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Nanofiltration for the Treatment of Oil Sands-Produced Water

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Abstract

This chapter summarizes nanofiltration (NF) studies focused on the treatment of thermal in-situ steam-assisted gravity drainage (SAGD)-produced water streams in the Alberta, Canada, oil sands industry. SAGD processes use recycled produced water to generate steam, which is injected into oil-bearing formations to enhance oil recovery. NF has potential applications in the produced water recycling treatment process for water softening, dissolved organic matter removal, and partial desalination, to improve recycle rates, reduce make-up water consumption, and provide an alternative to desalination technologies (thermal evaporation and reverse osmosis). The aim of this study was to provide proof-of-concept for NF treatment of the following produced water streams in the SAGD operation: warm lime softener (WLS) inlet water, boiler feed water (BFW), and boiler blowdown (BBD) water. Commercial NF membranes enabled removal of up to 98% of the total dissolved solids (TDS), total organic carbon (TOC), and dissolved silica, which is significant compared to the removal achieved using conventional SAGD-produced water treatment processes. More than 99% removal of divalent ions was achieved using tight NF membranes, highlighting the potential of NF softening for oil sands-produced water streams. The NF process configurations studied provide feasible process arrangements suitable for integration into existing and future oil sands and other produced water treatment schemes.

Keywords: nanofiltration, produced water treatment, oil sands, SAGD, membrane processes

1. Introduction

A significant amount of research and development is currently underway to improve oil sands water treatment processes to allow for higher levels of water recycle and to reduce the

energy associated with water treatment and steam generation. Part of this water use reduction effort is focused on water consumption in the steam-assisted gravity drainage (SAGD) process. SAGD is a thermally enhanced heavy oil recovery method, which is widely practiced for bitumen extraction from oil sands in Alberta, Canada. In this process, steam is injected through a horizontal well into the bitumen-containing formation to decrease the viscosity of the bitumen and allow its extraction. An emulsion of steam condensate and heated bitumen flows down the periphery of the steam chamber to the production well, which is located below the injection well. This emulsion is pumped to the surface where the bitumen and water are separated, and the water subsequently treated for reuse as boiler feed water for steam generation.

In a typical SAGD plant (**Figure 1**), the produced emulsion is first sent through a series of gravity separation vessels to remove gases and separate the bitumen and water. The de-oiled produced water is mixed with make-up water (fresh and/or brackish) and recycled boiler blow-down (BBD) prior to treatment in a warm lime softener (WLS) to remove silica. Treated fluids from the WLS are further processed through ion exchangers (IX) to remove Ca^{2+} and Mg^{2+} to generate boiler feed water (BFW) suitable for steam generation. Unlike power generation and utility steam drum boilers, SAGD plants use robust, oilfield-style once-through steam generators (OTSG's), which can tolerate high amounts of TDS (8000–12,000 mg/L) and TOC (300–1000 mg/L). Only hardness and silica removal are necessary for OTSGs, not desalination. To compensate for the relatively low-quality feedwater, OTSG's typically produce a low-quality steam (75–80% steam), resulting in a large volumetric rate of boiler blowdown (BBD). A portion of the BBD is recycled back to the WLS, while the balance is sent to deep disposal wells, third-party waste disposal operators, or processing in zero liquid discharge (ZLD) facilities.

The conventional WLS-IX water treatment configuration does not reduce the amount of dissolved organic matter (DOM) or total dissolved solids (TDS) in the boiler feed water, and only partially removes silica. In spite of the robust nature of SAGD OTSGs, high levels of DOM and TDS in OTSG feed water can cause operational and maintenance problems due to fouling and scaling of steam generators and disposal wells [1–3]. Boiler feed water from WLS-IX processes requires blowdown rate management to mitigate scale formation; this causes a higher recycle of low-quality BBD water back to the process [3]. To reduce the volume of disposal water, evaporators are sometimes used as a downstream BBD water recovery process [4]. Evaporators are also used in SAGD to directly desalinate produced water for higher-quality BFW, allowing the use of more efficient, smaller oilfield drum or hybrid boilers. However, evaporation results in high operational costs (chemical cleaning and electrical energy). In light of the above, industry is pursuing replacement of the WLS-IX and produced water evaporator schemes with emerging membrane-based processes, which can separate almost all silica and divalent ions, and reject more than 90% of DOM and TDS in a single step, while consuming less energy than if desalination evaporators were used.

Membrane separation processes are an emerging technology for oil sands-produced water treatment due to their distinct advantages over traditional processes, primarily lower operating

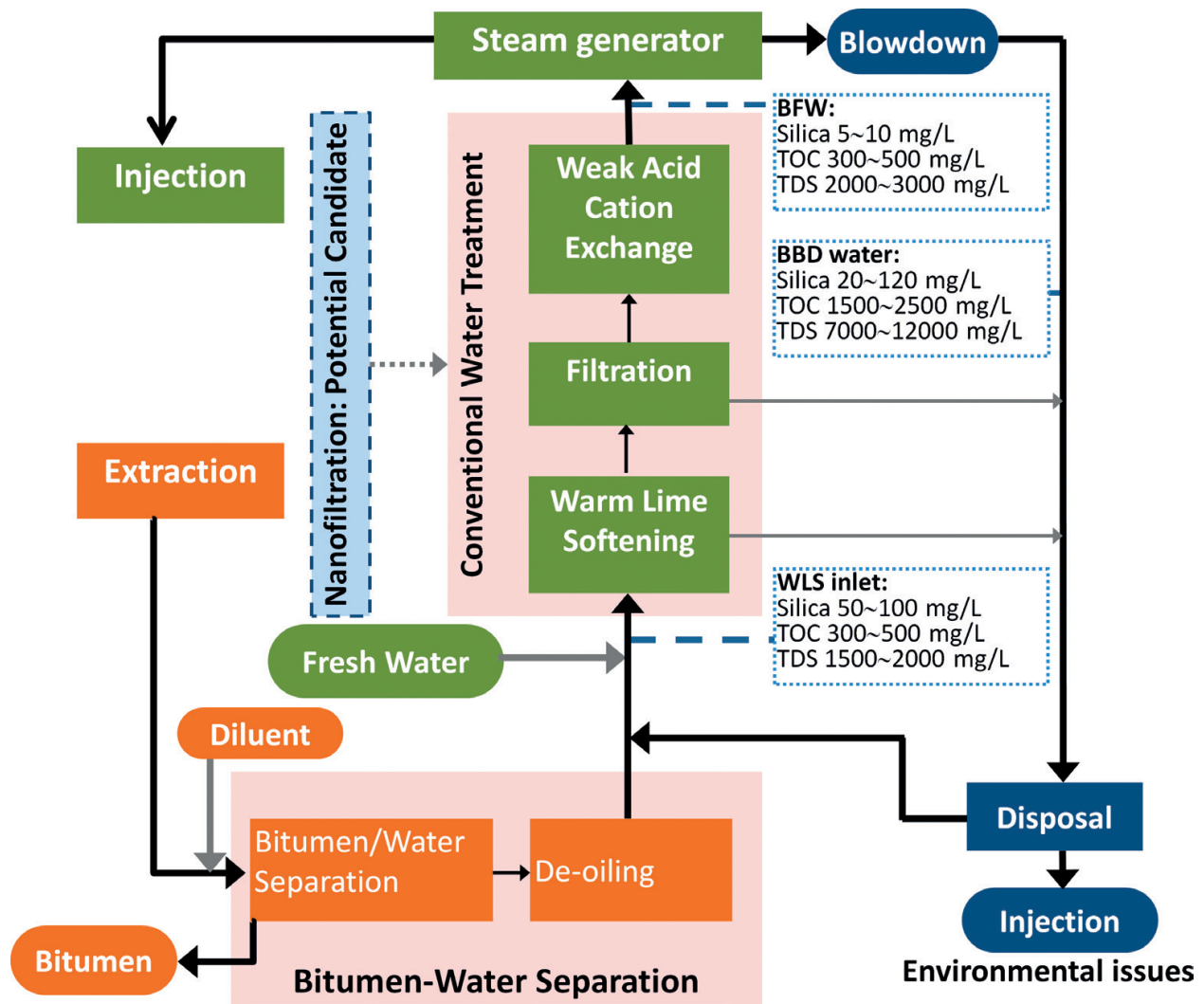


Figure 1. Main steps in SAGD-produced water treatment operations.

costs, compact design, and high filtrate quality [5]. Among membrane processes, nanofiltration (NF) is increasingly deployed for the removal of solutes ranging from colloidal particles and organic molecules to salts in a single unit operation. NF membranes provide a higher water flux and lower rejection of monovalent ions (<90%) as compared to reverse osmosis (RO) membranes. Tight NF membranes are similar to RO membranes, while loose ones can be categorized as ultrafiltration (UF) membranes [6]. NF membranes are the best candidates for water softening as they provide a high rejection of divalent ions (>99%). For SAGD-produced water or blowdown treatment, removal of scale-forming divalent ions such as hardness and silica is more important than NaCl removal when OTSG's are used. Treatment with NF membranes may reduce operational costs of operating OTSG's and WLS-IX processes, and also enable direct blowdown reuse as BFW instead of requiring disposal. Further treatment to drum boiler quality requires further research, but will likely require RO treatment to reach required TDS levels like those achievable by evaporators.

In this chapter, we aim at evaluating the performance of NF processes for the treatment of SAGD-produced water and blowdown streams. First, all emerging technologies that can be applied for the treatment of oilfield-produced water are presented. Then, a critical literature review on the application of NF for the treatment of oil sands-produced water is provided. After that, the methodology for a typical NF experiment and analysis of results are described. Finally, membrane permeation results are discussed on the basis of membrane characteristics including hydrophilicity, zeta potential, and roughness.

2. Emerging technologies for the treatment of oilfield-produced water: overview and perspective

The potential technologies for oilfield-produced water treatment can be classified into five main groups [7–9]:

- i. *Physical treatment* such as adsorption, media filtration (anthracite, sand, walnut shell), evaporation, distillation, gas floatation, and hydrocyclones
- ii. *Chemical treatment* such as precipitation (WLS), chemical oxidation (by chlorine, hydrogen peroxide, ozone, and permanganate), and electrochemical processes (electrocoagulation)
- iii. *Biological treatment* such as activated sludge, anaerobic reactors, aerated lagoons, and wetlands
- iv. *Membrane filtration* such as microfiltration (MF), ultrafiltration (UF), NF, RO, and electrodialysis (ED)
- v. *Hybrid processes* such as membrane bioreactor (MBR), micellar-enhanced UF (MEUF), coagulation/MF, and oxidation/flocculation/membranes

Among these processes, adsorption (by activated carbon, zeolites, clays, resins, and synthetic polymers) [10–12], oxidation (chemical, photocatalytic, and sonochemical) [12–14], biological treatment [15–17], and membrane processes [18–20] represent emerging technologies in Canada's oil sands industry. Adsorption processes are used for the removal of a broad range of compounds in oilfield-produced water, including DOM, oil, and heavy metals [21]. The principal shortcomings noted for adsorption processes are low adsorption capacity and the high costs for disposal, cleaning, and regeneration of spent media [7, 21]. In oxidation process, pollutants are degraded through a series of direct oxidation and radical reactions. Radicals are produced by using chemicals like ozone (ozonation), hydrogen peroxide (Fenton), chlorine, and permanganate. The formation can be intensified by UV light (photocatalytic oxidation) and ultrasound (sonochemical oxidation). The application of oxidation in oilfield water treatment is limited by inefficient radical generation, poor reaction kinetics, and interference from background TOC concentrations and high concentrations of salt and radical scavengers (chloride and bicarbonate) in oilfield-produced water. Incomplete pollutant removal and high energy costs limit the application of oxidative treatment [7, 21]. Biological treatment, primarily activated sludge, is widely used in the treatment of municipal and refinery wastewaters,

but its application is limited for the treatment of more complex industrial effluents, especially those with high salinity high temperatures, and the presence of inhibitory organics [21]. Membrane processes have been broadly applied in industrial and municipal wastewater treatment. Numerous previous studies have mainly considered the use of looser MF and UF membranes for oily produced water treatment [22–24]. For the separation of DOM, salt, and silica from oil sands-produced water, it is essential to use tighter NF and RO membranes [25].

3. Oil sands-produced water treatment by nanofiltration

An overview of published studies on oil sands-produced water treatment using NF membranes is presented in **Table 1**. Although NF membranes are widely applied in water softening, there are few records in the literature for their application in oil sands-produced water treatment. This is mainly due to the high susceptibility of these membranes to fouling by the high TDS and TOC of oilfield-produced water. Meanwhile, these waters are mostly at high temperature and pH, which can affect the membrane integrity of current commercial membranes. In some applications, these streams must be cooled or pH tuned solely to accommodate a membrane separation process, after which the processed fluid will be readjusted back to an initial condition (e.g., pH) to optimize steam production reliability [26–28]. This temperature and pH adjustment requires a significant amount of energy and chemicals. Applying hydrophilic membranes with antifouling properties as well as thermal and chemical resilience (up to 70°C and pH 2–11), for example, sulfonated polyethersulfone (PES) developed by hydranautics, will facilitate the practice of NF in the oil sands-produced water treatment.

From the data presented in **Table 1**, it can be seen that NF was studied for the treatment of produced water generated from two main oil sands operations, namely open-pit mining and SAGD [5, 25, 29–31]. Sadrzadeh et al. [5] and Hayatbakhsh et al. [25] treated SAGD WLS

Ref	Produced water	Feed characteristics				Contaminant removal
		pH	TDS (mg/L)	TOC (mg/L)	Ca/Mg (mg/L)	
[5]	SAGD BFW	9.8–10.5	1800	500	0.84	Up to 98% TOC, TDS, and silica rejection
[25]	SAGD WLS inlet	9.0	1200	420	2.5	>86% rejection of the salt, silica, and DOM
[29]	SAGD BBD	11.6–12.2	14,900–36,200	2480–5060	Up to 700	Up to 80% DOC and 45% TDS removal
[30]	Mining OSPW	7.3–8.5	1549–4920 μ S/cm	46–85	30–80	>95% rejection of TOC and divalent ions.
[31]	Mining OSPW	8.0–9.0	2477	48.3	73	~69% and 82% NaCl removal w/ and w/o pretreatment

Table 1. Overview of earlier studies on oilfield-produced water using NF membranes.

inlet and BFW using various types of NF membranes. TOC, TDS, and silica rejection of up to 98% and divalent cation removal greater than 99% was obtained at different pH values from pH 7.0 to pH 10.5. Pulsation of pH was proposed as an effective technique for mitigation of membrane fouling and water flux recovery. Hurwitz et al. [29] investigated NF processes with and without upstream coagulation and pH adjustment for the treatment of SAGD BBD water. Dissolved organic carbon (DOC) and TDS removal as high as 80 and 45%, respectively, were obtained. It was also found that neither coagulation nor acidification as pre-treatment processes improved the separation performance of the NF process. Peng et al. [30] and Kim et al. [31] worked on oil sands process-affected water (OSPW) associated with surface mining extraction of bitumen. OSPW is the water contained in tailings ponds in oil sands mining operations. Significant reductions in permeate hardness, TOC (>95%), and NaCl (up to 82%) was reported. In contrast to the Hurwitz et al. [29] study, Kim et al. [31] demonstrated that applying pre-treatment methods, for example, coagulation, resulted in improved desalination performance. As will be discussed further in subsequent sections of this chapter, the high native pH of the BBD stream (>11) compared to the lower pH of the OSPW streams (<9) was likely the main reason for the differences in the effectiveness of pretreatment. However, differences in the nature of the DOM may also have been important. Earlier studies revealed that the DOM in mining OSPW consists primarily of naphthenic acid-like compounds [32–34]. The type of DOM present is different for in situ processes compared to mining OSPW, likely due to the different water temperatures and pressures, as well as solvents used (diluent versus naphtha or paraffins). It was shown that the DOM in SAGD-produced water are more representative of humic acids than naphthenic acids [3, 35]. Each organic matter fraction has specific physicochemical properties, for example, charge and molecular conformation, which governs the fouling rate and thus the performance of membrane processes [36]. Hence, membrane fouling propensity changes vastly from mining to SAGD water treatment as the type and concentration of organic matter and produced water chemistry are significantly different.

Here we present the materials and methodologies (sections 4), as well as, experimental results (section 5) related to the treatment of SAGD produced water which have been already published in peer-reviewed journals [5, 25, 29].

4. Summary of NF experiments on SAGD water treatment

4.1. Produced water

SAGD-produced water was obtained from different SAGD water treatment plants located in the Athabasca oil sands region of Alberta, Canada. Concentrations of salt, organic matter, silica, and other inorganic ions were measured in the samples. **Table 2** presents the properties of BFW, WLS inlet, and BBD as the main process-affected streams in a SAGD water treatment plant (**Figure 1**).

4.2. Nanofiltration membranes

Commercial NF membranes are mostly thin film composite (TFC) membranes consisting of three layers: a thin polyamide (PA) or sulfonated polyethersulfone (PES) active layer (100–300 nm), an intermediate microporous layer (~40 μm), and a mesoporous polyester fabric

Elements	Units	WLS Inlet	BFW ^ε	BBD ^ς
pH	—	9	10.5	11.9
Conductivity	mS/cm	1.68	3.50	15.4
TDS	mg/L	1200	1800	14,900
TOC	mg/L	420	500	2890
Dissolved Silica (Si)	mg/L	89	21	331
Sodium (Na ⁺)	mg/L	350	880	2980
Calcium (Ca ²⁺)	mg/L	1.9	3.30	490
Magnesium (Mg ²⁺)	mg/L	0.59	0.37	212
Iron (total Fe)	mg/L	0.39	2.12	11.4

^εModel BFW is prepared by the dilution of BBD.

^ςPlant 1 in Hurwitz et al. study [29], Silica in this study is total silica.

Table 2. Properties of WLS inlet water, BFW, and BBD water [5, 25, 29].

support (~100 μm) [37]. The active layer of TFC membranes governs the membrane separation performance and fouling behavior. The top active layer is typically synthesized by an interfacial polymerization reaction between two monomers (e.g., m-phenylenediamine and trimesoyl chloride for the synthesis of polyamide), which are dissolved in two immiscible solvents [38, 39].

Membrane properties	NF270 (Filmtec) [25]	NF90 (Filmtec) [25]	ESNA (Hydranautics) [25]	HYDRACoRe ^ε (Hydranautics) [40]
Membrane type	TFC-PA	TFC-PA	TFC-PA	TFC-Sulfonated PES
Maximum operation pressure (kPa)	4136	4136	4136	4136
Maximum operation temperature (°C)	45	45	45	70
pH range	2.0–11.0	2.0–11.0	2.0–10.0	1.0–13.5
Salt rejection (%)	40–60	85–95	75–92	10–70
MWCO (Da)	330 ± 48	201 ± 25	223 ± 37	720–3000 [29]
Contact angle (θ°)	34 ± 5.5	62 ± 6.7	60 ± 6.2	62 ± 3.0 [41]
Zeta potential (mV)	–12.1 at pH 4, –21.6 at pH 7, –24.0 at pH 9	5.1 at pH 4.5, –24.9 at pH 7, –27.3 at pH 9	0 at pH 4.5, –11.5 at pH 7, –11.0 at pH 9	–85 mV over a pH range of 3–11 –36.8 at pH 7 [41]
Isoelectric point (IEP, KCl 10 ^{–3} M)	3.0 ± 0.2	4.0	4.9 ± 0.1	N/A
Mean roughness (nm)	5 ± 0.25	65 ± 2.2	50 ± 3.5	9.8 [41]

^εThe properties of this membrane are obtained from the membrane manufacturer's published literature [40] unless otherwise stated.

Table 3. Properties of NF membranes tested for SAGD-produced water treatment.

The main characteristics of NF membranes, which have been used for SAGD-produced water treatment are summarized in **Table 3**.

The fouling propensity of a membrane primarily depends on its surface charge, roughness, hydrophilicity. The hydrophilicity and surface charge of membranes are obtained by measuring their zeta potential and contact angle. In general, more hydrophilic and more negatively charged membranes are less susceptible to fouling by more hydrophobic DOM and negatively charged organic and inorganic dissolved materials present in water. The surface roughness of a membrane also plays a significant role in fouling. Rougher surfaces cause the entrapment of more foulants in the eddy zones created behind the peaks. The blockage of valleys on the surface of NF membranes results in a substantial loss of water flux [25].

4.3. Nanofiltration test apparatus

The NF experiments were conducted using bench scale cross-flow filtration systems (**Figure 2**). A typical system consisted of a feed tank, a membrane cell, a pump, a temperature controller to keep the feed temperature at a specific value, a back pressure regulator, and a bypass valve to adjust the applied pressure and cross-flow velocity. A weighing balance or a digital flow-meter were utilized to measure the permeate flow rate. Permeate and retentate are recycled to the feed tank to maintain a constant feed concentration over time.

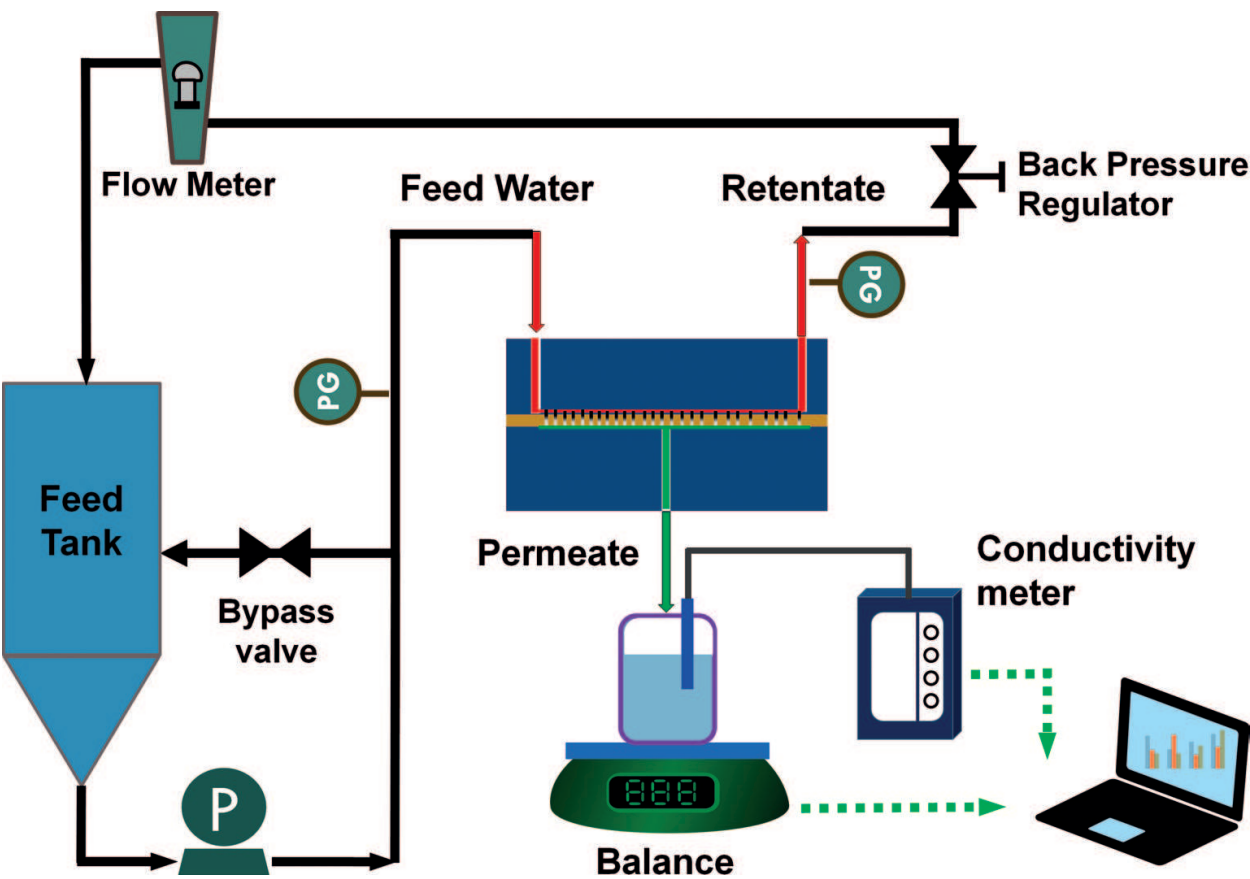


Figure 2. Schematic of a bench scale cross-flow NF setup.

Water flux (J_w) at steady state is obtained by measuring the mass or volume of water (ΔV) passed through the membrane with active surface area A during a certain period Δt :

$$J_w = \frac{\Delta V}{A \Delta t} \quad (1)$$

The rejection of contaminants (TDS, TOC, silica, and divalent ions) is calculated by measuring their concentration in the permeate solution as follows:

$$R(\%) = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (2)$$

where C_p and C_f are the constituent concentration in the permeate and feed solutions, respectively.

5. Results and discussion

Membrane performance was evaluated based on permeation flux and removal of the target constituents. The fouling propensity of a membrane is typically evaluated by measuring the rate of flux decline over time. Fouling decreases the performance of a membrane by reducing the water permeation flux and ultimately shortening membrane life (complete replacement or increased cleaning interval) [36]. Therefore, fouling mitigation is a major challenge for sustainable application of membrane processes. A facile method to mitigate fouling during filtration is an abrupt change of operating conditions such as solution pH, temperature, and ionic strength [42]. The impact of changing pH on water flux and rejection of contaminants during SAGD water treatment has, therefore, been investigated [5, 25, 29].

5.1. Treatment of WLS inlet water by various NF membranes

Water flux through NF270, ESNA, and NF90 membranes and TDS/TOC rejection over 360 min at 50°C and pH of 9.0 are shown in **Figure 3(a)**. The initial water flux of 35 LMH was adjusted for all membranes at transmembrane pressures of 276, 552, and 552 kPa for NF270, ESNA, and NF90, respectively. Water flux was found to decline gradually due to combined silica/organic matter/divalent ion fouling. Based on the data presented in **Table 2**, the concentration of divalent ions in the WLS inlet water is negligible compared to the total concentration of silica and organic matter (~500 mg/L). Hence, combined colloidal and organic fouling was the principal fouling mechanism in this study. The adsorption of silica and DOM onto the membrane surface reduced the permeate flux due to pore blocking, formation of silica/DOM gel, and induced hydrophobic properties [25].

The bar chart in **Figure 3(a)** shows that the initial flux decline for the NF270 membrane was lower than the other NF membranes. Fouling is mainly affected by the feed properties (e.g., pH, ionic strength, and concentration) [43], operating conditions (e.g., pressure and cross-flow velocity) [44], and the physicochemical properties of the membrane (e.g., hydrophilicity and charge) [25].

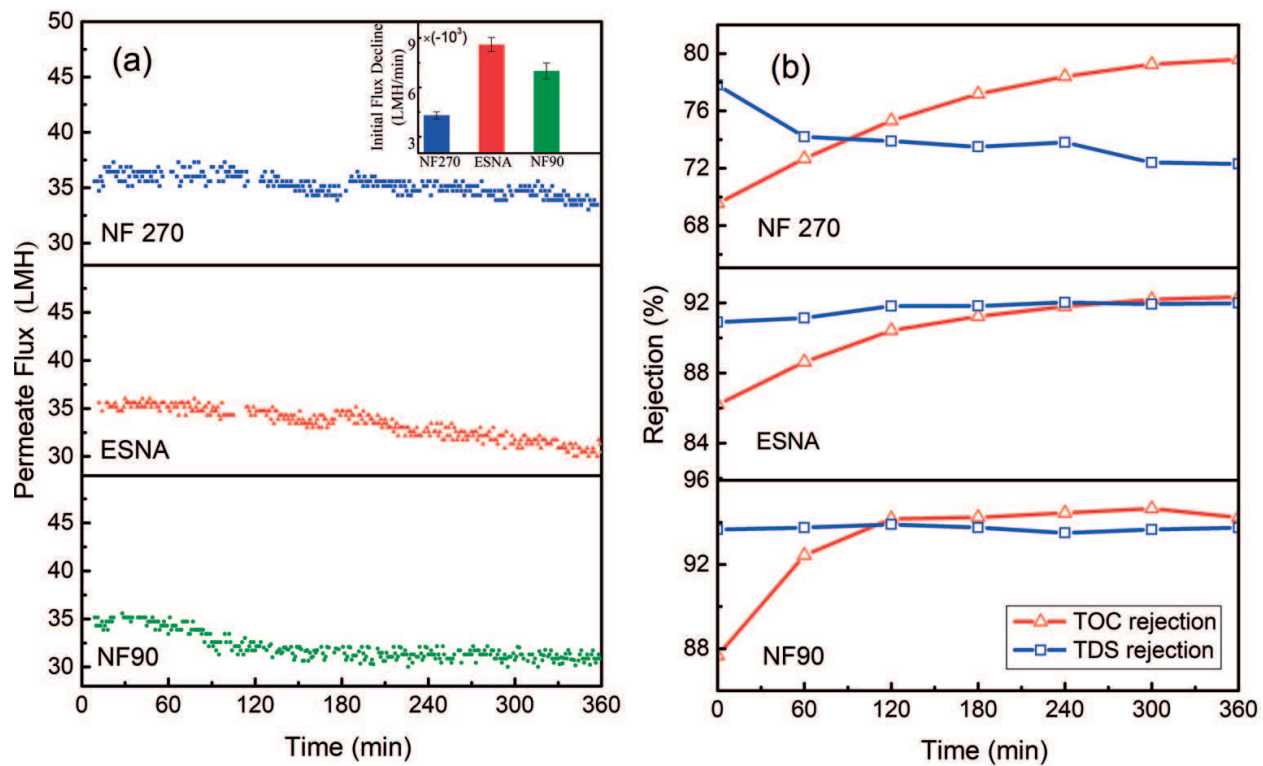


Figure 3. (a) Water flux over time and (b) TOC/TDS rejection for WLS inlet water filtration using NF270, ESNA, and NF90 membranes at pH 9.0 and 50°C [25]. Copyright 2016, Reproduced with permission from Balaban Desalination Publications, Rome, Italy.

Hence, at a constant initial permeate flux, feed flow rate, and feed solution chemistry, the rate of flux decline strongly relates to the surface properties of the membrane. The surface roughness and contact angle data in **Table 3** shows that NF270 is smoother and more hydrophilic than ESNA and NF90. The zeta potential of NF270 is similar to NF90 and is more negative than that of ESNA [25]. It is widely accepted that membranes with higher hydrophilicity and more negatively charged surfaces are less prone to fouling by DOM and silica due to the lower hydrophobic interaction and higher electrostatic repulsion between the foulants and the membrane surface [45].

Figure 3(b) displays the variation of TOC/TDS rejection with time. For all NF membranes tested, TOC rejection increased over time. Earlier studies revealed that the adsorption of DOM on the membrane surface increases its hydrophobicity [45, 46]. This phenomenon enhances the layering attachment of DOM on previously deposited organic matter through hydrophobic interactions that subsequently increase TOC rejection. Rejection of TDS, however, remained constant for the tighter NF90 and ESNA membranes, and decreased for the looser NF270 membrane. Based on the cake-enhanced concentration polarization (CECP) mechanism, both flux and salt rejection should decrease as fouling progresses [47]. Deposited foulants on the membrane surface prevent back diffusion of salt from the surface to the bulk solution and thus increases the salt concentration at the membrane surface significantly. The enhanced concentration-gradient across the membrane increases the passage of salt ions toward the permeate side. In this study, however, TDS rejection remained constant for the denser NF membranes [25]. A possible explanation is that there was clogging of membrane hot spots (the valleys on the surface of membranes with the lowest thickness and the highest local water flux) by the DOM, which restricted the transport of salt [48, 49].

The effect of pH on the performance of the NF90 membrane was studied. The pH of WLS inlet water was progressively decreased from 9 to 7 after 120 min, then increased to 10 after 240 min. As can be seen in **Figure 4(a)**, by reducing the pH from 9 to 7 the water flux declined sharply, then recovered by increasing the pH from 7 to 10. The variation of flux with pH can be attributed to a change in the surface properties of the membrane and by changes to the solution chemistry [25]. At lower pH values, the protonation of the functional groups of DOM, as the major constituent in the WLS inlet water (**Table 2**), decreases the negative charge and ultimately reduces the electrostatic repulsion between DOM molecules [50–52]. Changing the pH also affects the DOM/membrane interaction. In general, the zeta potential of membranes becomes less negative as pH decreases. The foulant/foulant and foulant/membrane attraction causes more deposition of foulants, and increases the thickness of the cake layer. These phenomena can explain the lower permeation flux observed at lower pH values [53]. It was also reported that pH varies the macromolecular conformation of DOM so that a smaller structure forms at a lower pH [50]. This leads to the formation of a denser cake layer and decreases the water flux accordingly.

The effect of pH on TOC/TDS rejection is shown in **Figure 4(b)**. As can be seen, TDS rejection increased after the pH was decreased from 9 to 7. The precipitation of silica and DOM at lower pH values has led to the formation of a closely-packed fouling layer that improved the TDS rejection. The effect of pH on TOC rejection was, however, insignificant. At pH 9, TOC rejection enhanced over time due to the cake filtration, then decreased marginally as pH decreased to 7. This rather contradictory result of TOC and TDS rejection is still unknown and calls for further investigation.

To select an appropriate membrane for the treatment of SAGD WLS inlet water, the trade-off relation between energy consumption and permeate water quality should be considered. Energy consumption in pressure-driven membrane processes is directly linked to the applied pressure. Therefore, a loose NF270 membrane is likely to be less energy-intensive than a tight NF90 or ESNA membrane. In this study, employing all NF membranes adequate Ca/Mg/Si removal is achieved to replace the current water treatment scheme. In addition, the NF270

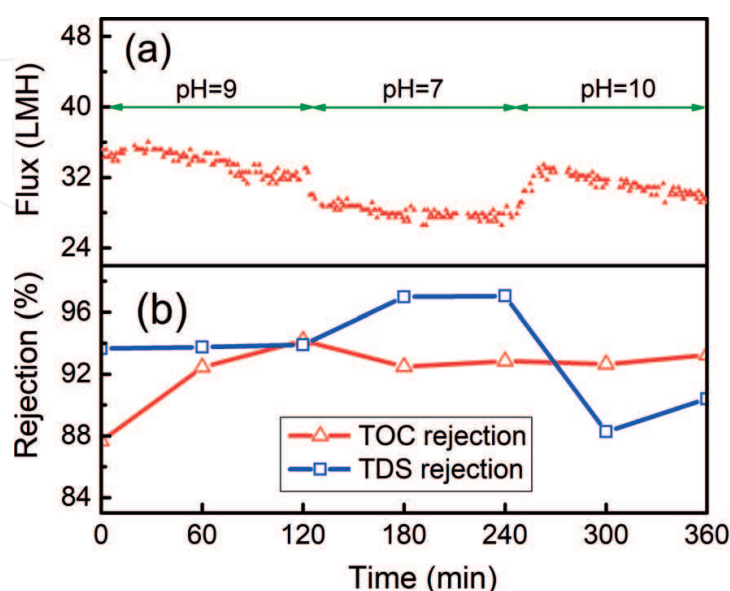


Figure 4. Effect of pH on performance of NF90 membrane for the filtration of WLS inlet water at 50°C [25]. Copyright 2016, Reproduced with permission from Balaban Desalination Publications, Rome, Italy.

membrane provided TOC/TDS rejection of more than 70% at pressures as low as 276 kPa. As a result, when highly purified water is not required, the NF270 membrane would be an excellent energy-efficient candidate. The ESNA and NF90 membranes provided 35 LMH water flux at the same transmembrane pressure of 552 kPa. The TOC/TDS rejection of the NF90, however, is slightly better than the ESNA (**Figure 3b**). Therefore, the NF90 membrane is proposed as the best candidate when a high water quality with reasonable energy efficiency is desired. In summary, replacing the current water treatment scheme with a properly designed cross-flow NF process (**Figure 1**) yields a higher quality of recycled water and consumes a lower amount of chemicals and energy. In addition, pH pulsation was found to be an efficient technique for the mitigation of membrane fouling and water flux recovery.

5.2. Treatment of model BFW by a tight NF membrane

Water flux and TOC/TDS rejection of the NF90 membrane at 50°C and pH 10.5 (raw BFW pH) are shown in **Figure 5(a)**. The normalized flux declined due to the combined fouling of silica and DOM in the model BFW (**Table 2**). In the treatment of model BFW, TDS rejection increased over time (from 80–95%), while TOC rejection remained constant (~98%), which is contrary to that observed for filtration of WLS inlet water [5]. This discrepancy demonstrates the effect of solution chemistry, primarily pH and ionic strength, on the rejection of salt and organic matter. Taking a closer look at **Table 2** reveals that the model BFW has a significantly higher pH and slightly higher salt concentration as compared to the WLS inlet water. Higher pH leads to the increased solubility of organic matter in the feed solution and less tendency to precipitation on the membrane surface. On the other hand, high salt concentration reduces the thickness of electric double layer around silica particles and thus facilitates the precipitation of silica and co-precipitation of DOM [54]. The latter effect seems to be dominant and results in the formation of selective fouling layer, which increases the TDS rejection over time. Also, an increase of TDS rejection again confirms the significance of organic fouling (plugging of hot spots by DOM) in the treatment of SAGD-produced water.

Figure 5(b) shows the effect of a step change in pH on flux and rejection at 50°C. Decreasing the pH from 10.5 to 8.5 reduced the flux by 20%, but enhanced the TDS rejection. Returning the pH back to 10.5 has quickly returned the water flux and TDS rejection to the previous trend. For all pH values, >98% of the organic matter was removed by NF90. Dynamic pH experiments showed that a more stable flux with higher TDS rejection can be obtained at lower pH values. However, higher overall water flux at higher pH values was achieved. The rapid change of flux and salt rejection by injecting acid or basic solutions into the feed stream demonstrates the significant impact of pH on fouling, particularly, in the presence of both silica and organic matter [5]. This behavior can be explained by a rapid change in foulant/foulant and foulant/membrane interactions by altering the pH as described earlier.

The results of scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) on NF90 membranes before and after filtration are shown in **Figure 6**. After NF, a layer of rejected solutes was formed on the membrane surface. More foulants were clearly deposited on the membrane when the pH of the solution was decreased to 8.5 (**Figure 6c, d**). Decreasing the pH resulted in precipitation of silica and co-precipitation of DOM, which were adsorbed on the surface of the membrane. EDX analysis revealed the presence of silica and iron in

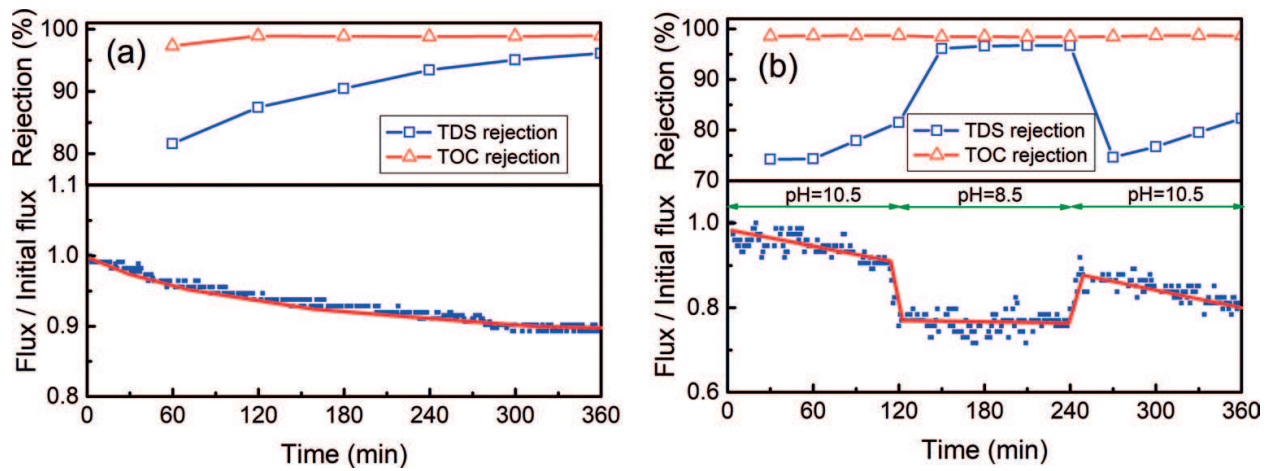


Figure 5. Water flux and TOC/TDS rejection for model BFW filtration using NF90 at (a) constant pH = 10.5, and (b) variable pH 10.5–8.5–10.5 at 50°C [5]. Copyright 2015, Reproduced with permission from Elsevier Science Ltd., Oxford, UK.

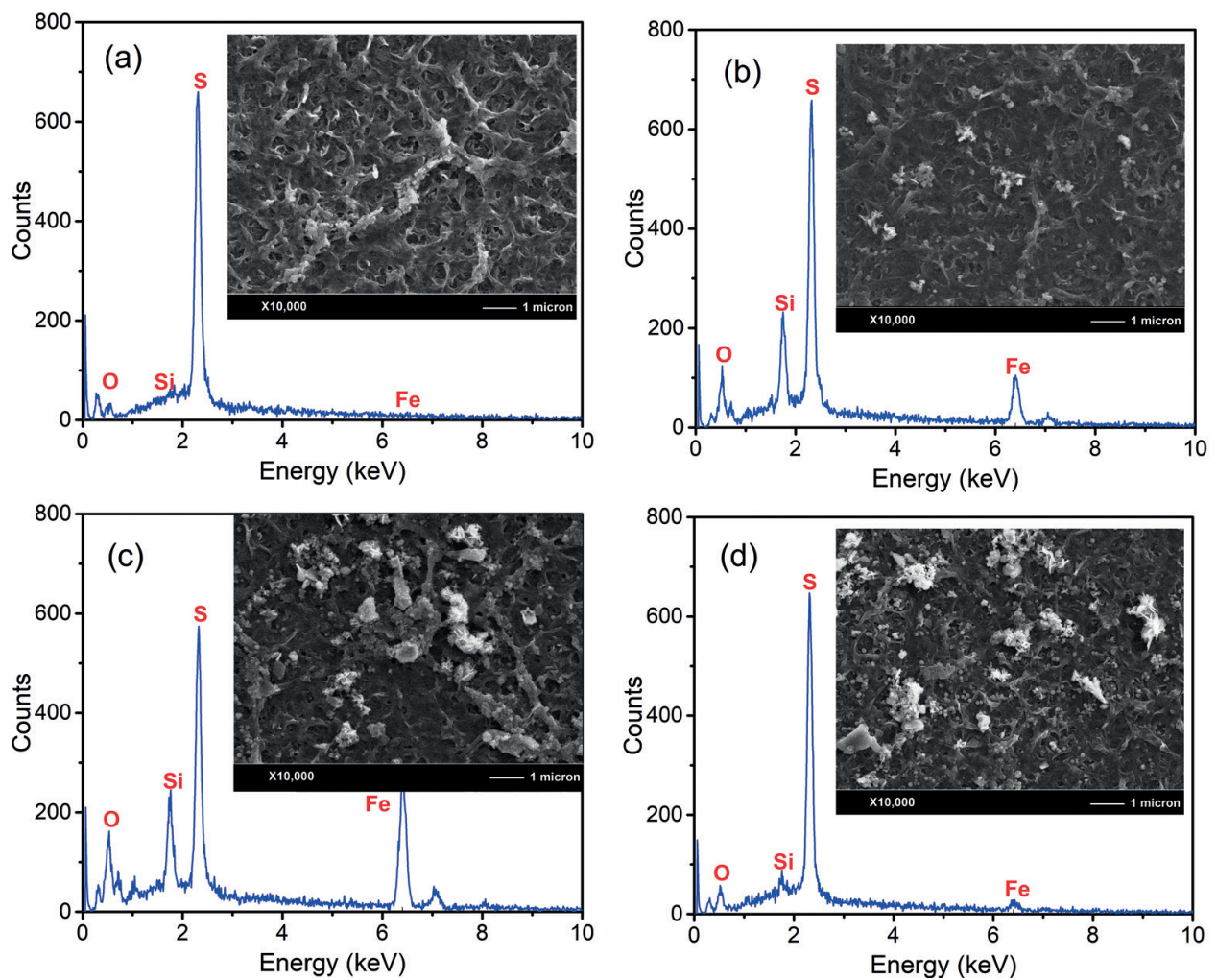


Figure 6. FESEM-EDX of (a) virgin membrane, and fouled membranes at (b) pH = 10.5, (c) pH = 8.5, and (d) pH = 8.5 then 10.5 [5]. Copyright 2015, Reproduced with permission from Elsevier Science Ltd., Oxford, UK.

the fouling material. The iron peak became larger as the pH decreased from 10.5 to 8.5. This indicates precipitation of more solutes on the membrane surface at a lower pH. As expected based on solubility considerations, when the pH of the feed solution increased from 8.5 to 10.5 both silica and iron peaks shortened noticeably which shows re-dissolving of these materials at higher feed pH. This result implies that fouling is reversible by increasing the pH [5]. It is worth noting that the intense sulfur peak in all EDX results is related to the PES support layer of NF90 membrane.

Removal of inorganic elements from model BFW was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis and the results are provided in **Table 4**. Almost 98% of the dissolved silica and more than 99% of divalent ions (Fe^{2+} , Ca^{2+} , and Mg^{2+}) were removed by NF90 [5]. With 98% rejection of silica its content in the BFW becomes more than 90% lower than typical BFW and, therefore, would significantly reduce the fouling propensity in steam generation. Such a low level of DOM, salt, and scale-forming species in the permeate would significantly reduce the fouling/scaling propensity of the BFW if NF was employed as a polishing stage in the current SAGD process train (see **Figure 1**). Production of higher quality BFW may significantly reduce capital and operating costs through reducing the membrane area required for water treatment.

5.3. Treatment of BBD water by chemically and thermally stable NF membranes

A further concern for oil sands producers is minimizing the volume of BBD water requiring disposal [55]. Therefore, a process configuration involving NF of BBD to remove silica, TOC, and TDS in which the permeate would be used for BFW with a reduced volume of concentrate sent to disposal. Hurwitz et al. [29] evaluated NF for this application. Direct NF treatment and NF with coagulation and acidification pre-treatment were evaluated. Direct nanofiltration of chemically unadjusted BBD at its original pH was found to be the optimal treatment option with respect to the flux stability and the removal of TOC and TDS. The high DOM concentration and high pH of the BBD made coagulation of the bulk DOM difficult. Without NF, a maximum DOC removal of 30–40% was possible, but this required either very high coagulant doses (>400 mg/L as Al) and/or very low pH (4–6) [29]. Although upstream removal of DOM can be beneficial in some membrane process configurations, in this case, neither pH reduction nor coagulation significantly improved the rejection of DOM or TDS. Additionally, acidification and/or coagulation consistently resulted in increased membrane surface fouling and flux

Elements (mg/L)	Model BFW	NF90 Permeate	Rejection (%)
Na^+	880	53	94
Cl^-	510	15	97
Mg^{2+}	0.18	<0.02	> 99
Ca^{2+}	0.66	<0.03	> 99
Iron, total	0.48	<0.03	> 99
SiO_2 , dissolved	21	0.4	98

Table 4. Rejection of inorganic materials by NF90 obtained by ICP-OES [5]. Copyright 2015, Reproduced with permission from Elsevier Science Ltd., Oxford, UK.

decline. Because of the naturally high pH of the BBD, prolonged operation with at elevated fluxes and recoveries was possible, while maintaining solute removal as high as 80 and 45% for DOC and TDS, respectively.

A specially formulated sulfonated PES TFC membrane (HYDRACoRe) was used to treat the BBD. The high thermal and chemical stability of these membranes as well as their high negative surface charge (see **Table 3**) make them well suited to the treatment of BBD water. The HYDRACoRe membrane with a MWCO of 720 Da (the tightest membrane in this series of commercial membranes) was utilized for filtration studies. Dead-end NF tests were conducted to determine the effect of coagulation and BBD pH on the performance of the membrane. Stable operation was observed for water flux and DOC/TDS rejection across the range of initial fluxes tested (**Figure 7**). No flux decline was observed for the high, middle, and low initial fluxes (**Figure 7b**). A slight increase in the water permeability over time for low and intermediate initial fluxes was attributed to the swelling of membrane caused by electrostatic repulsion between the charged solutes (ions and charged DOM) and the membrane itself [29]. Likewise, neither elevated temperature nor initial flux had a significant effect on solute rejection (**Figure 7b**). Between 60 and 85%, DOC rejection was obtained over the range of initial fluxes. Interestingly, no loss in rejection was detected over the 60 min test period. This might be attributed to the very low total suspended solids (TSS) of BBD water (2 ppm) which mitigates the effect of cake enhanced concentration polarization and thus diffusion of organic matter toward permeate side. Applying a moderate initial flux of 60 LMH resulted in 80% DOC removal from BBD sample. Very high pH of BBD water minimizes the deposition of silica and DOM that reduces the effect of cake filtration on DOC rejection. In fact, NF membrane just strains out a certain molecular weight of organics without any deposition of foulants. Similarly, the TDS rejection was not significantly affected by the initial flux and feed solution temperature. Optimal TDS rejection was 40–50%, which obtained at a moderate initial flux. Operation at the middle initial flux, 60 LMH, was reported to provide the most sustainable combination of minimal fouling and maximum DOC/TDS rejection.

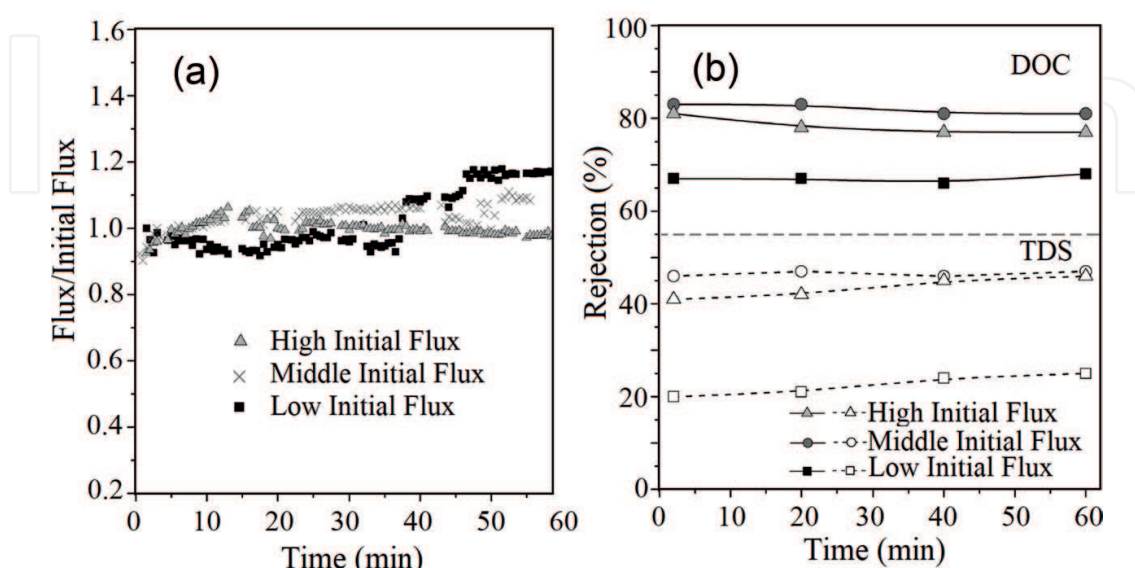


Figure 7. Effect of the initial flux on (a) the flux decline and (b) DOC/TDS rejection using 720 Da MWCO HYDRACoRe NF membrane at 70°C [29]. Copyright 2015, Reproduced with permission from ACS Publications, Washington, DC, USA.

6. Conclusion

The Alberta oil sands industry is actively developing and deploying technologies that reduce operating costs per barrel of product, as well as the amount of energy and fresh water consumed during resource extraction. Development of tailored NF membranes has created new interest in the application of membrane separation processes for the treatment of oil sands-produced water. In this chapter, several studies of NF membranes being tested for oil sands-produced water treatment were presented. Based on these studies, three scenarios for the application of NF membranes in the SAGD-produced water treatment train are suggested: (i) replacing the current WLS-IX process scheme with a cross-flow NF membrane softening process that gives higher-quality boiler feed water with lower energy consumption, (ii) integrating a NF process as a polishing stage downstream of the current WLS-IX processes to produce higher-quality BFW and thus increase the reliability of the boilers, and (iii) using NF to treat OTSG BBD water in the current WLS-IX scheme to increase the reuse of produced water and reduce BBD disposal rates. The major challenge for NF membrane processes in SAGD-produced water applications was found to be fouling by high concentrations of organic matter. pH pulsation was suggested as an effective method for the fouling reduction and water flux recovery. Treatment with loose NF membranes was found to remove more than 70% of the TDS and DOM. Tight NF membranes rejected more than 86% of the TDS and TOC. NF membranes for the treatment of SAGD-produced water should be selected based on the required trade-off between energy consumption and permeate water quality required for steam generation.

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