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Liangxiong Li[a]; Robert Lee[a]
[a] Petroleum Recovery Research Center, New Mexico Institute of Mining and Technology, Socorro, NM, USA

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Purification of Produced Water by Ceramic Membranes: Material Screening, Process Design and Economics

Liangxiong Li and Robert Lee
Petroleum Recovery Research Center, New Mexico
Institute of Mining and Technology, Socorro, NM, USA

Abstract: Produced water, generated from underlying formations during the recovery of hydrocarbons, constitutes the largest waste stream associated with oil and gas production. Currently, over 90% of produced water is reinjected into the formation, either in support of enhanced oil recovery or for disposal. In arid areas, reclamation of produced water for beneficial uses such as irrigation or tower cooling may be an attractive alternative if the produced water can be purified to an adequate quality, specifically through the removal of dissolved components including inorganic compounds (salts, heavy metals, and radiochemicals) and organic compounds (fatty acid, aliphatic, and aromatics).

Membranes technologies show advantages in both energy efficiency and high water quality. Due to the presence of dissolved organics, reverse osmosis with organic membranes is highly limited. Research efforts focus on developing new materials that are less prone to fouling and are easy to regenerate. Novel ceramic membranes are relatively new classes of material that show promising application in produced water purification due to their extreme stability in harsh environments and optional choices for regeneration. This paper details the results of investigations of produced water purification by microporous ceramic membranes, including metal oxide membranes, clay membranes, and zeolite membranes. Techniques for membrane fabrication, process design, and economic aspects are also discussed.

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Address correspondence to Liangxiong Li, Petroleum Recovery Research Center, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA. Tel.: (575) 835-6721. E-mail: Li@prrc.nmt.edu

Keywords: Beneficial use, inorganic membranes, produced water, purification, reverse osmosis

INTRODUCTION

Oil and gas reservoirs usually have a natural water layer, the formation water, underlying the hydrocarbons. During oil and gas production, the formation water will inevitably be produced along with the hydrocarbons. Natural gas in coal beds (coalbed methane, or CBM) has been adsorbed onto the surface of the coal. A large quantity of water basically provides the necessary pressure to maintain adsorption equilibrium. To release the adsorbed CBM from coal, the water must be removed by being pumped to the surface in order to break the adsorption equilibrium by lowering the pressure in the reservoir. "Produced water" designates all the waters produced from formations during oil, gas, and CBM production, constituting the major waste effluent in oil/gas production.

For the purpose of disposal or beneficial reuse, separation technologies need to be deployed for treating the produced water to an appropriate quality for meeting the purposes of disposal and industry uses. Produced waters are conventionally treated by removing the suspensions and floating oil. More than 90% of this purified produced water is then injected into oil zones for enhanced oil recovery/enhanced coalbed methane (EOR/ECBM) or into specially designated reinjection horizons for disposal, which are deemed to be geologically isolated (1,2). Methods for removing suspended solid and oils include gravity separation, hydrocycloning, centrifuging, gas floatation, and filtration (3). Suspended particles with particle size of 5.0 μm or above can be removed with these commercial processes (4). As petroleum companies and regulatory agencies initiate more stringent regulations for water disposal and reinjection, removal of suspensions with large particles will be not sufficient for meeting the requirements. Advanced technologies must be developed to remove both fine particles and dissolved components. For example, the European Standard for effluents from onshore petroleum activities requires less than 5 mg/l total hydrocarbons and less than 10 mg/l suspended solids (5). More stringent water quality is also regulated by petroleum companies for produced water reinjection into low-permeability formations, to avoid or minimize damages to the injectivity. The Daqing oilfield, China's largest oilfield, has established water quality criteria for waterflooding: less than 5.0 mg/l total hydrocarbons, less than 1.0 mg/l suspended solids, and less than 1.0 μm media particle size for suspensions (6). Apparently, the conventional purification processes (i.e., sedimentation and floatation) cannot attain such high standards for water quality.

In addition, surface disposal and beneficial uses such as irrigation and tower cooling require removal of dissolved components, which has a major impact on the receiving environment, due to toxicity and corrosion problems (7). Membrane filtration processes, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, have the potential to generate high quality water by removing suspensions and dissolved components. Zaidi (8) reviewed micro/ultrafiltration membranes for removal of oil and suspended solids to obtain sufficiently high quality of water for reinjection or surface disposal. He suggested that membrane technology is the best available technology for treating oilfield brine. Both laboratory study and field tests have indicated that polymeric membranes are problematic for application in produced water purification, due to fouling and membrane degradation (9). Thus, multistage pretreatment of the waters and periodic chemical cleaning of the membranes are recommended (10). Recently, produced water desalination with inorganic membranes has been reported and laboratory testing of these membranes has shown promising results in cleaning produced water (5,11).

This article investigates micro- and mesoporous inorganic membranes, specifically clay membranes and zeolite membranes, on desalination of produced water. In addition, research results and practice of produced water purification by other type of inorganic membranes, i.e., metal oxide membranes and porous stainless steel, are reviewed. The membrane material selection, water quality for beneficial uses, and economic efficacy of different membrane technologies are discussed for treating produced water cost-effectively.

EXPERIMENTAL

Chemical and Materials

Chemicals used in this study include tetrapropylammonium hydroxide (TPAOH) (1 M solution, Aldrich), sodium hydroxide (NaOH) (99.99%, Aldrich), fumed silica (SiO_2) (99.98%, Aldrich), Hydrogen Peroxide, (34–37%, Fisher), Sodium Chloride (>99.5%, ACROS), Wyoming Na-bentonite (Wyo-Ben Hydrogel) clay with particle size <0.2 µm, aluminum isopropoxide (98 + %, Aldrich), and deionized (DI) water.

Porous ceramic membranes investigated in this research include macroporous α-alumina (pore size = 0.2 µm, Pall), disk-shaped stainless steel (0.5 µm, Mott), and Zr-coated stainless steel (pore size = 0.1 µm, Pall). Other inorganic membranes investigated in this study are MFI-type zeolite membranes on porous α-alumina supports and laboratory fabricated clay membranes.

Membrane Fabrication and Characterization

Zeolites are aluminosilicates with well-defined pore sizes determined by the number of oxygen member-rings. Zeolite membranes usually have a thin layer of zeolite film on porous supports such as α-alumina or stainless steel. MFI-type zeolite membranes with Si/Al ratio of 50 were fabricated for reverse osmosis test in this study. Synthesis of thin and defect-free zeolite films on porous supports is accomplished through a two-stage crystallization process at hydrothermal conditions. First, porous substrate is polished and dipped into a synthesis solution containing an organic template (TPAOH solution) for zeolite crystallization (11). During this process, a thin zeolite layer ($\sim$1.0 μm) is crystallized on a porous support followed by drying and sintering at 450°C to remove the organic template and open the zeolitic pores for mass transport. Permeation tests have indicated that the zeolite layer formed by this process has a high density of micro defects and exhibits low ion rejection efficiency. Thus, a secondary growth is necessary to promote zeolite in-plane growth and form a defect-free thin layer. The secondary growth is carried out at 175°C by dipping the seeded substrate into a solution with chemical composition of $1.0\ SiO_2 + 41.5\,H_2O + 0.38\ NaOH + 0.02\ Al_2O_3$ for 3 hr at hydrothermal conditions: zeolite crystals grow further and form a dense layer on porous support. Figure 1 shows the fabrication process of zeolite membranes and zeolite crystal morphology after each synthesis step.

Mesoporous bentonite clay membranes are prepared on porous α-alumina supports by a sol-gel method using refined clay nanopowders. The Al-pillared clay is prepared by adding dropwise 0.2 M KOH to 0.2 M $AlCl_3$ at vigorous stirring to an OH/Al ratio of 2.0. The OH/Al ratio is adjusted to below 2.5 to avoid formation of larger oligomers. After aging at 50°C for 10 hours, the pillaring solution is further added to 1.0% bentonite clay suspension till Al/clay ratio reaches 10 mmol/g under vigorous stirring. The final pillared clay suspension is aged overnight at 40°C and washed with deionized water until conductivity of supernant of centrifuge is below 10 μs/cm. The suspension formed therein is ready for membrane fabrication by dip-coating with the detail procedure described in the literature (11).

The supported clay membranes are sintered at 450°C for 3 hr by using a heating rate of 0.5°C/min and a cooling rate of 1.0°C/min. Figure 2 gives the SEM images of supported clay membranes on porous α-alumina substrates.

Membrane microstructure and morphology are studied by scanning electron microscope (SEM) and water permeation is investigated through a standard cross-flow experiments in which feed water is forced to flow across membrane surface and the permeate is collected as purified water.

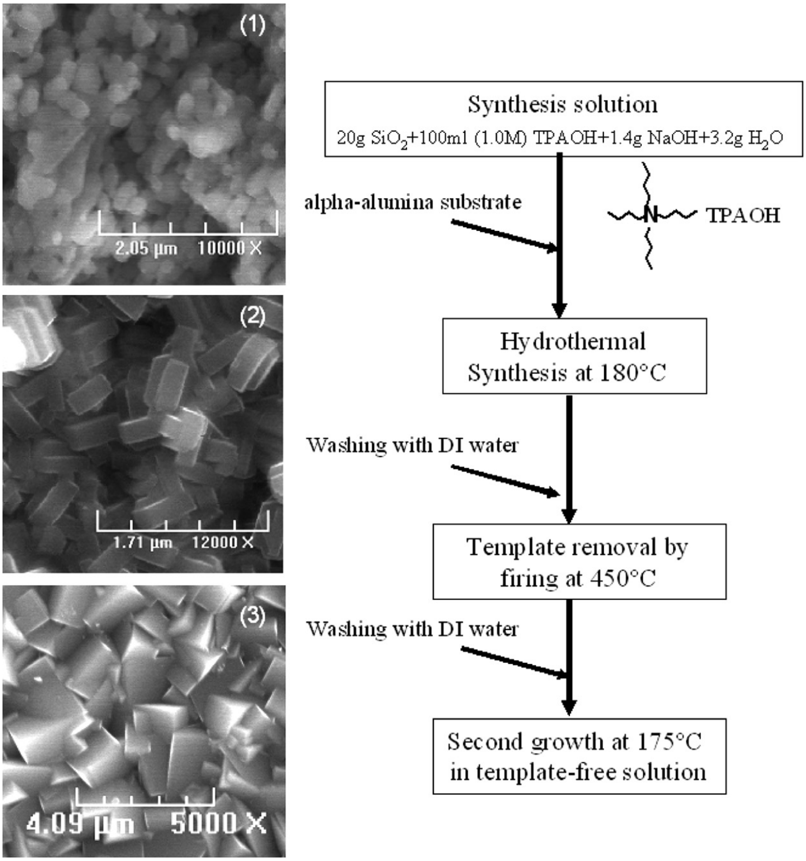


Figure 1. Synthesis process of a zeolite membrane by two-step crystallization. (1) SEM image of substrate, (2) seeded substrate, and (3) zeolite membrane.

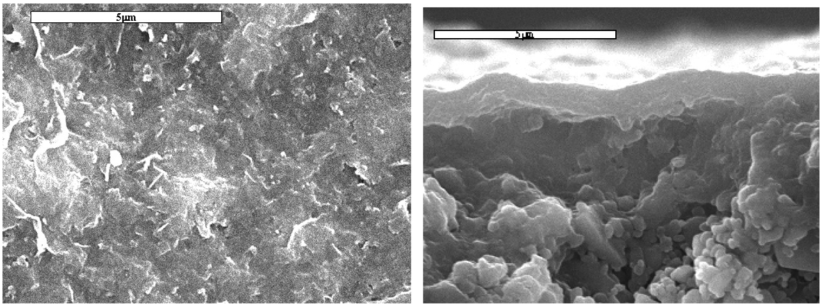


Figure 2. Clay membranes fabricated on porous alpha-alumina support.

Under hydrostatic pressure, water molecules permeate through membranes while ions are rejected at mechanisms of size exclusion and electrostatic repulsion. Scaning electron microscopy (SEM, JEOL 5800LV) with energy dispersive spectrometer (EDS) is studied for determination of aluminium contents in zeolite membranes. Ion concentrations of both feed solution and permeate solution are studied by ion chromatograph with computer data acquisition system (Dionex, I-20).

CHARACTERISTICS OF PRODUCED WATER

Suspensions in Produced Water

Suspensions in produced water contain clay particles, fine coal powder, and oil droplets. Figure 3 gives the particle size distribution of a typical CBM produced water that was studied by dynamic light scattering particle analysis (DLS, Microtrac 3000). Most of the fine coal powders in CBM produced water have a particle size in the range of 1.6 – 6.5 μm.

Particle separation by gravity is determined by Stoke's equation,

$$\nu = g \cdot \frac{\Delta\rho(d_p)^2}{18\mu_L}$$

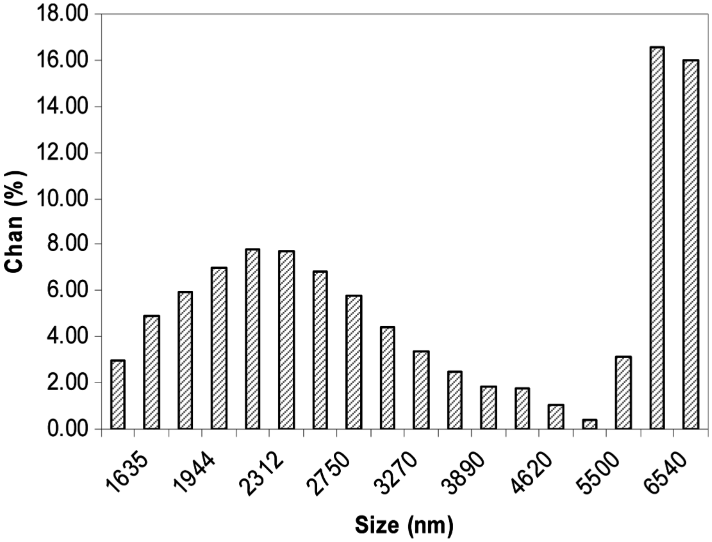


Figure 3. Particle size distribution of suspensions in produced water.

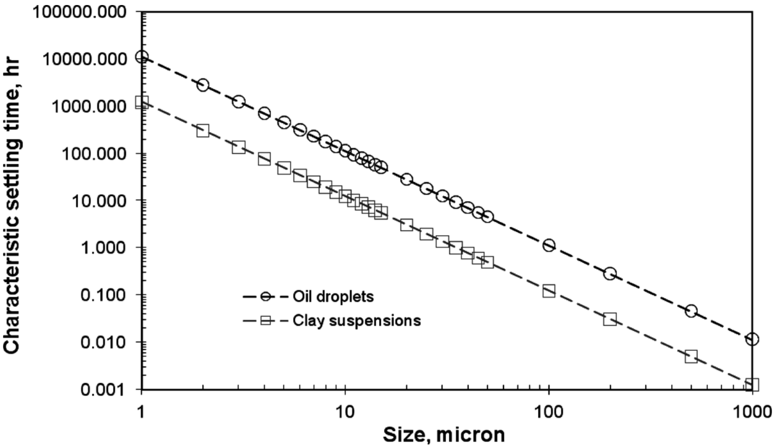


Figure 4. Characteristic settling time as a function of particle size in produced water.

where $\Delta\rho$ is the density difference between the suspension and water, g is the accelerating gravity, 9.80665 m/s^2, d_p is diameter of the particulates, and μ_L is the water viscosity.

The settling velocities of clay suspensions and oil droplets as a function of particle size, therefore, can be calculated. For particles with size less than 10.0 μm, separation by gravity becomes difficult. Mechanical devices for increasing the gravity accelerator or flocculants for agglomerate suspensions can enhance the separation efficiency. Even under centrifugal condition (i.e., hydrocyclone), gravitational separation show difficulty in separating suspensions with particle size less than 3 μm. Figure 4 gives characteristic settling time of oil droplet and clay suspension in a 2-meter tall tank as a function of particle or oil droplet diameter. The oil density is assumed at 910 kg/m^3 and clay density is set as 1826 kg/m^3.

Dissolved Components in Produced Water

Produced water from oil and gas production has a complex solution composition, which varies over the life of a well production. The dissolved salts contain different cations and anions in varying concentrations. The primary cations from dissolved salts include Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+} and Fe^{2+}; the anions are mainly F^-, Cl^-, SO_4^{2-}, CO_3^{2-} and HCO_3^-. Produced water from CBM is considerably different from that in oil and gasfields due to the difference in formation, coal type and depth (12).

Table 1. Characteristics of produced water compared with seawater

Component	San Juan basin (CBM), mg/L	Permian basin (Oilfield), mg/L	Typical seawater, mg/L, (14)
Bicarbonate (HCO_3^-)	5870.3	1538.1	107
Hydrogen sulfide (H_2S)	65	22.5	N/A
Chloride (Cl^-)	2389.5	130636	19352.9
Sulfate (SO_4^{2-})	24.1	4594.1	2412.4
Sodium (Na^+)	4169.3	80421.2	10783.8
Potassium (K^+)	35	398.6	399.1
Magnesium (Mg^{2+})	19	894.1	1283.7
Calcium (Ca^{2+})	11	4395.5	412.1
Strontium (Sr^{2+})	6.3	88.9	7.9
Iron (Fe^{2+})	0.65	65.3	15.5
Total Dissolved Solids (TDS)	12590.2	223054.3	34774.4

Specific concentrations of dissolved salts and organics in oilfield and CBM produced waters vary considerably with the geographical location and history of the well (13). Table 1 gives chemical compositions of produced waters from different formations. For comparison, the chemical composition of typical seawater is also listed.

Dissolved organics in oil/gas field produced waters are mainly fatty acids (C2-C5), phenols, aromatic hydrocarbons, and aliphatic components (9). The presence of organics in produced water is determined by the type of reservoir (oil/gas/CBM) and environmental conditions. Therefore, solubility-sensitive factors, including temperature and pH, all affect the concentration and type of dissolved hydrocarbons (15). Usually, CBM produced water contains higher amounts of low molecular weight aromatic hydrocarbons such as BTEX than are found in oilfield produced water (2), and thus has more impact on the receiving environments. Other factors including type of oil, artificial lift technique, and age of production, also show considerable influence on the characteristics of produced water. Table 2 compares dissolved organic components in produced water from different sources.

It should be noted that produced waters from gasfield and CBM operations have relatively lower TDS but higher levels of hydrocarbons. Further investigation of gasfield produced water indicated that benzene is the major contribution of the organic load; the remaining organic loads come from polar fatty acid and phenols. In some areas, production chemicals, such as corrosion and scale inhibitors and emulsion breakers, will also affect the organic components in

Table 2. Organic content of produced waters from different formations (13)

Components	Typical concentration, mg/l Oil field	Gas field	CBM
Aliphatic			
Aliphatic, C_2-C_5	1	1	
Aliphatics, $>C_5$	5	10	
Aromatic			
BTX	8	25	120
Naphthalenes	1.5	1.5	3
Polar compounds			
Phenols	5	5	
Fatty acids			
C_2-C_5	300	150	
$>C_5$			

BTX: benzene, toluene, and xylene.

produced water. These factors all play a crucial role in the selection of appropriate technologies for produced water treatment.

THE REQUIREMENTS FOR PRODUCED WATER PURIFICATION

The end use of the purified produced water determines the level of water quality required and the methods of treatment. Generally, the energy consumption and operating costs for the treatment are directly related to the ultimate water quality—they will increase with increase in water quality. For example, both onshore and offshore disposals need to meet increasingly stringent standards that are generally regulated by the U.S. Environmental Protection Agency (EPA) under the Clean Water Act (CWA) (5). Onshore disposal of produced water will only be allowed for agriculture and wildlife propagation, for which the maximum daily effluent limitation for oil and grease is 35 mg/l and total dissolved solid (TDS) is less than 2000 mg/l (16,17). Deep well injection for disposal or enhanced oil recovery is the most common option for produced water cleaned by current treatment methods. The water must be injected into an isolated formation to avoid any contamination of the groundwater or surface water system. Industry operators usually have their own standards for suspensions and solid contents in treated produced water, because these can cause formation

Table 3. Produced water disposal and water quality

	Water quality requirement		
Uses	Suspensions	Dissolved component	Main concerns
offshore disposal	Solid <10 mg/l Oil <5 mg/l Oil <5 mg/l	No limitation	Environmental impact
Reinjection	Solid <1 mg/L D < 1 μm	No limitation	Formation Damage
Irrigation (17)	Oil & grease <35 mg/l	TDS: 500–2000 mg/l	Salinity, trace elements, chlorine residue, and nutrients
Cooling water (16)	N/A	TDS <2700	Corrosion, biological growths, and scaling
Chemical process (16)	N/A	TDS <1000	Low turbidity, suspended solids, and silica

Note: D = median particle size.

damage and harm injectivity (18). Table 3 summarizes the potential uses of produced water and the water quality requirements for these.

CERAMIC MEMBRANES FOR LIQUID SEPARATION

Membrane filtration is the most studied process for produced water demineralization and volume reduction. In membrane separation, feedwater flows across a membrane surface. Under hydraulic pressure, water molecules permeate through the membrane while particles, dispersed oil, or even ions and organic molecules are rejected through the mechanism of size exclusion. The permeate will be collected as purified water for beneficial uses and the small volume of concentrate with high concentration of salt and organics are disposed of by conventional methods such as deep well injection or evaporation. Figure 5 gives the schematic diagram of the membrane filtration process.

Membranes can be classified as polymeric or inorganic membranes according to the materials used. Polymeric reverse osmosis membranes dominate the membrane market, but are less efficient for treating wastewater containing strong organic solvents and radioactive elements, due to their tendency to degradation and fouling (19). Porous ceramic membranes have shown promise for produced water purification because of

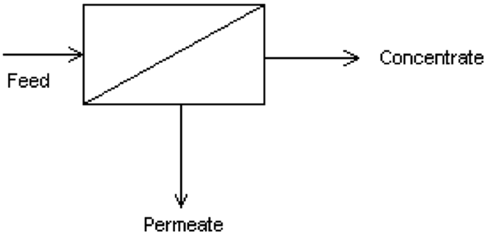


Figure 5. Diagram of a RO membrane separation process.

their extraordinary properties, such as thermal stability, high mechanical strength and ease of regeneration after fouling (20). According to their pore size distribution, ceramic membranes can be classified as microporous membranes (pore size $<2.0\,\text{nm}$), mesoporous membranes ($2.0\,\text{nm} \geq \text{pore size} \leq 50\,\text{nm}$), and macroporous membranes (pore size $>50\,\text{nm}$).

A few preliminary studies have indicated that nanofiltration ceramic membranes have the ability to separate salt and organics from oil-containing wastewater and oilfield brine (21). For water desalination using porous inorganic membranes, surface charges play an important role in the separation performance. The electrostatic interaction between ions and membrane surface charge, which is referred to as the Donnan exclusion, is the main mechanism for electrolyte separation by inorganic nanofiltration membranes (20). Therefore, the factors that affect the surface charge, such as ion valence, ionic strength, and pH, can drastically change the separation performance of micro- or mesoporous ceramic membranes (22). As a result, nanofiltration membranes are only efficient for ion removal from low-concentration solutions or for separating multivalent ions through the mechanism of the Donnan exclusion. In addition, current nanofiltration ceramic membranes usually have a wide pore size distribution, which lowers separation efficiency for dissolved components (20). Zaidi (8) summarized the desirable characteristics of ceramic membranes for produced water desalination—high porosity, surface hydrophilicity, and adequate temperature and pressure tolerance. As he pointed out, however, no one material in the available nanofiltration membranes has been proven to be the most suitable for produced water purification because of severe flux decline and relatively low separation efficiency for concentrated solutions. In the search for new materials with desirable properties, a computer simulation performed by Lin and Murad suggested that molecular sieve zeolite membranes might have high separation performance in the desalination of high concentration solutions (23). In their simulation, 100% Na^+ rejection was achieved with a ZK-4 zeolite membrane, based on the mechanism of size exclusion.

Moreover, decent water flux was achieved in an RO separation of water/ethanol mixture through the same type of zeolite: a 44% rejection of ethanol and a water flux of $0.058\,\mathrm{kg{\cdot}m^{-2}{\cdot}h^{-1}}$ under an applied feed pressure of 1.5 MPa were reported (24).

Permselectivity and water flux are two important factors determining the separation performance of microporous membranes. Carbon nanotube membranes were reported to have much faster water permeation than allowed for by conventional fluid flow theory (25,26). The rapid transport of water molecules through carbon nanotubes is attributed to the friction-free surface, cylindrical pore geometry, and surface hydrophobicity (26). Contrary to water permeation behavior in carbon nanotube membranes, water flux in zeolite membranes increases considerably with the increase of membrane surface hydrophilicity (27). All these materials show promising application in novel membrane fabrication. But, more experiments are needed for better understand the water and ion transport in the confined spaces, i.e., micropores of zeolite.

Meso- and Macroporous Ceramic Membranes for Suspension Removal

Produced water reinjection and drilling fluid recycling typically require the removal of oil and suspended solids. Porous ceramic membranes with pore sizes ranging from nanometer to micron provide the best technology for achieving this goal at relatively low cost because of their well-defined pore size distribution, tolerance for high temperatures, and their strong solvent, chemical and mechanical stability.

Typically, ceramic membranes have an asymmetrical structure with an effective top layer formed by coating or casting. Figures 6 and 7 show the surface and cross-section images of ceramic membranes with pore sizes of 40 nm and 200 nm, respectively. The mesoporous thin layer with thickness of $0.5 - 1.0\,\mu\mathrm{m}$ will exclude any suspensions larger than the pore size. Zaidi (8) has summarized the application of ceramic membranes for oil/gasfield produced water purification, suggesting that the oil and grease level can be reduced from 583 mg/L to less than 10 mg/L after ceramic membrane filtration.

Among the many flux-influencing factors, including feed water quality, concentration of suspensions, membrane porosity, pore size distribution, and thickness of the effective top layer, pore size is the determining parameter of permeate water quality and water flux. Figure 8 shows water flux for ceramic membranes versus membrane pore size. Water flux increases exponentially with an increase in pore size. Selection of ceramic membranes with appropriate surface properties, pore structure, and size distribution is crucial to the achievement of high water flux and

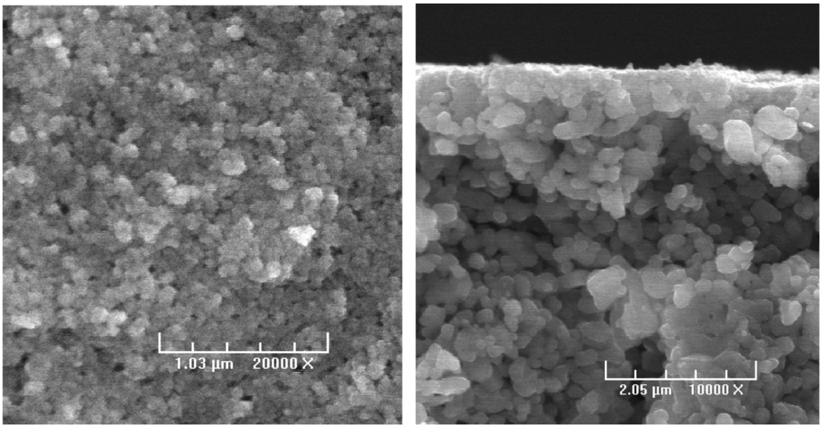


Figure 6. Mesoporous zirconia membranes (pore size = 40 nm) on a porous α-alumina support.

acceptable water quality. Zaida suggested that zirconia and silica based membranes could be more efficient and fouling-resistant due to their high hydrophilicity and minimized plugging with tighter pore size (8).

Microporous Clay Membranes for Ion Separation

Produced water cleaned for beneficial uses, including irrigation, surface disposal, and tower cooling, must meet stringent standards for salinity, total chemical oxygen demand (COD), oxygen biochemical demand

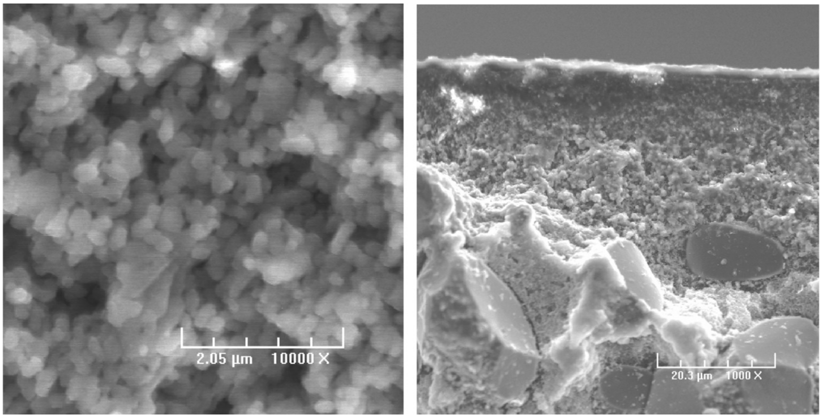
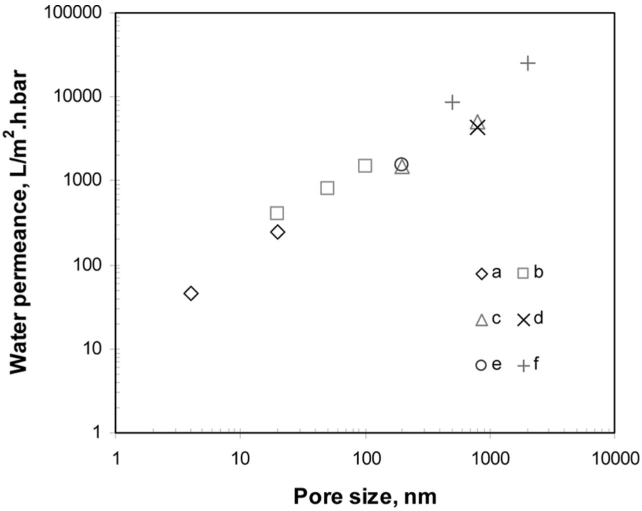


Figure 7. Macroporous α-alumina membranes (pore size = 200 nm).



	Membrane	Manufacturer	Material	Support material	Reference
a	Tubular	Gaston County	ZrO_2	carbon	[28]
b	Multi-channel	Alcoa	ZrO_2	a-alumina	[28]
c	Tubular	Homemade	ZrO_2	a-alumina	[29]
d	Tubular	Alcoa	a-alumina	a-alumina	(8)
e	Tubular	Pall Process Filtration Co.	a-alumina	a-alumina	Lab testing
f	Disc-shaped	Mott Corporation	Stainless steel	no support	Lab testing

Figure 8. Water flux of ceramic membranes as a function of pore size.

(BOD), and dissolved organic carbon (DOC), which are determined by concentration of dissolved components. Removal of salts and dissolved hydrocarbons by membrane technology is the most promising process for achieving the water quality criteria. Ceramic membranes can overcome many disadvantages of polymeric membranes, i.e., the need for sophisticated pretreatment and their structural instability, as well as limited operating lifetime (10), and thus attract much research interest for produced water desalination.

Naturally occurring clays are crystalline materials with a layered structure composed of octahedral flat sheets, which are thermally stable up to 700°C. The major constituents of clays are Al_2O_3 and SiO_2 with small quantities of other metal oxides. The thickness of a single clay sheet is around 0.9–1.0 Å for montmorillonite and bentonite (30). The clay surface is negatively charged due to ion isomorphous substitutions. Therefore cations, mostly Na^+ or Ca^{2+}, exist in the interlayer space as charge compensators. These cations can be readily exchanged in aqueous solutions to alter chemical and physical properties of the clay surface after appropriate post-treatment (31,32).

When contacting water, the clay sheets are propped open by absorbing water molecules. The clay sheets collapse under deep dehydration at high temperature, eventually eliminating the interlayer space (31,33). The interlayer space can be adjusted by placing nanometer or subnanometer molecular species between the layers. This process is called “pillaring” and the resultant clay is called “pillared clay” (PILC). The pillaring process normally includes two major steps—first, impregnation of the hydroxide pillaring precursor and next, conversion of the precursor into strong oxide pillars. The PILC contains slit-shaped micropores whose size (interlayer distance) can be conveniently adjusted between 3 Å to 50 Å by different metal oxide pillars (34).

Most of the porous clay membranes reported in the literatures are compacted membranes of unpillared clay, formed by sandwiching clay particles between porous stainless steel plates under high pressures (~50 MPa). These membranes have been used to study osmosis and reverse osmosis of salt solutions (35–37). A typical clay membrane with dimensions of 10 cm × 20 cm is shown in Fig. 9.

For practical application, supported clay membranes have been fabricated on porous supports. Hu et al. (38) prepared porous glass-supported Al_2O_3-PILC membranes by deposition of uncalcinated PILC from suspensions. After firing, the membrane was treated by impregnation and carbonization of polyvinyl alcohol (PVA) to reduce

Figure 9. Compacted clay membrane formed by compacting under high pressure.

the intercrystalline pores. Good separation performance was obtained for N_2-aromatic vapor mixtures by a competitive diffusion process. Vercauteren et al. (39) synthesized Al_2O_3-pillared montmorillonite membranes on top of mesoporous γ-alumina membranes by coating with 0.1 wt% unpillared clay suspensions and a subsequent pillaring process. After firing, the PILC membranes were 0.2 – 0.5 μm thick. A very dilute clay suspension was used to avoid the easily-formed flocs. Although the original clay particle size was large, 0.2–0.5 μm by light scattering, the resultant membranes were microporous with $dp = 0.8$ nm, micropore volume of 0.04 – 0.12 $cm^3\,g^{-1}$, and surface area of 266–540 $m^2\,g^{-1}$. The ratio of the microporous area to the mesoporous area was around 100/15. The main reasons causing the microporous structure were suggested to be effective pillaring, small primary layer plates (~0.1 μm), and the oriented stacking of clay plates (40). The microporous membranes achieved H_2/N_2 selectivity of 3.6, which is close to the Knudsen factor (3.74). However, permeance was low (2×10^{-8} mol $m^{-2}\,s^{-1}\,Pa^{-1}$ for N_2) because the interlayer pores were parallel to the surface, increasing the tortuosity, and pores were at the clay-γ-alumina interface by the overlying clay plates. Ion separation by clay membranes have been studied since the early 1970 s (41). Recently, supported clay membranes have been fabricated on porous support and exhibit a comparable ion separation performance at much lower operating pressures compared to the compacted membranes (11). Table 4 summarizes ion separation performance of different types of clay membranes.

Ion separation by clay membranes is attributed to Donnan repulsion due to the overlapping of the charged double layer between the interparticle spaces. In an aqueous solution, the charged surface and adsorbed ion layer with the opposite charge form a localized electrical field, or "double layer." The ion entering and transporting across the interior of the microchannel in a clay membrane is thus restricted by the overlapping of the double layers and a stream potential across the membrane thickness (36). A common problem encountered involving the Donnan

Table 4. Desalination performance of clay membrane

Type of membranes	Solution	Thickness, μm	Flux, $kg/m^2.h$	Ion rejection, %	Reference
Compacted	0.60 M NaCl	2200	0.088	60.0	(41)
Compacted	0.80 M NaCl + 0.15 M $CaCl_2$	5000	0.452	60.0	(42)
Compacted	0.10 M NaCl	60	7.22	62.9	(37)
Supported	0.10 M NaCl	2	5.5	44.5	(11)

Figure 10. Tubular zeolite membranes on α-alumina supports.

repulsion mechanism is the shrinking of the double layer and subsequently, decreasing ion rejection at elevated solution concentrations (37).

Reverse Osmosis Zeolite Membranes

The laboratory-synthesized zeolite membranes show high ion rejection efficiency (>95%) and high water flux (>1.0 kg/m^2.h). Figures 10 and 11 show zeolite membranes fabricated on a commercial α-alumina substrate

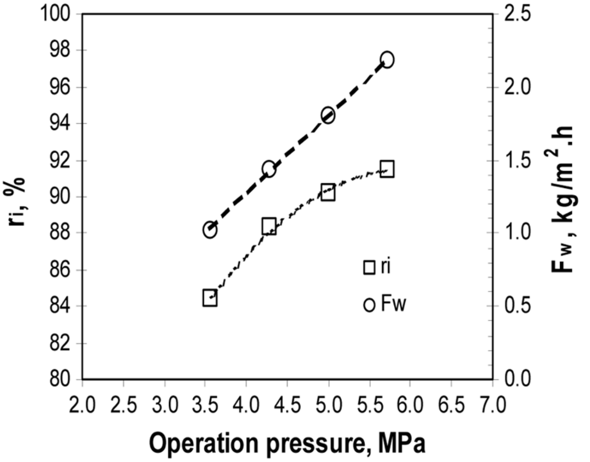


Figure 11. Ion separation performance of zeolite membranes.

and their separation performance with a CBM produced water obtained from the San Juan Basin in New Mexico. The produced water had total dissolved solids (TDS) of 2.1×10^4 mg/L and was filtrated before the desalination test by a 0.22 μm filter for particulate removal. The zeolite membranes showed an overall ion rejection of 95.2% at a water flux of 1.47 kg/m^2.h at transmembrane pressure of 5.0 MPa.

Ion rejection by zeolite membranes is mainly attributed to the size exclusion of hydrated ions whose dynamic sizes are larger than the zeolitic pores. Since the ion hydration number is independent of feed ion concentration, ion separation by zeolite membranes is less affected by solution chemistry and thus is expected to show advantages for produced water desalination. However, a considerable decline in ion separation was observed as feed concentration increased (27). This behavior was attributed to the inherent intercrystalline pores in all polycrystalline zeolite membranes. The nano- or subnano-intercrystalline pores will reject ion species through electrostatic repulsion and are thus less efficient at increased ion concentrations. Modifying the intercrystalline pores by using ion oligomer deposition was suggested to be effective for enhancing ion separation efficiency from feed solutions with high ion concentration (43).

MEMBRANE DESIGN AND MODULES

Zeolite membranes usually have an asymmetric cross-section with a multilayer structure to reduce mass flow resistance. Figure 12 shows the inorganic supports for MFI-type zeolite fabrication: α-alumina with different geometry and Zr-coated stainless steel.

Advantages of inorganic membranes include high stability at elevated temperatures and in the presence of strong organic solvents. Module design needs to meet the requirements for application at harsh

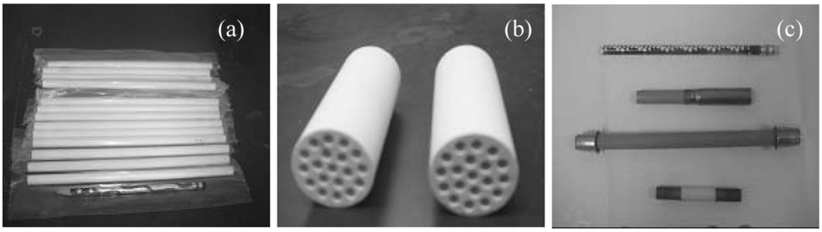


Figure 12. Inorganic membranes having different modules: (a) α-alumina (pore diameter = 0.2 μm, Pall Process Filtration Co.), (b) multi-channel α-alumina (pore diameter = 0.5 μm), and (c) Zr-coated stainless steel (pore diameter = 0.1 μm, Pall Process Filtration Co.).

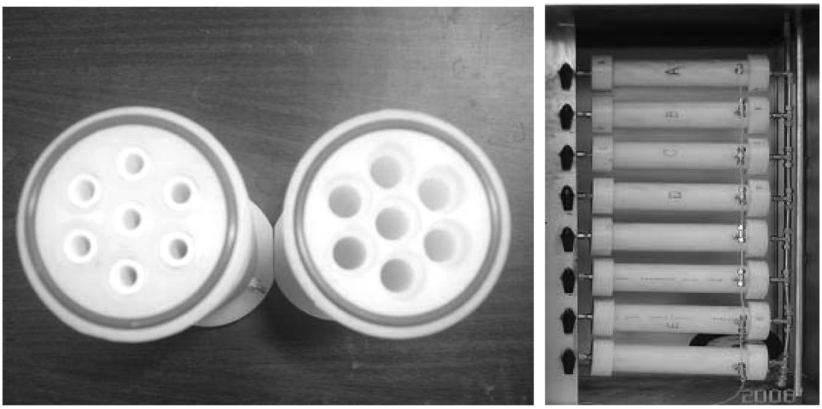


Figure 13. Cross-flow reverse osmosis module for zeolite membranes.

conditions. The module and seal should be applicable for the specific environment, i.e., a strong solvent or oxidative solution, elevated temperature, and high pressure. A reverse osmosis separation vessel has been designed for produced water separation use, containing a cylindrical multichannel body and lab-fabricated tubular zeolite membranes, as shown in Fig. 13. The tubular zeolite membranes are fixed into the pipes in the cylindrical vessel body by O-ring sealing at both ends. Under the hydrostatic transmembrane pressure, water transports across the zeolite membrane and accumulates in the permeate side while large ions and organic species are excluded. The material for preparation of the module body can be nylon, which shows sufficient strength for operating at high pressure and chemical stability in the produced water environment.

FLUX ENHANCEMENT AND CHEMICAL REGENERATION

Flux Losses and Membrane Fouling

Common problems for produced water purification by membranes are fouling and flux decline, both of which significantly increase operating costs. Membrane fouling is associated with the composition of produced water, i.e., the concentration of suspended particulates, floating oil droplets, dissolved salts, scale deposition onto the membrane surface, and adsorption of dissolved hydrocarbons.

Microfiltration membranes for oil and solid suspension removal generally have pore sizes ranging from 0.2 μm to 5 μm. These membranes are commercially deployed for produced water filtration (5,8) and are only

Table 5. Decline of water flux in the presence of oil and solid suspensions

Membrane	Pore size	Operating style	Initial flux, L/m^2.h	Stabilized flux, L/m^2.h	Oil rejection	Reference
α-Al_2O_3	0.8 μm	Cross-flow, 1–5 m/s	800–1200	150	98.3%	(8)
ZrO_2	0.2 μm	Cross-flow, 3–5 m/s	1500	93	99.9%	(29)
α-Al_2O_3	0.2 μm	Cross-flow, 3–5 m/s	400	22	99.8%	(29)
ZrO2	0.2 μm	Cross-flow, 2.56 m/s	240	120	96.1%	(44)
α-Al_2O_3	0.2 μm	Cross-flow	301	25	99.4%	(45)
α-Al_2O_3	0.8 μm	Cross-flow	998	40	99.7%	(45)

slightly affected by dissolved components because their pore sizes are considerably larger than the ion species and organic molecules in produced water. The major fouling comes from oil droplets and solid suspensions. Drastic decline in water flux was widely observed for microfiltration ceramic membranes in the presence of oil and solid suspensions, as shown in Table 5.

A comprehensive summary of methods to enhance flux rate and minimize fouling of the microfiltration operation was performed by Zaidi and coworkers (8). The strategy for flux enhancement is to reduce the interaction between the foulant and the membrane surface. Technologies for flux enhancement include pulsed/reversed flow, turbulence promoters, rotating/vibrating membrane, crossflow electrofiltration, ultrasonic enhancement, additions of disinfectants, antiscaling agents, and membrane surface modification. Still, as membranes gradually become fouled, periodic cleaning is necessary to maintain constant water flux values. An alternating hot caustic wash, fresh water rinse, and acid wash were found to be effective in regenerating of ceramic membranes (8).

Reverse osmosis ceramic membranes, i.e., zeolite membranes, have a much smaller pore size ranging from subnanometer (i.e., 0.56 nm for MFI-type zeolite) to a few nanometers. Both suspensions and dissolved components contribute to membrane fouling and flux decline. Figure 14 shows the water flux of zeolite membranes as a function of elapsed permeating time. The water flux first increased and then declined with elapsed operating time. After 35 days of testing, the water flux reached a relatively stable value at $\sim$1.0 kg/m^2.h. The ion rejection declined continuously from $\sim$90% to 40% after operating for about two months, as shown in Fig. 15. The initial increase in water flux was also observed for the NaCl solution, which was attributed to surface ionization (27).

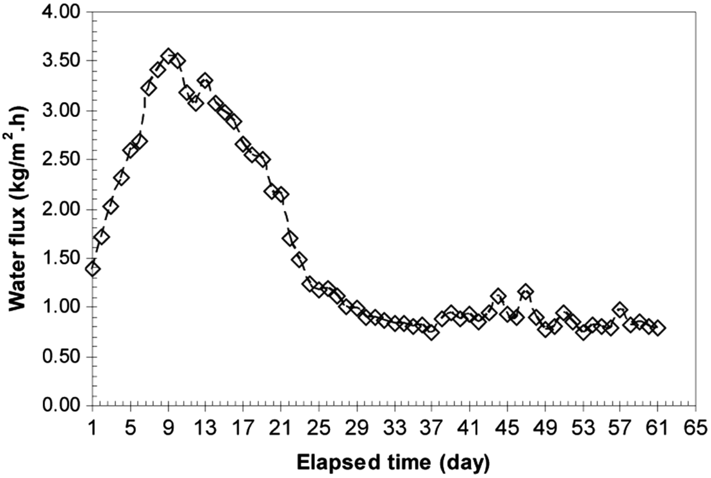


Figure 14. Water flux variation as a function of elapsed RO permeation time.

As the zeolite membrane contacts with water, the zeolite adsorbs cations and anions from the aqueous solution by releasing protons or hydroxide ions, resulting in surface hydroxylation (46). The formation of a large quantity of hydroxyl groups on the zeolite surface when it is contacted with produced water results in considerable enhancement in surface hydrophilicity as well as water flux. Unfortunately, the adsorbed ion species also increase the ion concentration gradient across zeolite

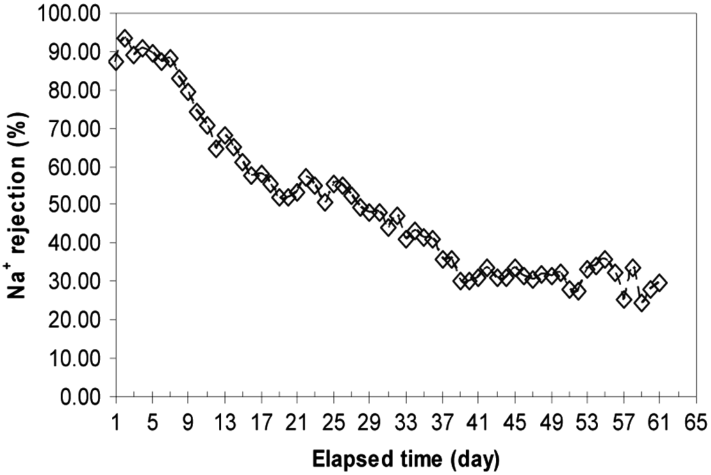


Figure 15. Ion rejection (Na^+) as a function of elapsed RO permeation time.

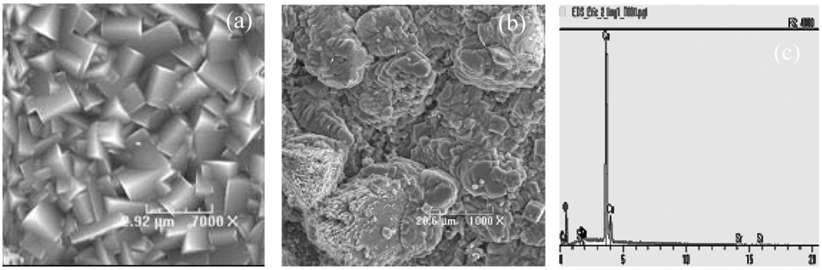


Figure 16. SEM images of zeolite membranes. (a) Zeolite membrane before fouling, (b) zeolite membrane with foulant, and (c) EDS for foulant element analysis.

membranes, resulting in a considerable increase in ion diffusion. As a result, ion separation efficiency decreases slightly at the early stage of RO permeation. The subsequent severe declines in water flux and ion rejection are attributed to the organic fouling and scale deposition on the membrane surface.

The zeolite membranes fouled by CBM produced water were washed thoroughly with DI water and dried at 120°C for further SEM and EDS analysis. Figures 16(a) and 16(b) give the SEM images of a zeolite membrane before and after fouling by permeating produced water for two months. The membrane with scale deposition has a thickness of $12-15\,\mu m$. Further random surface searching and EDS analysis indicated that the chemical composition of the scale was mainly $CaCO_3$ and $SrCO_3$ crystals, as shown in Fig. 16(c).

Flux Enhancement and Chemical Cleaning of Ceramic Membranes

Flux losses are the major obstacles in the application of ceramic membranes for produced water purification. Oil droplets and colloidal suspensions cause major fouling of nanofiltration membranes. Increasing interfacial liquid flow rate over the membrane surface will enhance water flux and hinder foulant deposition, particularly by hydrodynamic processes, such as cross-flow with imposed fluid agitation (47), rotation of tubular membranes (48), and bubbling (49). Alternative technologies that can potentially reduce the interaction between the membrane surface and foulants such as oil droplets and suspended particulates, are enhanced by water flux. These include using an external electric field (50) and membrane surface modification (51).

Flux decline of zeolite membranes during a long-term permeation test of produced water is attributed to scale deposition and organic sorption. The conventional convection-diffusion model suggests that a concentration polarization forms near the membrane surface during the separation process, which is governed by fluid chemistry, membrane properties and hydrodynamics (52,53). Our separation experiments indicated that the crossflow shearing at a flow rate of 0.2 m/s is not sufficient to break the concentration polarization. Serious scale precipitation was observed on the zeolite membrane surface after 60 days permeation. As suggested by the EDS analysis, the major chemical composition of the scale is $CaCO_3$ and $SrCO_3$; thus, acid cleaning is effective to remove surface scale. Figure 17 shows the SEM images of the fouled membranes before and after acid cleaning by 0.1 M HCl for 10 minutes.

Unfortunately, only 42% water flux was recovered after the acid cleaning, so further treatment is necessary to remove organic adsorption from produced water. Oxidative regeneration for organic removal was investigated for membrane regeneration after produced water treatment. A toluene-fouled membrane was treated by being dipped into 15% H_2O_2 solution for 2 hr. The water flux and ion rejection before and after H_2O_2 oxidative regeneration are shown in Fig. 18. The zeolite membrane had an initial water flux of 4.86 kg/m^2.h and ion rejection of 97.9%. The water flux gradually declined to 3.71 kg/m^2.h while the ion rejection slightly decreased to 97.2% in the presence of dissolved organics. After oxidative regeneration, the water flux was recovered to 4.60 kg/m^2.h while the ion rejection decreased slightly to 94.1%.

Despite the vast efforts to reduce membrane fouling, such as surface modification, pretreatment, and enhancement of hydrodynamic surface

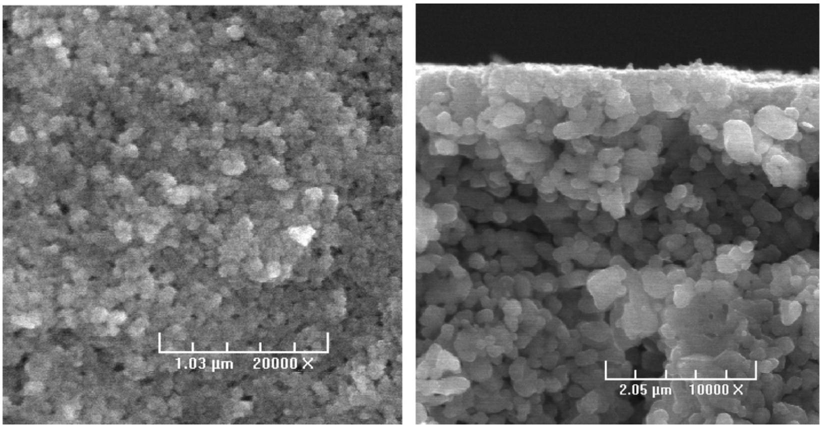


Figure 17. SEM images (cross-section) of zeolite membrane before and after acid cleaning with 0.1 M HCl solution.

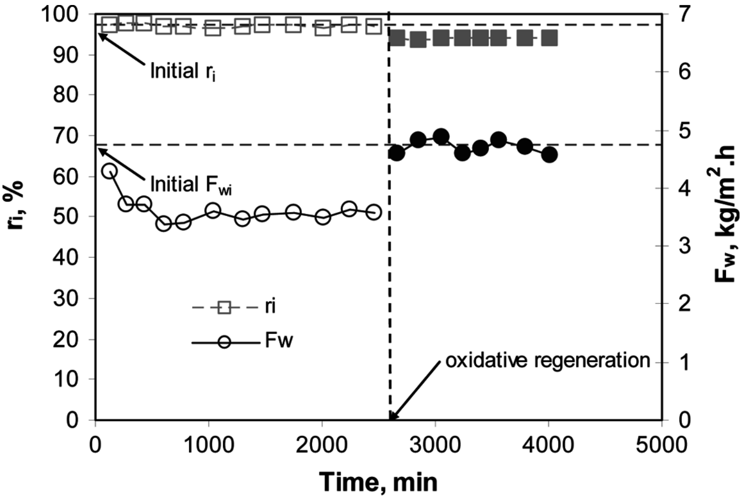


Figure 18. Oxidative regeneration of zeolite membranes after organic fouling.

shearing, fouling is essentially inevitable, particularly for produced water containing large amounts of fine clay powders and dissolved organics. In addition, many CBM produced waters contain high concentrations of bicarbonate ions that promote scale deposition on the membrane surface during reverse osmosis. Thus, periodic chemical cleaning, i.e., acid treatment or in-situ oxidative regeneration, is necessary to ensure a sustainable operation and extend the lifetime of inorganic membranes.

ECONOMIC CONSIDERATIONS

The major disadvantage of inorganic membranes is the high membrane cost. For example, zeolite membranes are about 10–50 times more expensive than the equivalent polymeric membranes. However, the unique capabilities of these membranes for produced water purification might be able to overcome the disadvantages. Specifically, the advantages of zeolite membranes include tolerance of organic solutions, corrosion resistance, and usefulness under extreme operating conditions, i.e., high temperatures, high surface shear rates, or the presence of oxidative solvents.

Currently, only a few types of zeolite membranes have been commercialized or demonstrated for industry applications. Typical examples of commercial application of zeolite membranes include alcohol dehydration by LTA zeolite membranes and CO_2 separation by DDR-type zeolite membranes (54). Recent research efforts have focused on MFI-type and

FAU-type zeolite membranes, which have larger pore sizes at 0.56 nm and 0.74 nm respectively and enhanced chemical stability. However, the commercialization of these zeolite membranes has faced difficulties because:

1. zeolite membranes usually have an asymmetric cross-section with a multilayer structure for the purpose of reducing mass flow resistance. Unfortunately, the membranes with layered structures have to be fired at each step of the synthesis, considerably increasing the production costs (54);
2. at least 70% of the zeolite membrane costs comes from the fabrication of the ceramic support. In addition, efforts to seek out cheaper, automated production of membrane supports have not been successful. Currently, only a few substrates were reported to be effective for fabrication of defect-free zeolite membranes, including α-alumina and stainless steel;
3. Module design needs to meet the requirement of application under harsh conditions.

Reproducibility was found to be a major challenge for upscale fabrication of zeolite membranes. Figure 19 shows water flux and ion rejection of MFI-type zeolite membranes synthesized under the same experimental

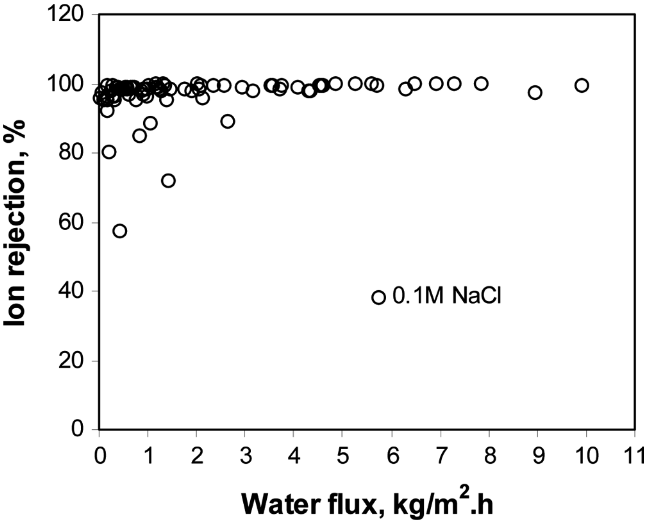


Figure 19. Ion separation performance of MFI-type zeolite membranes fabricated on porous α-alumina support.

conditions. Over 90% of zeolite membranes have ion rejection above 95% for 0.10 M NaCl solution. However, high variation in water flux was observed from 0.12 to 10.2 kg/m^2.h. Obviously, nearly two orders of magnitude of variation in water flux are difficult to attribute to changes in membrane thickness. The cross-section of SEM/EDS test suggests no significant changes in aluminium content for these membranes. Factors governing water transport in nano- or subnanometer scale micropores need to be investigated further.

CONCLUSIONS

In order to mitigate environmental and economic impacts associated with produced water treatment, one strategy is to purify the produced water for beneficial uses. Inorganic membranes, including microfiltration ceramic membranes, microporous clay membranes, and molecular sieve zeolite membranes, were investigated for purifying produced water to a quality adequate for meeting a variety of end use requirements.

Ceramic membranes are new classes of materials that show promising application in produced water purification due to their extreme stability in harsh environments and options for regeneration. Microporous ceramic membranes are very effective for reducing concentrations of oil and suspended solids from produced water. Increasing water flux and reducing fouling are crucial for the economic feasibility of microporous ceramic membranes. Hydrodynamic processes are generally deployed to enhance the surface shear flow rate and eliminate surface fouling by precipitation.

Clay and zeolite are microporous materials that show promising application in novel membrane fabrications that have potential for use in produced water deionization. MFI-type zeolite membranes formed on commercial tubular substrates give over 99% ion rejection at a water flux of ~10 kg/m^2.h. However, the scale-up of zeolite membrane fabrication faces difficulties due to the large variations in water flux and the sophisticated—therefore costly— membrane fabrication process.

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