical cleaning is the most important method for controlling and minimising irreversible fouling (Basile and Nunes, 2011). A wide range of chemicals can be used to clean the membranes primarily depending on the type of foulant as well as the membrane material.

Ceramic membranes may be an alternative material for polymeric membranes in MF/UF applications. Ceramic membrane has a greater resistance to chemicals, extreme thermal condition and high mechanical force than polymeric membranes (Weber *et al.*, 2003). Hence they are expected to be able to coop with harsh cleaning agents and sterilized at high temperatures without sacrificing the performance.

Ceramic MF/UF membranes are commonly applied as pre-treatment before Reverse Osmosis(RO) to minimising the fouling behaviour during RO treatment (Bartels *et al.*, 2005; Flemming, 1997). Due to high foulant concentration in sewage, fouling in the ceramic membranes and in the subsequent RO membranes are main concern in this ceramic membrane application.

On account of the availability and cost consideration, NaClO has been commonly used in many treatment plant and shows a good performance in the restoration of membrane permeability (Kimura *et al.*, 2004; Shang *et al.*, 2017; Kramer *et al.*, 2015). However, in previous research damage onto the ceramic NF membranes was observed, resulting a permeability decline and MWCO increase, and therefore two hypothesis for damage on the membranes are put forward.

- Filtration layer was not heated enough to remove all the polymeric substances, that were introduced in membranes when applying sol-gel method;
- Chemical cleaning has an effect on the sealing at the edge of membranes.

To test and verify these hypothesis, commercial available ceramic membranes were heated with 450°C, cleaned with chemicals, NaClO and NaOH, and glued with epoxy glue.

2

Literature Review

2.1. Basics of Ceramic Membrane

2.1.1. Emergence of Ceramic Membrane

Membrane separation is a process where a membrane is used as a barrier to retain or separate some components in feed water from the other components. There are different mechanisms necessary to achieve separation, with membrane distillation being based on differences in vapour pressure, reverse osmosis on differences in solubility and on the diffusivity of water and salt and electrodialysis on ion transport in charge selective ion-exchange membranes (Mulder, 2012). External energy is required to make the separation processes function. The selectivity of different membranes or process particularly depends on the mechanisms applied in the process and the type of membranes. For porous membranes, which are widely applied in MF and UF, the selectivity can be affected by pore size, pore size distribution, electric charge and membrane affinity. Dense nonporous membranes applied in gas separation and pervaporation, are not considered here.

Membranes play an important role in separation industry, nevertheless, they were not considered technically important until mid-1970 (Bhave; Mulder, 2012). Since the middle of twentieth century, synthetic membranes are gaining more attention and have been successfully used in many industry (Basile and Nunes, 2011). The success of membrane filtration is due to its performances and feasibility of use.

Most commercially utilized synthetic membranes used in water treatment process are made of polymeric structures. However, as fouling is the most significant problem during filtration process, a lot of chemicals are used to clean the membranes, depend on what kind of the fouling is and how severe it is. When more chemicals are introduced into cleaning step, the chemical stability of membranes become more important, since they are expected to be stable even in aggressive media, such as acids and alkali. As previous research indicated, polymeric membranes cannot handle high concentration of chemicals while ceramic membranes are relatively stable even in aggressive situations (Heijman and Bakker, 2007).

Ceramic membranes are made of inorganic material, usually Al_2O_3, TiO_2 and ZrO_2,

Table 2.1: The corresponding MWCO of different filtration membranes

Membrane type	**MF**	**UF**	**NF**	**RO**
MWCO	>100 kDa	3-100 kDa	1-2 kDa	<1 kDa

which enable it to superior chemical, thermal and mechanical properties. Historically, ceramic membranes are much less used owing to their higher fabrication costs and lower packing densities than the polymer-based membranes (Baker, 2000). However, as the result of technology development in ceramic membranes, a cheaper, more effective and more compact ceramic membranes can be formed, potentially provoking the widening of their applications.

2.1.2. Micro Structure

Membranes can be categorized according to their (i) structure, (ii) material, (iii) production method, and (iv) applications. Depending on their identical structure, membranes can be defined as dense, porous or asymmetric membranes. Furthermore, for porous membranes, there are a variety of membranes according to their pore size difference, namely microfiltration(MF), ultrafiltration(UF), nanofiltration(NF) and Reverse osmosis(RO) membranes. Usually the molecular weight cut off, defined as the largest molecular weight species for which the membrane has more than 90% rejection, is used as a measure of pore size. Therefore, the difference in MWCO of four main types of membranes was also given in table 2.1 (Basile and Nunes, 2011). It should be noted that there is no conclusive definitions to distinguish different membrane types (Kramer *et al.*, 2015). In this study, ceramic membranes with a MWCO 450 Da were defined as NF membranes.

Both polymeric and inorganic material are used to produce membranes, which might have a dense or porous layer depending on their use an applications. Ceramic membranes are generally a porous membrane which consists of several layers with different properties and composites. As figure 2.1 shows (Duscher, 2013), usually a ceramic membranes has a ceramic support layer, such as SiO_2, onto which several porous separating layers, often silica, alumina or zirconia (Gobina, 2006; Ku *et al.*, 2008) with decreasing pore sizes are deposited until designed pore sizes are reached. The supporting sub-layer plays the function of providing adequate mechanical strength. This kind of combination of structures allows high selectivity with good permeation fluxes.

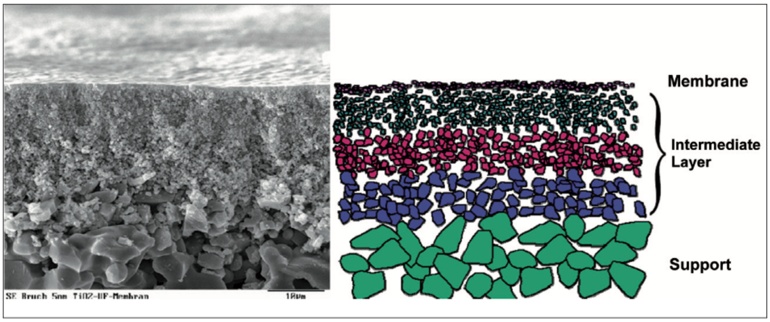


Figure 2.1: Typical structure of a ceramic membrane

2.2. Fabrication Process

2.2.1. Main Stages

Fabrication of composite ceramic membranes differs due to the different requirements for structures and quality and morphology properties of membranes. Generally, there are three main stages to form ceramic membranes: preparation of the ceramic powder paste; shaping of the ceramic powder into the desired geometry; and heat treatment including calcination and sintering (Li, 2007). After the main steps, some modification, such as adding additional deposited layer, can be made by further heat treatment.

2.2.2. Pore modification method

Layer deposition after main steps is relatively more important than the previous treatment for altering the microstructure of ceramic membranes. There are many techniques applied in layer deposition: dip or spin coating; sol-gel method and ALD coating etc..

- **Dip coating**
  Dip coating or spin coating is a method that a dry porous support base which is production from main steps, is dipped into a ceramic powder suspension and withdrawn from it after certain duration (Gu and Meng, 1999). Due to the capillary forces between the ceramic particles and suspension, the liquid would be sucked into the support pores resulting a uniform layer skin on virgin membrane. Dip coating is a novel fabrication method to produce porous membranes waiting for further research to develop a complete model to interpret some effects of different aspects,such as dipping time and withdraw speed of substrate (Babaluo *et al.*, 2004).

- **Sol-gel method**
  Sol-gel method is involved when membranes with pores size range of $1-100\ nm$ representing a higher selective, so called nanofiltration membranes, is required

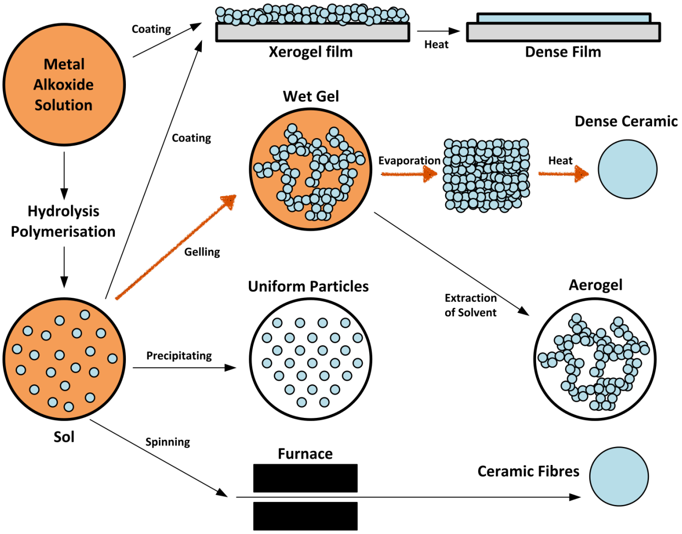


Figure 2.2: Schematic representation of the different stages and routes of the sol-gel technology

(Das and Maiti, 2009). Sol-gel method is a wet-chemical technique widely used for the fabrication of materials starting from a colloidal solution, often metal alkoxide or salts. The colloidal solution acts as a precursor, which gradually evolves towards the formation of gel-like phase system (Uche, 2013). The fraction of particle in the colloidal is usually too low to recognize a gel-like property, therefore a subsequent drying process to remove the remaining liquid is required. Afterwards, a thermal treatment, often sintering, is necessary to enhance the mechanical strength and structure stability. As figure 2.2 illustrates, there are several approaches to applying sol-gel method, among which the route with orange arrow represents the process described above. The distinct advantages of Sol-gel method as opposed to the traditional processing techniques is a much low temperature during thermal treatment process.

- **Atomic layer deposition method**
  Atomic layer deposition(ALD) is a self-limiting gas-phase thin film technology that atomic scale thin layers of metal, polymer and many other materials are grown on support substrate. ALD is based on a reactions between two precursors, which are separated strictly and then absorbed on pore wall or reacting with previously absorbed precursor (Li *et al.*, 2012). Between each surface reaction, there is a purge step with inert gas to remove unreacted precursors and by-products (Marichy *et al.*, 2012). ALD is a special variant of well-known chemical vapour deposition(CVD) method while the difference between them is obvious: The reaction between two precursors takes place at the same time and precursors can decompose in CVD

method (Pinna and Knez, 2012).

- **Plasma ALD method**
  Plasma came to light in 1992, when De Keijser and Van Opdorp of the Philips Research Laboratories in Eindhoven published a report on atomic layer deposition of GaAs using H radicals (De Keijser and Van Opdorp, 1991). However, the method was not developed until the end of 1990s, when semiconductor industries began being interested in ALD method. In plasma ALD, also referred as plasma-enhanced ALD(PEALD), the surface of bulk is exposed to the species generated by a plasma during reaction steps. One of the most significant difference between plasma ALD and thermal ALD is that the reactant species generated by plasma gas during plasma steps are mainly radicals, one kind of species which are more reactive than hydroxide species.

2.3. Fouling Phenomenon

Membrane fouling is the major limiting factor in membrane filtration process. Fouling, caused by the deposition of trapped substances in feed water onto membranes surface and/or pores within membranes, is responsible to a long term flux decline and decrease of water quality investigated in filtration process. Generally, there are four major types of fouling: scale, silt, bacteria and organic (Baker, 2000).

Scale is caused by deposition of dissolved metal salts on membrane surface. With the salts removed in permeate water, the salts concentration in feed water gradually increases. When the ion concentration in feed water exceed the solubility limits, salts begin to precipitate on membrane surface as scale. Scale can be easily removed by adding acids into feed water, therefore it is not a major issue concerning the fouling phenomenon.

Silt is a kind of formation of particulates present in feed water. Typical sources of silt are organic colloids, iron corrosion products, precipitated iron hydroxide, and fine particulate matter. Usually the SDI (Silt Density Index) is chosen as a predictor indicating the possibility of one kind of feed water to produce fouling by silt. The acceptable value of SDI depends on the membrane material and module design, but 5 is the maximum desired value most of the time.

Fouling can also form by the growth of bacteria on membrane surface, also known as biofouling. This type of fouling happens quite often in cellulose acetate membranes because they are a good nutrient resource for bacteria. If uncontrolled, the cellulose acetate membranes can be completely destroyed by biofouling. Therefore, sterilization is required before filtration process running with cellulose acetate membranes, or other materials susceptible to bacteria. Chlorination is a common way to sterilize the feed water to cellulose acetate membranes to make sure no biofouling occurs.

Organic fouling is the attachment of organic substances, such as oil and grease onto the membrane surface. Filtration and carbon adsorption are used in removal of organics in feed water.

2.4. Cleaning Method

Cleaning method can be categorized into tow main types: physical method and chemical method. As the name indicating, physical cleaning method removes reversible foulants from membrane surface by mechanical force. Commonly used physical method includes: back washing, forward flush, air flushing, rinsing and sponge ball cleaning.

For chemical cleaning, the species of chemicals used in cleaning can be in a wide range. For instance, acids may be used to removal scale, and alkalis is commonly used for removing organic fouling (Zondervan and Roffel, 2007) and whey protein (Bartlett *et al.*, 1995). Ozone and oxidants have also been used to remove organic fouling.

The way to control and prevent membrane fouling is greatly depend on the particles composition in feeding, plant operation system and membranes properties. In reality, the cleaning method applied in each water treatment plant is always a combination of the two method. When it comes to the wastewater treatment, chemical cleaning dominates the regular cleaning schedule due to the high contamination of feed water. Among those chemicals, hypochlorite is highly chosen due to its ready availability, reasonable price and high efficiency (Arkhangelsky *et al.*, 2007). Since new UF material is claimed to be highly resistant to oxidants, hypochlorite is then widely recommended as a popular ingredient of cleaning recipe (Pilutti and Nemeth, 2003; Liu *et al.*, 2001).

3

Materials and Methodology

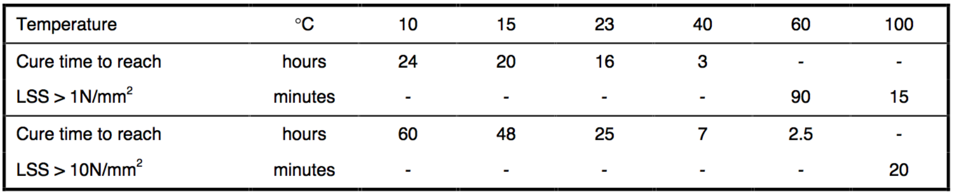
3.1. Materials

3.1.1. Substrate membranes

Commercial ceramic nanofiltration(NF) membranes (Inopor GmbH, Germany) were used in this study. The Inopor membrane is a single-channel tubular membrane, with inner diameter of 7 mm and outer of 10 mm and a length of 100 mm. The effective filtration area is 0.00163 m^2. The inner layer, which is separation layer, has a porosity of 30%, as described by the manufacturer. Different materials are used to produce one single membrane. The separation layer is made of titanium dioxide (TiO_2) while the support layer, which is located in the outside, is made of alumina (Al_2O_3). These NF membranes used in this experiment are claimed to have a MWCO of 450 Da by the supplier.

3.1.2. Epoxy glue

The Epoxy glue, Araldite® 2020 (Huntsman Corporation) was used in experiment to seal the edge of tubular ceramic membrane. Araldite® 2020 is a mix of two component curing, XW 396 and XW 397, with low viscosity and suitable for bonding a wide range of metals, ceramics,rubbers and so on. It can be activated in low temperature (0-100 °C) with cure time ranging from 15 minutes to 60 hours, as the data in figure 3.1 shows Although the processing temperature and cure time various during the experiment, the glue strength should be the same as long as the cure time matches the corresponding temperature.



Temperature	°C	10	15	23	40	60	100
Cure time to reach	hours	24	20	16	3	-	-
LSS > 1N/mm^2	minutes	-	-	-	-	90	15
Cure time to reach	hours	60	48	25	7	2.5	-
LSS > 10N/mm^2	minutes	-	-	-	-	-	20

Figure 3.1: Times to minimum shear strength, LSS = Lap shear strength

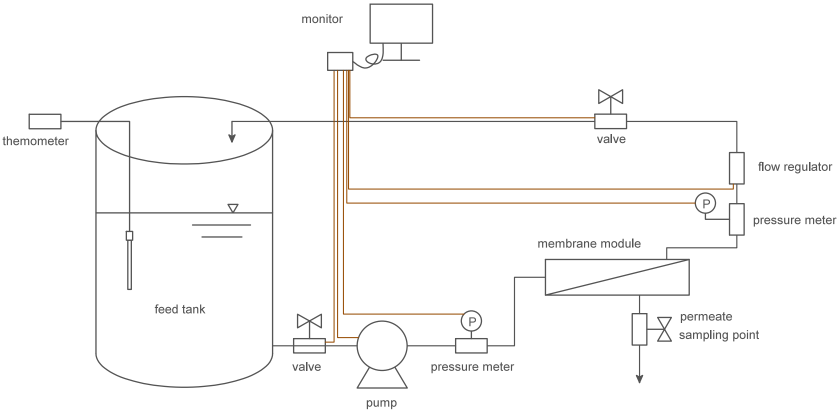


Figure 3.2: Schematic overview of the cross-flow ceramic NF filtration system(Kramer *et al.*, 2015)

3.2. Filtration Set-up

3.2.1. Experiment protocol

The filtration experiments were conducted in the Waterlab at TU Delft, where an OSMO water filtration system was installed. The OSMO system consists of a feed tank of 150 capacity and a filtration part. The picture and schematic overview of OSMO installation is shown in figure 3.3 and 3.2. A cross-flow with constant flowrate 150 L/s and flow velocity 1.08 m/s were applied. Only the concentrate was fed back into the feed tank since the permeate volume is relatively negligible compared to the feed water volume ($< 2\%$). Temperature in feed water increased over time therefore temperature correction was applied in calculation.

- Heating treatment

  Some of membranes were kept in oven at 450 °C for one hour.

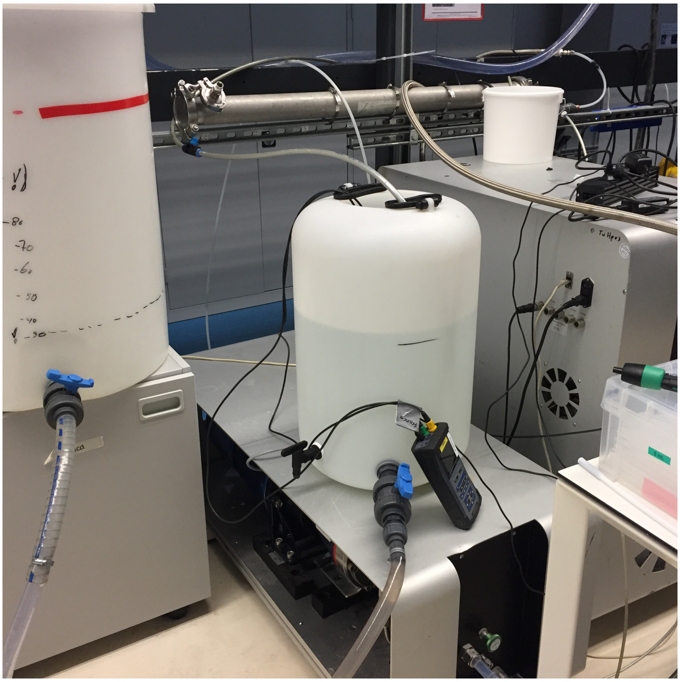


Figure 3.3: Cross-flow ceramic NF filtration system in WaterLab at TU Delft

In order to examine the influence of chemical cleaning and high temperature on membranes, treatments of chemical cleaning and oven heating were combined. The detailed scheme of various treatments on membranes are shown in experiment scheme table 3.1.

3.3. Membrane characterization

3.3.1. Permeability

Water filtration performance was examined by temperature-corrected permeability. Demineralized water was filtered through substrate membranes at a constant TMP of 4 bar. Three samples were collected during filtration experiment to determine water flux and feed water temperature was monitored. An increase of water temperature was observed, which could be a result of heat transfer from the cross-flow pump, and therefore a temperature-corrected permeability equation was calculated using equation 3.1 (Shang *et al.*, 2017).

$$L_{p,20^\circ C} = \frac{J}{\Delta P} \cdot \frac{\eta_T}{\eta_{20}} = \frac{J \cdot e^{-0.0239 \cdot (T-20)}}{\Delta P} \tag{3.1}$$

Table 3.1: Experiment scheme for substrate membranes

Membrane	**Treatment**			
F1	Oven	Glue	NaClO	Glue
F2	Oven	Oven		Glue
F3	Oven	Glue	NaClO	Glue
F4			NaClO	Glue
F5	NaOH			
F6	NaOH			
F7	NaOH	Glue		
F8	NaOH			
F9	NaOH			
F10	NaOH			
F11	NaOH			
G02			NaClO	Glue

NaOH: soaking in 2 % NaOH for 30 minutes , at 97 $^\circ C$
NaClO: soaking in 1 % NaOH for 100 hours , at 25 $^\circ C$
Glue: glue with epoxy glue
Oven: heated in oven at 400 $^\circ C$

where: $L_{p,20^\circ C}$ – permeability at $20^\circ C$, $Lm^{-2}h^{-1}\text{bar}^{-1}$
J – measured membrane flux, $Lm^{-2}h^{-1}$
η_T – permeate viscosity at measured water temperature
η_{20} – permeate viscosity at $20^\circ C$
T – measured water temperature, $\circ C$
ΔP – measured TMP, bar

3.3.2. Molecular weight cut-off (MWCO)

MWCO, namely Molecular weight cut-off, is defined that the tracer molecule whose weight is larger than MWCO would be removed in permeate at least 90% . A mixture of Polyethylene glycols (PEGs) solution with a a concentration of 0.6 g/L was filtered through substrate membranes at room temperature and under constant trans-membrane pressure(TMP) of 4 bar. The molecule weight of PEG feed solution ranged from 100 Da to 1000 Da. Because the PEG molecules are non-charged, their rejection by membrane is the result of steric rejection. That means, the PEG molecules which are larger than the pore size of membrane would be rejected in the concentration while smaller ones could pass through the membrane. In each filtration test, both permeate and feed solution were sampled and also temperature was monitored.

To calculate the MWCO, the permeate and feed solution samples were analysed by a high-performance liquid chromatography system (HPLC, Shimadzu, Japan) equipped with a size exclusive chromatography columns (SEC, 5 μm 30 Å , PSS Polymer Standards Service GmbH, Germany). SEC, also known as gel permeation chromatography or gel filtration chromatography, separates particles on the basis of molecular size. It is used primarily for the analysis of large molecules such as proteins and polymers. The separation mechanism is like adsorption that smaller molecules are trapped into the solid adsorbent material inside chromatography column while larger molecules simply pass by the adsorbent as they are too large to be adsorbed into the pores in adsorbent. That means larger molecules come out of the column earlier than smaller molecules and give a short retention time.

With calibration samples, which are the permeates from feeding single size of PEG solution, tested in HPLC, a series of corresponding retention time of different PEG molecule can be found. Using a exponential model to fit the curve(molecule weight in function of retention time) gives the calibration curve, as figure 3.4 shows, where each elution time is corresponded to a specific molecules weight. The corresponding rejection curves were then plotted by determining the rejection rate of a PEG with certain molecular weight using equation 3.2 (Shang *et al.*, 2017). Afterwards, the experimental retention curves were described by a log-normal model as function of MW and MWCO, given by equation 3.3 (Shirley *et al.*, 2014; Van der Bruggen and Vandecasteele, 2002). This model is on the basis of size exclusion of uncharged molecules and negligible diffusion rate during filtration experiment.

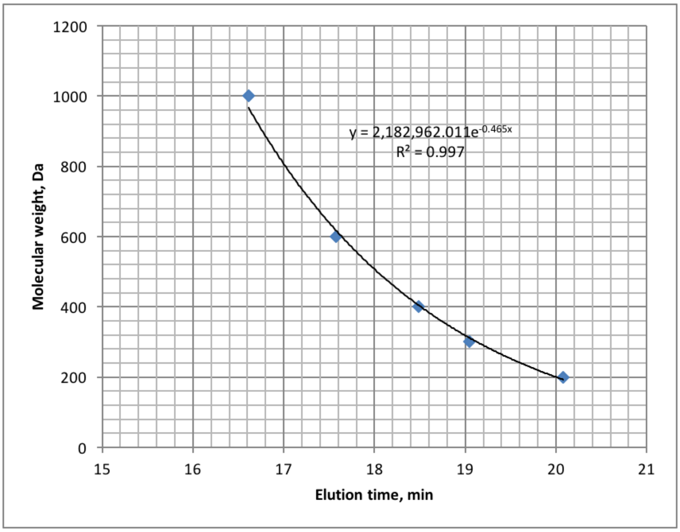


Figure 3.4: Calibration curve for 450 Da nanofiltration membranes

$$R_i(\%) = \frac{C_{i,feed} - C_{i,permeate}}{C_{i,feed}} \tag{3.2}$$

where: $R_i(\%)$ – retention of PEG molecule i, %
$C_{i,feed}$ – PEG concentration in feed solution, mg/L
$C_{i,permeate}$ – PEG concentration in permeate solution, mg/L

$$\sigma(MW_s) = \int_0^{MW_s} \frac{1}{S_{MW}\sqrt{2\pi}} \frac{1}{MW} \exp[-\frac{(\ln(MW) - \ln(MWCO) + 0.56S_{MW})^2}{2S_{MW}^2}]dMW \tag{3.3}$$

where: $\sigma(MW_s)$ – reflection coefficient, %
S_{MW} – standard deviation of molecular weight retention, Da
$MWCO$ – molecular weight cut-off, Da

4

Results and Discussion

4.1. Characterization

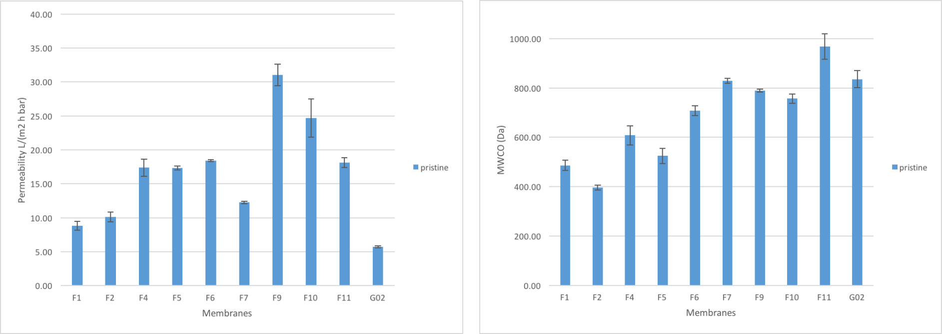
All membranes were characterized by MWCO test and permeability test before any treatment. The characterization results of pristine membranes are shown in figure 4.1a and 4.1b. It can be seen that permeability fluctuates from 6 to 31 $L/(m^2 \cdot h \cdot bar)$. Moreover, the MWCO measured of most of membranes except F1 and F2 are over 450 Da which is the claimed MWCO by supplier. Thus it can be expected that the performance of these membranes are considerably different from each other.

4.2. Heating treatment

4.2.1. Oven

As a preparation for NaClO cleaning treatment,new membranes F1, F2 and F4 were extra sintered and the permeability and MWCO were tested, showed in figure 4.3a and 4.3b. The main reason that heating treatment was performed here was that we considered there were impurities in filtration layer due to the imperfect performance of sol-gel method and therefore extra heating might remove the polymers from the filtration layer to strengthen the filtration layer. The three membranes were heated with a fixed temperature profile where temperature increased gradually from 0 to 450 $^\circ C$ within 8 hours and stayed at 450 $^\circ C$ for one hour. The maximum temperature was similar to sintering temperature of supplier and was chosen in a way that the membrane structure would not be damaged or changed (Burnat *et al.*, 2014).

It can be seen that permeability increased significantly and a small growth of MWCO can be noticed. Among these membranes, F2 was selected to be heated second time and a further but smaller increase both in permeability and in MWCO can be found. The increase of permeability suggested the resistance decrease on the top layer of ceramic membrane and a possible damage on the the structure of membranes. However, it is common to know that ceramic membranes have a high thermal stability (Lee *et al.*, 2015b). But we knew there was a glass sealing at the edges of tubular membrane, covering both ends of membranes. The glass sealing, which might not be able to resist to high thermal conditions, was likely the cause of the drop of the resistance of membranes.



(a) Permeability

(b) MWCO

Figure 4.1: Membranes characterization for pristine membranes

Therefore we decided to glue the membranes with epoxy glue at both ends of membranes F1, F2 and F4.

4.2.2. Glue

A broken sealing was suspect of the cause of increase of permeability and MWCO. Therefore the heated membranes were glued by epoxy glue around the membrane edge at both ends, as figure 4.2. The result is shown in figure 4.3a and 4.3b. It seemed that the glue worked well and proved the original sealing was to some extent damaged. When we looked at the membrane F2, it could be noticed that the MWCO after glue was still much higher than that before oven treatment, compared with membranes F1 and F4. This further indicated that broken sealing might not be the only reason of the drops of resistance and increases of MWCO and to some extend proved that membranes structure were damaged.

In previous researches, Larbot (Larbot *et al.*, 1988) reported that the lowest sintering temperature for titania membranes was 400°C. However, on the contrary, A.C. Pierre (Pierre, 1997) described that the temperature applied in sintering process usually did not exceed 400 °C. And in Nandi's research (Nandi *et al.*, 2008), high temperature of 950°C was used. The substrate membranes combined titania and alumina material, and therefore it was hard to predict that what the porosity actually is after oven treatment, due to the different properties of titania and alumina. Some previous researches proved that the porosity of membrane would decrease as the sintering temperature increases (Pierre, 1997; Ricardo *et al.*, 1999; Lee *et al.*, 2015b), while others showed the other way around (Larbot *et al.*, 1988; Othman and H. Mukhtar, 2000; Brodsky and Ko, 1994). If the membranes react in thermal treatment as the same in the sintering process in terms of pore deformation, our work would follow the theory of M. Othman (Othman and H. Mukhtar, 2000) that the porosity level would increase as the temperature increases but the me-

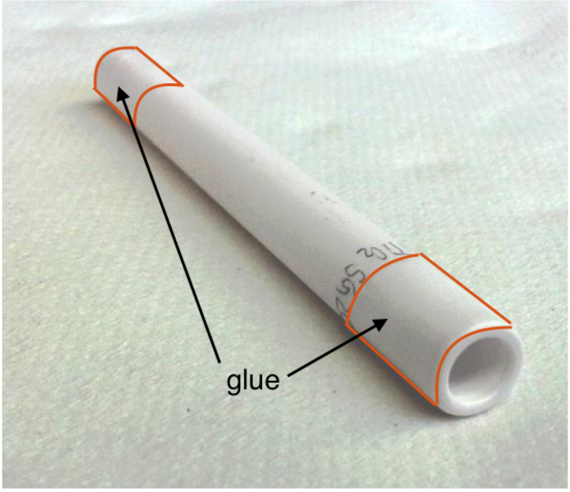


Figure 4.2: Glue on both ends of membrane

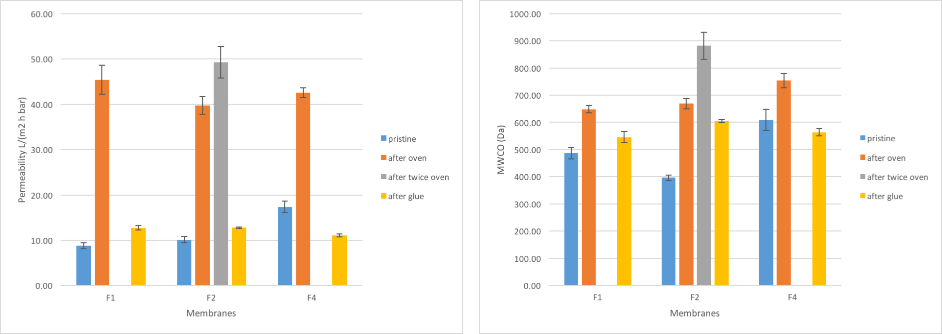
chanical strength falls significantly. M. Othman also indicated that this phenomenon is further exacerbated when membrane materials are not free from impurity and too thick.

4.3. Chemical cleaning treatment

4.3.1. Chemical cleaning

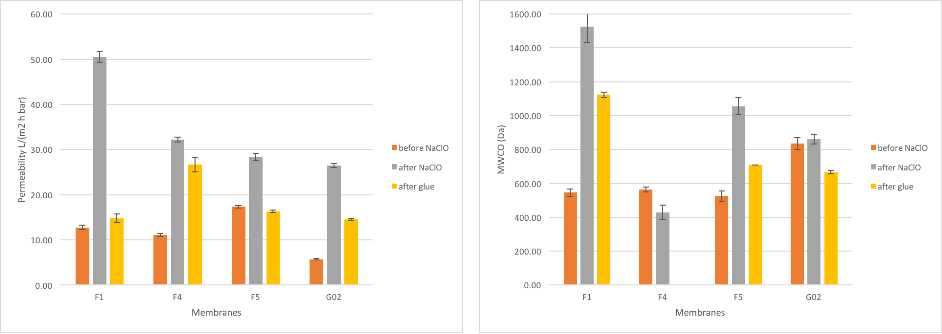
Chemical cleaning was conducted with two kinds of chemicals, NaClO and NaOH. Membranes F1, F4, F5 and GO2 were subjected to one time soaking in 1% NaClO solution at 25 $^{\circ}C$ for 100 hours, while membranes F6, F7, F9, F10 and F11 were soaked in 2% NaOH solution at 97 $^{\circ}C$ for 30 minutes. Among those, which were treated with NaClO, some (F1, F4) were preheated at 450 $^{\circ}C$ and the others (F5, GO2) were totally new membranes before they were soaked in the NaClO solution. All membranes, which were cleaned with NaOH solution, were totally new. The results are illustrated in figure 4.4a, 4.4b for NaClO cleaning and figure 4.5a, 4.5b for NaOH cleaning.

It can be seen that, except membrane F9, all membranes revealed an dramatic increase of permeability after chemical cleaning test. The result was a sign of severe corrosion of membrane surface or membrane grain. This was further proved by the change in MWCO. It was worth noticing that all membranes, except membrane F4, showed an increase in MWCO, with increasing rate ranging from 3% to 213%. Strangely, membrane F9 showed a slight decrease in permeability. The reason for the decrease is not clarified yet but might be fouling by a small amount of corrosion products (Buekenhoudt, 2008), or that there was too much glue on the membranes making the membrane area smaller and thus the permeability got lower.



(a) Permeability (b) MWCO

Figure 4.3: Membranes characterization after heat treatment

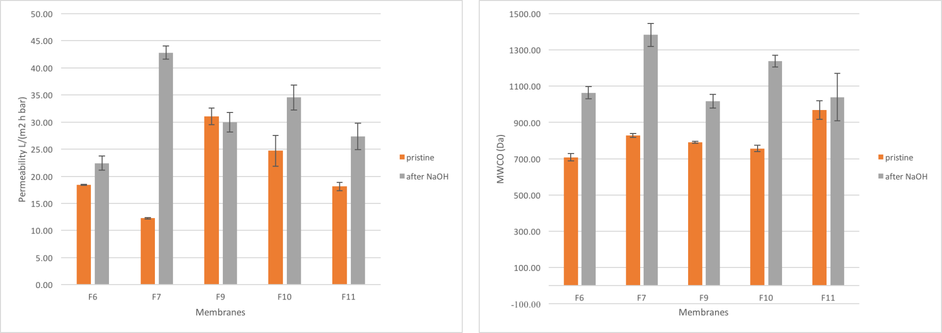


(a) Permeability (b) MWCO

Figure 4.4: Membranes characterization after NaClO soaking and glue

However, the result is somehow conflict to some previous research, where TiO_2 showed a superb chemical stability. Van Gestel (Van Gestel *et al.*, 2003) performed corrosion tests on microporous TiO_2 membranes calcined in 450 $^{\circ}C$. Both static (Van Gestel *et al.*, 2002) and dynamic corrosion tests (Van Gestel *et al.*, 2003) showed that membranes were highly chemical stable in caustic solution with a pH up to 13. Therefore, it is expected that the Al_2O_3 support and TiO_2 top layer membrane can be stable during the NaClO tests.

If the big degradation or corrosion did not point to membrane surface or grain due to its high chemical stability, then the cause might be the sealing. Buekenhoudt mentioned in his research that correct sealing material was also important. Usually, teflon(PTFE) or glass sealing is recommended in industrial use (Buekenhoudt, 2008).



(a) Permeability (b) MWCO

Figure 4.5: Membranes characterization after NaOH soaking

4.3.2. Glue

Due to the bad performance of original sealing in heating treatment, the sealing was considered one of the possible causes of the increase of MWCO and permeability. Therefore both ends of membranes were glued by epoxy glue. The performance after glue treatment recovered slightly, but the permeability and MWCO were still higher than that before chemical cleaning treatment. One thing should be remarked is that the glue of membrane F4 peeled off badly during filtration test, seeing figure 4.6, and therefore the data for F4 after glue was missing.

Figure 4.4a, 4.4b summarizes MWCO and permeability of membranes after glue treatment. It can be seen that both permeability and MWCO recovered in different degrees. Membrane F5 almost recovered to the state before chemical cleaning. This proved that the original sealing is in a poor quality and it can be damaged during filtration. However, except F5, others just recovered part of MWCO and permeability, indicating that some corrosion took place in membrane surface or bulk part.

Apart from the poor sealing condition, the increases of permeability and MWCO can be explained as follows. Firstly, the impurity within a membrane would significantly increase the risk of degradation of membranes, even though the material TiO_2 itself is capable of surviving extreme conditions (Buekenhoudt, 2008); Secondly, the material phase, usually related to calcination temperature, makes a big difference. The anatase phase of TiO_2, which is a completely form of crystalline, is much more stable than its amorphous phase. The complete crystalline form requires higher sintering temperature. Moreover, the effect of phase transition on membranes stability would be exaggerated when the membranes contained multilayer configurations (Van Gestel *et al.*, 2002). Because the fabrication procedure in not revealable, the method parameters, such as temperature, is unknown. Thus, the real reasons are not clear now.

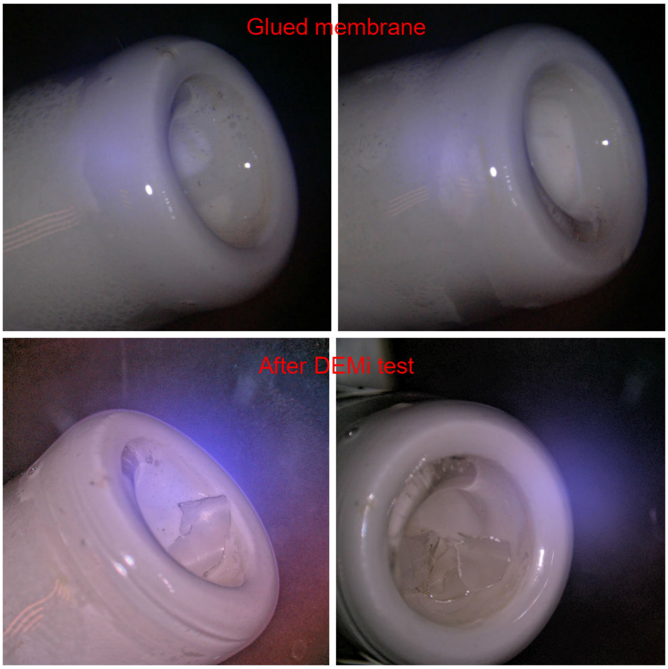


Figure 4.6: Photos of membrane F4 before and after permeability test

5

Conclusion

Ceramic NF membranes were treated thermally and chemically to test their quality.

In thermal test, the membranes showed an increase of permeability and MWCO after heated at 450 $^\circ C$ for an hour. Afterwards, membranes performance partially recovered with glue covering on both ends of membranes, which meant that glue can only fix part of the problem. The rapid irreversible degradation of the membrane performance indicated a severe corrosion on the membrane surface or membrane grain. Many aspects can affect the final thermal stability of membranes, such as sintering temperature, contact time, viscosity of precursors. Even small changes of any of them would shift the outcome.

In chemical cleaning test, the membranes showed a similar behaviour as in thermal test. Glue still improved some of the performance in terms of permeability and MWCO. This can explained in two ways: impurity of materials and the correct form of materials. Impurity within membranes decrease the homogeneity of membranes, and thus make the properties unpredictable. Another interesting found is when membranes contain several layers, such as support, intermedia layer and top layer, the sandwich configuration of membrane can also be seen as impure. Therefore, a multilayer membranes require one kind of membranes with higher stability compared with unsupported membranes. As commonly known, TiO_2 material is stable chemically and thermally when it is in its anatase form, which is completely crystalline. If TiO_2 is not completely crystallized, both the chemical and thermal stability would dramatically decrease.

From both thermal test and static chemical test, we can draw following conclusions in terms of thermal stability and chemical stability, as confirmed by experiments:

- The original sealing were not able to suffer temperature of 450 $^\circ C$ and either the caustic solution.
- The NF membranes did not show high chemical and thermal stability as expected. High temperature of 450 $^\circ C$ and caustic solution (2% NaClO and 2% NaOH solution) could damage the structure of membranes.

Bibliography

M. Lee, Z. Wu, and K. Li, *Woodhead Publ. Ser. Energy* (2015) pp. 43–82.

M. Lee, Z. Wu, and K. Li, *Advances in ceramic membranes for water treatment* (Elsevier Ltd, 2015).

B. Van der Bruggen and C. Vandecasteele, *Distillation vs. membrane filtration: overview of process evolutions in seawater desalination,* Desalination **143**, 207 (2002).

K. S. Ashaghi, M. Ebrahimi, and P. Czermak, *Ceramic Ultra- and Nanofiltration Membranes for Oilfield Produced Water Treatment : A Mini Review,* , 1 (2007).

P. Lens, P. N. Lens, G. Zeeman, and G. Lettinga, *Decentralised sanitation and reuse: concepts, systems and implementation* (IWA publishing, 2001).

A. Basile and S. P. Nunes, *Advanced membrane science and technology for sustainable energy and environmental applications* (Elsevier, 2011).

R. Weber, H. Chmiel, and V. Mavrov, *Characteristics and application of new ceramic nanofiltration membranes,* Desalination **157**, 113 (2003).

C. R. Bartels, M. Wilf, K. Andes, and J. Iong, *Design considerations for wastewater treatment by reverse osmosis,* Water science and technology **51**, 473 (2005).

H.-C. Flemming, *Reverse osmosis membrane biofouling,* Experimental Thermal and Fluid Science **14**, 382 (1997).

K. Kimura, Y. Hane, Y. Watanabe, G. Amy, and N. Ohkuma, *Irreversible membrane fouling during ultrafiltration of surface water,* Water research **38**, 3431 (2004).

R. Shang, A. Goulas, C. Y. Tang, X. de Frias Serra, L. C. Rietveld, and S. G. Heijman, *Atmospheric pressure atomic layer deposition for tight ceramic nanofiltration membranes: Synthesis and application in water purification,* J. Memb. Sci. **528**, 163 (2017).

F. C. Kramer, R. Shang, S. G. Heijman, S. M. Scherrenberg, J. B. van Lier, and L. C. Rietveld, *Direct water reclamation from sewage using ceramic tight ultra-and nanofiltration,* Separation and Purification Technology **147**, 329 (2015).

J. Mulder, *Basic principles of membrane technology* (Springer Science & Business Media, 2012).

R. R. Bhave, *Inorganic membranes-synthesis, characteristics, and applications.*

S. G. J. Heijman and S. Bakker, *Ceramic microfiltration as the first step in surface water treatment* (KIWA Water Research, 2007).

R. W. Baker, *Membrane technology* (Wiley Online Library, 2000).

S. Duscher, *Ceramic membranes in chemical and pharmaceutical applications,* Ceramic Applications **1**, 19 (2013).

E. Gobina, *Apparatus and method for separating gases,* (2006), uS Patent 7,048,778.

A. Y.-C. Ku, J. A. Ruud, J. L. Molaison, L. A. Schick, and V. Ramaswamy, *Functionalized inorganic membranes for gas separation,* (2008), uS Patent 7,396,382.

K. Li, *Ceramic membranes for separation and reaction* (John Wiley & Sons, 2007).

Y. Gu and G. Meng, *A model for ceramic membrane formation by dip-coating,* Journal of the European Ceramic Society **19**, 1961 (1999).

A. A. Babaluo, M. Kokabi, M. Manteghian, and R. Sarraf-Mamoory, *A modified model for alumina membranes formed by gel-casting followed by dip-coating,* Journal of the European Ceramic Society **24**, 3779 (2004).

N. Das and H. S. Maiti, *Ceramic membrane by tape casting and sol–gel coating for microfiltration and ultrafiltration application,* Journal of Physics and Chemistry of Solids **70**, 1395 (2009).

D. O. V. Uche, *Sol-gel technique: A veritable tool for crystal growth,* Adv Appl Sci Res **4**, 506 (2013).

F. Li, Y. Yang, Y. FAN, W. XING, and Y. Wang, *Modification of ceramic membranes for pore structure tailoring: The atomic layer deposition route,* Journal of Membrane Science **397-398**, 17 (2012).

C. Marichy, M. Bechelany, and N. Pinna, *Atomic Layer Deposition of Nanostructured Materials for Energy and Environmental Applications,* Advanced Materials **24**, 1017 (2012).

N. Pinna and M. Knez, *Atomic layer deposition of nanostructured materials* (John Wiley & Sons, 2012).

M. De Keijser and C. Van Opdorp, *Atomic layer epitaxy of gallium arsenide with the use of atomic hydrogen,* Applied physics letters **58**, 1187 (1991).

E. Zondervan and B. Roffel, *Evaluation of different cleaning agents used for cleaning ultra filtration membranes fouled by surface water,* Journal of Membrane Science **304**, 40 (2007).

M. Bartlett, M. Bird, and J. Howell, *An experimental study for the development of a qualitative membrane cleaning model,* Journal of Membrane Science **105**, 147 (1995).

E. Arkhangelsky, D. Kuzmenko, N. V. Gitis, M. Vinogradov, S. Kuiry, and V. Gitis, *Hypochlorite cleaning causes degradation of polymer membranes,* Tribol. Lett. **28**, 109 (2007).

M. Pilutti and J. E. Nemeth, *Technical and cost review of commercially available mf/uf membrane products,* Int. Desalin. Assoc. Cong., BAH03-029 (2003).

C. Liu, S. Caothien, J. Hayes, T. Caothuy, T. Otoyo, and T. Ogawa, *Membrane chemical cleaning: from art to science,* Pall Corporation, Port Washington, NY **11050** (2001).

J. Shirley, S. Mandale, and V. Kochkodan, *Influence of solute concentration and dipole moment on the retention of uncharged molecules with nanofiltration,* Desalination **344**, 116 (2014).

B. Van der Bruggen and C. Vandecasteele, *Modelling of the retention of uncharged molecules with nanofiltration,* Water Res. **36**, 1360 (2002).

B. Burnat, G. Dercz, and T. Blaszczyk, *Structural analysis and corrosion studies on an iso 5832-9 biomedical alloy with tio2 sol–gel layers,* Journal of Materials Science: Materials in Medicine **25**, 623 (2014).

A. Larbot, J. P. Fabre, C. Guizard, and L. Cot, *Inorganic membranes obtained by sol-gel techniques,* J. Memb. Sci. **39**, 203 (1988).

A. Pierre, *Porous sol-gel ceramics,* Ceramics international **23**, 229 (1997).

B. K. Nandi, R. Uppaluri, and M. K. Purkait, *Preparation and characterization of low cost ceramic membranes for micro-filtration applications,* Appl. Clay Sci. **42**, 102 (2008).

N. P. S. Ricardo, N. P. S. Ricardo, R. Holmes, and C. Price, *Synthesis and Characterization,* Engineering **39**, 543 (1999).

M. Othman and H. Mukhtar, *Review on development of ceramic membrane from sol-gel route: parameters affecting characteristics of the membrane,* (2000).

C. J. Brodsky and E. I. Ko, *Effect of Drying Temperature on Physical Properties of Titania Aerogels,* **4**, 651 (1994).

A. Buekenhoudt, *Stability of Porous Ceramic Membranes,* Membr. Sci. Technol. **13**, 1 (2008).

T. Van Gestel, C. Vandecasteele, A. Buekenhoudt, C. Dotremont, J. Luyten, B. Van Der Bruggen, and G. Maes, *Corrosion properties of alumina and titania NF membranes,* J. Memb. Sci. **214**, 21 (2003).

T. Van Gestel, C. Vandecasteele, A. Buekenhoudt, C. Dotremont, J. Luyten, R. Leysen, B. Van der Bruggen, and G. Maes, *Alumina and titania multilayer membranes for nanofiltration: Preparation, characterization and chemical stability,* J. Memb. Sci. **207**, 73 (2002).