

Salt rejection in nanofiltration for single and binary salt mixtures in view of sulphate removal

H.M. Krieg^{a*}, S.J. Modise^b, K. Keizer^c, H.W.J.P. Neomagus^a

^aSST, North-West University, Private Bag X6001, 2520 Potchefstroom, South Africa
Tel. +27 (18) 299-2360; Fax: +27 (18) 299-2350; email: chehmk@puknet.puk.ac.za

^bDepartment of Chemistry, Private Bag X021, Vaal University of Technology, 1900 Vanderbijlpark, South Africa

^cFaculty of Natural Sciences, University of Twente, PO Box 217, 7500AE, Enschede, The Netherlands

Received 13 January 2004; accepted 5 May 2004

Abstract

Three commercial membranes (NF70, NF90 and TFC-SR) were firstly characterized in terms of pure water flux and the rejection of uncharged (alcohols and sugars) compounds. Subsequently, the rejection of monovalent (sodium and chloride) and divalent (calcium and sulphate) ions in single (NaCl, CaCl₂ and Na₂SO₄) and binary (NaCl/Na₂SO₄, CaCl₂/CaSO₄, NaCl/CaCl₂ and Na₂SO₄/CaSO₄) salt mixtures was studied. According to the pure water permeability the TFC-SR membrane is a loosely packed NF membrane (12.3 L·m⁻²·h⁻¹·bar⁻¹), while both NF70 and NF90 are tightly packed (2.6 and 3.6 L·m⁻²·h⁻¹·bar⁻¹). According to the uncharged solute rejection, the MWCO_{NF70} = 60, MWCO_{NF90} = 200 and MWCO_{TFC-SR} > 500. NF70 and NF90 were equally efficient in rejecting 1-2, 1-1 and 2-1 salts (>90%), while TFC-SR showed typical negatively charged surface behaviour, i.e., *R* (1-2) salt > *R* (1-1) salt > *R* (2-1). Sulphate rejection decreased in the presence of sodium chloride more significantly than in the presence of calcium chloride due to the more efficient retention of the bivalent calcium.

Keywords: Membranes; Nanofiltration; Salt rejection; Characterisation

1. Introduction

While nanofiltration (NF) is a relatively new membrane process, it is already widely used for water treatment in different parts of Europe, Israel and the US [1–4]. Striving towards improved membrane quality, efficiency and appli-

cability, research is continuing in an attempt to understand and model the varying parameters involved during NF [5–7]. However, while NF rejection behaviour for single components (salts, pesticides, microorganisms, etc.) is largely understood, the behaviour in multi-component systems becomes complex and less predictable [8]; if an NF membrane is sought for a specific application,

*Corresponding author.

say for the removal of sulphates from mine waste streams (acid mine drainage), many membranes have to be screened in order to find a suitable membrane. A technique that is often used for the evaluation of membranes is the flux and rejection behaviour of uncharged and charged solutes [9,10].

The rejection of uncharged solutes seems to be a function of both solute (size and polarity), as well as membrane properties (pore size, membrane material and membrane charge) [11,12]. Although the mechanism of uncharged solute rejection is not yet clearly understood, it has, for example, been shown that rejection usually remains constant and/or drops slightly with increasing feed concentration [13,14].

Similarly, the rejection of charged solutes is also determined by both the solute and the membrane properties. Additionally, however, there is the added effect of the charged solute and its interaction with the charged surface of the membrane, since it is well known that the surface charge of NF membranes is also influenced by the solution (solutes) in contact with the membrane [10,15].

It is the aim of this study to evaluate and explain the rejection behaviour of three commercial NF membranes in the presence of various single — but especially binary — salt mixtures containing sulphates. The membranes are characterized in terms of pure water permeability and uncharged solute rejection to give a more comprehensive insight into the membrane properties.

2. Experimental

From the membranes recommended by suppliers for the removal of sulphates, the following three were chosen: TFC-SR from Koch Membrane Systems and NF70 and NF90 from Filmtec (Dow). The specifications of the membranes are given in Table 1.

A bench-scale dead-end module with a capacity of ~1 L was used with a flat-sheet

Table 1
Membrane specifications according to suppliers

	TFC-SR	NF-70	NF-90
Supplier	Koch Membrane Systems	Filmtec (Dow)	Filmtec (Dow)
Membrane type	Flat sheet	Flat sheet	Flat sheet
Max. temp., °C	45	35	35
Design or pressure range, bar	17	17	41
MW cut-off, Da	— ^a	200	200
pH range	—	3–9	3–9

^aNot provided.

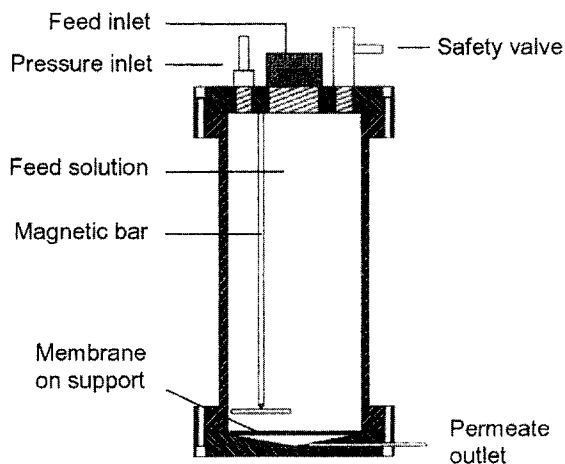


Fig. 1. Dead-end filtration unit.

membrane (effective membrane area is 0.0044 m², see Fig. 1). The unit was operated at pressure differences up to 20 bar, using pressurized nitrogen gas as a driving force. A magnetic stirrer was used to homogenize the feed solution. All experiments were performed at room temperature and the membranes were immersed in water for 1 h before each experiment. The solutions were prepared using deionized water. All experiments were conducted at neutral pH (± 7).

Table 2
Properties of the uncharged solutes used in the retention measurements

	Molar mass, g.mol ⁻¹	Diffusion coefficient, 10 ⁻⁹ m ² .s ⁻¹	Stokes radius, nm
Ethanol	46.1	1.24	0.20
Isopropanol	60.1	1.02	0.24
t-Butanol	74.1	0.88	0.28
Galactose	180.2	0.67	0.32
Maltose	342.3	0.52	0.42
Raffinose	504.5	0.43	0.57

2.1. Water permeability and uncharged solute rejection

The membranes were characterized in terms of pure water permeability, porosity as well as rejection (R) of uncharged solutes. The permeability studies were performed at transmembrane pressure differences ranging from 5 to 20 bar. The permeate flow (g.s⁻¹) was measured using a Sartorius BP2100 balance.

For the uncharged solute rejection, 0.1 vol% of the alcohols ethanol; t-butanol and isopropanol; and 0.1 wt% of the sugars galactose, maltose and raffinose were filtered through the membranes at 10 and 20 bar transmembrane pressure differences. An overview of the solutes (alcohol and sugar) used is given in Table 2.

The diffusion coefficients in water (D_i) were used to calculate the Stokes radius (r_s) with the Stokes-Einstein equation:

$$r_s = \frac{k \cdot T}{6 \cdot \pi \cdot \eta \cdot D_i} \quad (1)$$

The concentrations (feed, permeate and retentate) of sugars and alcohol were determined using high performance liquid chromatography (HPLC) and gas chromatography (GC), respectively.

2.2. Charged solute rejection

The salts used in this study (NaCl, Na₂SO₄, CaCl₂ and CaSO₄) were purchased from Merck (South Africa). The concentrations of the anions in the feed and permeate was measured using a colorimeter for the single salts (HACH DR/890), and an ion chromatograph for the binary salts (Waters Model 510 with Waters column IC-Pak anion HC). The concentrations of the cations were determined using an atomic absorption analyser (AA Varian 250+).

The single-salt experiments (NaCl, CaCl₂ and Na₂SO₄) were done at 5–20 bar and concentrations ranging from 20 to 200 ppm (total anion concentration). The binary salt mixture experiments were done at 10 bar using mixtures of NaCl/Na₂SO₄, CaCl₂/CaSO₄, NaCl/CaCl₂ and Na₂SO₄/CaSO₄. The ion ratios used were 1:9, 3:7, 5:5, 7:3 and 9:1. The total concentration of the common ion was set to 200 ppm.

3. Results and discussion

3.1. Water permeability and uncharged solute rejection

Water flux through a membrane can be described by Darcy's law [13]:

$$J_w = A_w \cdot (\Delta P - \sigma \Delta \pi) \quad (2)$$

If the feed and the retentate contain pure water, i.e., the osmotic pressure difference across the membrane becomes zero, then Eq. (2) reduces to:

$$J_w = A_w \cdot \Delta P \quad (3)$$

For the three membranes the pure water permeability was determined from the plot of (L.m⁻².h⁻¹) vs. bar.

Another approach for expressing water flux through a membrane is by using the Hagen-Poiseuille equation [13]:

$$J_w = \frac{\varepsilon \cdot r^2}{8 \cdot \eta \cdot \tau} \cdot \frac{\Delta P}{\Delta x} \quad (4)$$

The tortuosity of the membrane can be approximated (for porosities between 30 and 70%) by

$$\tau \approx \frac{1}{\varepsilon} \quad (5)$$

By combining the Darcy and Hagen-Poiseuille equations [Eqs. (3) and (4)], an equation for quantifying the water permeability is obtained:

$$A_w = \frac{\varepsilon}{\tau} \frac{r^2}{8 \cdot \eta \cdot \Delta x} \quad (6)$$

By combining Eqs. (5) and (6), it follows that:

$$(\varepsilon \cdot r)^2 = A_w \cdot 8 \cdot \eta \cdot \Delta x \quad (7)$$

Hence, if the permeability and the thickness of a membrane is known, the $\varepsilon \cdot r$ (a porosity factor) of the membrane can be calculated. The thickness of the active layer of the membranes was determined by scanning electron microscopy and was on the order of 1 μm [16]. Eq. (7) was used to calculate the porosity factor ($\varepsilon \cdot r$) from the pure water flux data for the three membranes (Table 3).

According to Mulder [13], the typical water permeability range for NF membranes is between 1.4 and 12 $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. This implies that the TFC-SR membrane is on the border between UF and NF membranes. On the other hand, both NF70 and NF90 membranes have typical NF flux, however close to the border between NF and RO membranes, with the NF90 membrane displaying the slightly higher flux of the two.

It has been shown previously that the rejection of uncharged solutes (for example, sugar and alcohol) is usually based on their molecular size [17]. According to Table 2, the uncharged solutes used in this study have a decreasing diffusion

Table 3

Pure water permeability and porosity factor of NF membranes

Membrane type	A_w , $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$	$\varepsilon \cdot r$, nm
TFC-SR	19.7	0.6
NF70	2.6	0.24
NF90	3.6	0.28

coefficient (D_i) and increasing Stokes radius with increasing molar mass. It is therefore expected that the rejection of solutes will increase with increasing molar mass and Stokes radius (0.2–0.57 nm). This correlation is confirmed in Fig. 2 where the rejection of the solutes is presented as a function of the Stokes radius. The rejection R (as % or fraction) was calculated using equation 8 [18]:

$$R = 1 - \frac{c_p}{c_f} \quad (8)$$

While there are more accurate methods than the Stokes radius to determine diameters of molecules (for example, molar diameters or diameters obtained from energy minimisation calculations [19]), the Stokes radius gives a rough estimate, which is adequate for the purpose of this study. According to Fig. 2, NF70 has the lowest MWCO at around 60, followed by the NF90 membrane with a MWCO of around 200. This means both membranes fall in the range as specified by the suppliers. However, according to van der Bruggen and Vandecasteele [20], the typical MWCO for NF membranes is in the range 100 to 2000 Da, confirming that both NF70 and NF90 are closer to RO than NF membranes. Of the $\text{MWCO}_{\text{TFC-SR}}$ it can only be deduced that it is >500 . When comparing the results of Fig. 2 and Table 3, the typical inverse proportionality between flux and rejection (selectivity) is

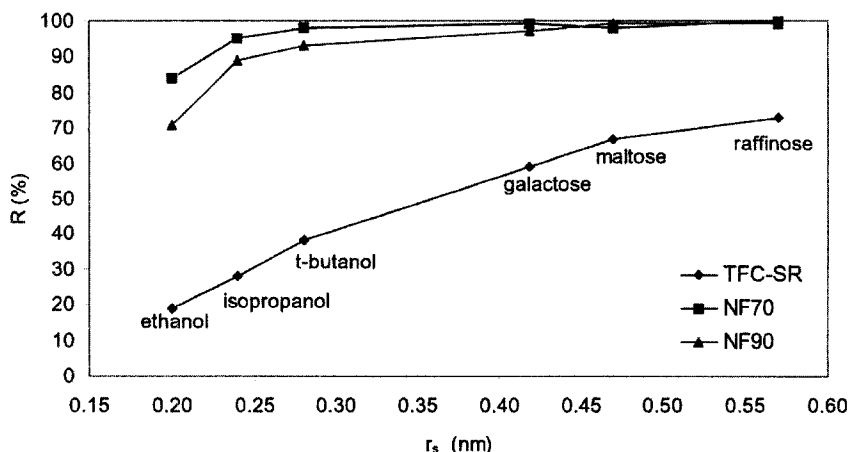


Fig. 2. Rejection of uncharged solutes as a function of solute size ($P = 20$ bar).

apparent, i.e., the membrane with the lowest permeability (NF70) also has the lowest MWCO. For NF70 and NF90 the measured solute size (r_s) for 90% rejection is quite close to the porosity factor as calculated in Table 3. This suggests that rejection behaviour of molecules and ions for these membranes is more a matter of void (pore) size than of charge of the membrane. That is not the case for the TFC-SR membrane. Therefore, it is interesting to note that while NF70 and NF90 have a sharp MWCO of around 60 and 200, respectively, the TFC-SR membrane displays a gradual (nearly linear) decrease in rejection with decreasing Stokes radius. This means that void size distribution of NF70 and NF90 is narrow and that of TFC-SR is relatively broad. This is in agreement with a looser packing of the polymer chains of TFC-SR in comparison with NF70 and NF90 and suggests that rejection of ions in TFC-SR is based more on charge of the membrane than on void size during filtration (swollen situation). This phenomenon is treated in the next paragraphs.

3.2. Charged solute rejection: single salts

From the original flux vs. pressure data (Fig. 3), the solvent permeability ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)

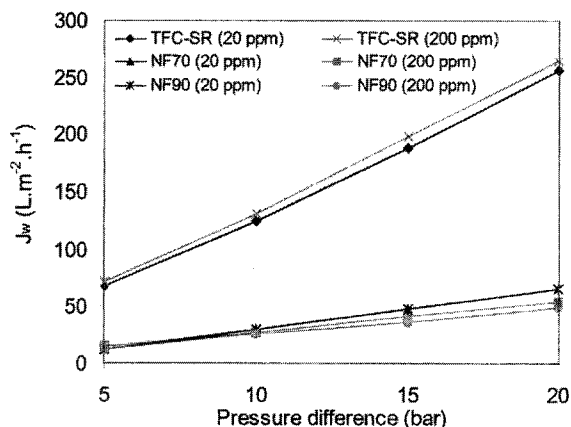


Fig. 3. Influence of varying NaCl concentrations on flux as a function of pressure difference.

for the three membranes at 20 and 200 ppm NaCl was calculated (TFC-SR = 12.5 and 12.9, NF70 = 2.7 and 2.7 and NF90 = 3.6 and 2.5). When comparing these results to the clean water permeabilities (Table 3) of TFC-SR (12.3), NF70 (2.6) and NF90 (3.6), it is clear that the salt concentration has little influence on the flux in the range of 0 to 200 ppm, while it has been shown that flux in NF membranes decreases at high (20–80 g/L) NaCl concentrations [21]. In the case of TFC-SR the permeability even increased slightly for this concentration range. The linearity of the

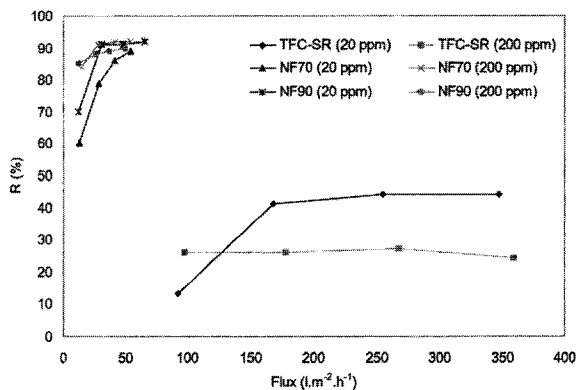


Fig. 4. Flux as a function of anion rejection for varying NaCl concentrations.

flux vs. pressure plot confirms that all three membranes obey Darcy's law [Eq. (2)] as was assumed for calculating A_w and $\epsilon.r$.

To illustrate the interrelationship of flux and rejection as a function of salt concentration, the flux vs. anion rejection plot for the permeation of NaCl at two concentrations (20 and 200 ppm) is shown in Fig. 4. The four data points for each membrane at each concentration were obtained at 5, 10, 15 and 20 bar.

As was observed for the uncharged solute rejection, TFC-SR not only had the highest flux, but also the lowest rejection irrespective of the pressure (5–20 bar) or concentration (20 and 200 ppm). Except for the 200 ppm TFC-SR rejection, all other results showed an increase in rejection with increasing flux sloping of towards a plateau giving an indication of the reflection coefficients (σ) of the membranes. While the rejection of chloride by TFC-SR in general was higher at lower concentrations, as is typical of NF membrane behaviour [8], both NF70 and NF90 displayed high rejection (>90%), especially at high concentrations and fluxes. At higher pressures, the flux of water increases, but the transport of salt does not increase since the driving force is not pressure but concentration dependent. This means that the actual salt concentration in the permeate is lower and therefore the rejection higher. The higher rejection at higher salt concen-

trations for NF70 and NF90 again suggests that the void size of the polymer when swollen is more important than the charge of the membrane. The high rejection of monovalent anions by NF70 has been shown for various monovalent anions and cations, for example: NO_3^- , Cl^- and Na^+ [22,23].

At low salt concentrations the flux has a larger influence on rejection than at high concentrations. This could be since the liquid flux is linear to the pressure difference (driving force), but the salt permeability is not linear to the concentration, but to the chemical potential difference that can be logarithmic related.

In Table 4 the rejection and solvent permeability of the two other single salts tested (CaCl_2 and Na_2SO_4) at 20 ppm and 20 bar is presented. The three salts used in this single salt permeation study represent the three salt types 2-1 (CaCl_2), 1-1 (NaCl) and 1-2 (Na_2SO_4).

The equally high rejection for all three salts by the NF70 and NF90 membranes could again be indicative of the RO character (*void size*) of these membranes as was mentioned earlier (pure water flux). While there is no significant difference in the rejection of the different salts for the NF70 and NF90 membranes, TFC-SR clearly shows the rejection sequence $R(1-2) \text{ salt} > R(1-1) \text{ salt} > R(2-1) \text{ salt}$, which is typical for negatively charged membranes, suggesting that in spite of its UF characteristics (high water permeability), the Donnan exclusion (charge effect) plays an important role during the separation on the TFC-SR membrane [24]. The high rejection of the divalent sulphate for all three membranes is very typical for NF membranes in general [25,26]. NF70 and NF90 showed high rejection ($R \geq 90\%$) for both monovalent and divalent anions.

For all three membranes, the highest solvent permeability was observed for the 1-1 salt NaCl, decreasing in the presence of divalent ions irrespective of whether the divalent ion was anionic or cationic.

Table 4
Anion rejection and solvent permeability for CaCl₂, NaCl and Na₂SO₄

	CaCl ₂		NaCl		Na ₂ SO ₄	
	R, %	A _w ^a	R, %	A _w	R, %	A _w
TFC-SR	29	17	44	17	96	16
NF70	92	2.4	89	2.7	99	2.4
NF90	93	2.4	92	3.6	93	2.8

^aWater permeability in L.m⁻².h⁻¹.bar⁻¹.

3.3. Charged solute rejection: Binary mixtures

In Fig. 5 the rejection of the two anions, sulphate and chloride, for the NaCl/Na₂SO₄ mixture is presented. Except for the sulphate rejection by TFC-SR, it can be said that as the concentrations of an anion decreased (both sulphate and chloride), the rejection of that anion decreased, which correlates to the anion rejection of the single salt experiments and further confirming the negative nature of the membrane (see Fig. 4).

In general, the retention of the monovalent chloride was lower for the salt mixtures than for the single-salt experiments. It seems that the presence of the high valence anion (SO₄²⁻) drives more chloride into the membrane, thus decreasing its retention. This behaviour was previously observed for nitrate rejection in the presence of sulphates [26]. This is further confirmed by the reasonable high chloride rejection at low sulphate concentrations (~80% for NF70 and NF90 and ~30% for TFC-SR) compared to the sulphate rejection at high sulphate concentrations (~50% for NF70, ~30% for NF90 and ~10% for TFC-SR).

In terms of sulphate rejection, the NF90 and NF70 membranes display comparable rejection patterns, i.e., decreasing rejection with decreasing sulphate concentration, the only difference being that while the rejection for NF70 decreases linearly with decreasing sulphate concentration, the rejection by NF90 decreases linearly only up

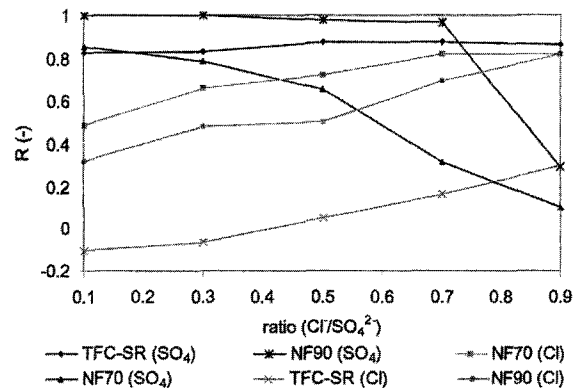


Fig. 5. SO₄²⁻ and Cl⁻ rejection of a NaCl/Na₂SO₄ mixture (pressure = 10 bar, total Na⁺ concentration = 200ppm).

to a Cl⁻/SO₄²⁻ ratio of 0.7, after which there is a sharp decline in rejection. Similarly to the rejection of chloride, the rejection of sulphate decreases with increasing chloride concentration. For TFC-SR the sulphate rejection remains approximately constant irrespective of its concentration, which is understandable when considering its partial UF properties (pure water permeability), i.e., the rejection of sulphate by TFC-SR seems to be also based on size exclusion and is therefore less influenced by the presence of chloride.

While the volume flux of the mixtures was lower than observed for the single salts, it remained constant for the various ratios. For TFC-SR, for example, the volume flux was

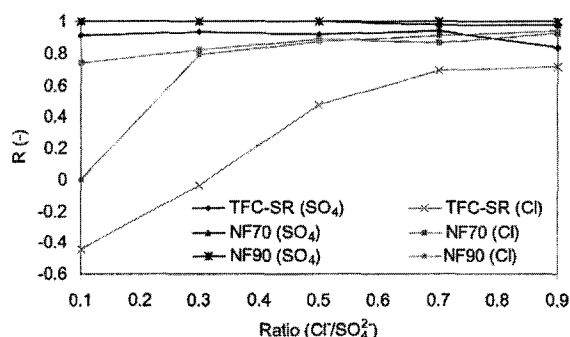


Fig. 6. SO_4^{2-} and Cl^- rejection of a $\text{CaCl}_2/\text{CaSO}_4$ mixture (pressure = 10 bar, total Ca^{2+} concentration = 200 ppm).

79 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 10 bar and 147 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 20 bar.

The results of the second binary mixture ($\text{CaCl}_2/\text{CaSO}_4$), presented in Fig. 6, differ from the previous system since the cation (Ca^{2+}) is divalent and larger in size than the monovalent sodium ion. However, the two anions, chloride and sulphate, are the same.

Chloride rejection in the presence of calcium is similar to the rejection in the presence of sodium, i.e., as the chloride concentration decreases (i.e., sulphate increases), its rejection decreases. However, while the relationship between chloride concentration and rejection was nearly linear in the presence of sodium for NF90 and TFC-SR, the relationship is more exponential in the presence of calcium, i.e., as the chloride concentration increases, its rejection increases exponentially, reaching a plateau at $\text{Cl}^-/\text{SO}_4^{2-}$ ratios of 0.3 and 0.7 for NF90 and TFC-SR, respectively. For TFC-SR, the chloride rejection decreased drastically in the presence of calcium at very low chloride concentrations (-10% and -50% in the presence of sodium and calcium, respectively). However, for all membranes, the chloride rejection was greatly improved at lower sulphate concentrations.

While rejection trends remained similar for chloride in the presence of calcium, the sulphate rejections improved drastically (~100% for NF70

and NF90), especially at low sulphate concentrations, compared to the decrease observed in the presence of sodium, phenomena also found by Wang et al. [25]. For the TFC-SR membrane, the rejection of sulphate remained approximately constant (~90%), decreasing slightly at very low sulphate concentrations.

The general improved rejection for both mono- and divalent anions can be explained by the presence of the divalent calcium anion. The divalent charge, the larger size and the strong hydration of calcium reduce its permeability compared to sodium's permeability. (The hydration energy of $\text{Ca}^{2+} = 1584 \text{ kJ}\cdot\text{mol}^{-1}$ compared to the 407 $\text{kJ}\cdot\text{mol}^{-1}$ for Na^+ [8].) As a result, more anions have to be retained on the feed side to maintain electron neutrality. Thus, for every calcium ion retained, two chlorides have to be retained as well. However, at high sulphate concentrations, sulphate effectively balances the charge of the calcium, and thus chloride is no longer required for electron neutrality, causing its retention to decrease.

When studying the cation rejection for the $\text{NaCl}/\text{CaCl}_2$ binary mixture, only TFC-SR displayed similar tendencies as was observed for the anionic co-ion rejections ($\text{Cl}^-/\text{SO}_4^{2-}$), i.e., both calcium and sodium rejections increased with increasing calcium and sodium concentrations respectively (Fig. 7). For all membranes, the calcium rejection was higher than the sodium rejection irrespective of their ratio. This confirms the conclusion derived for the $\text{CaCl}_2/\text{CaSO}_4$ system where an increase in both sulphate and chloride rejection was observed in comparison to the sulphate and chloride rejection for the $\text{NaCl}/\text{Na}_2\text{SO}_4$ system.

The calcium rejection by NF70 and NF90 is ~90%, remaining approximately constant with increasing calcium concentrations, i.e., retention does not increase with increasing high valence concentration. The retention of calcium by TFC-SR is ~75%, decreasing slightly at low calcium concentrations. The high retention of

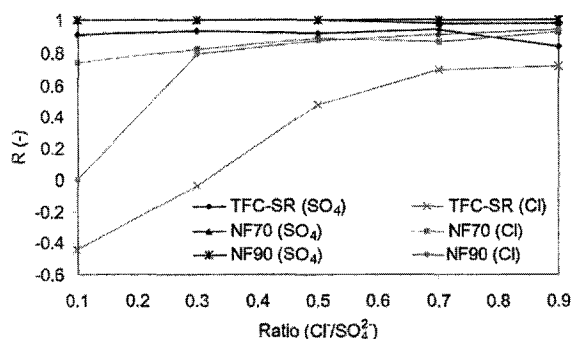


Fig. 7. Na^+ and Ca^{2+} rejection of a $\text{NaCl}/\text{CaCl}_2$ mixture (pressure = 10 bar, total Cl^- concentration = 200 ppm).

calcium, in spite of its divalent opposite charge to the membrane charge, is likely due to the bulkiness of the atom.

The high retention of both cations (Na^+ and Ca^{2+}) by the NF90 and NF70 membranes results in the improved rejections of the monovalent anion, which is a co-ion in this case. The retention of sodium decreases with increasing concentration at low divalent cation concentrations. This is an opposite effect to a decrease in retention in chlorides at high divalent cation concentrations. Also, there would be reduced retention of cationic divalents as compared to the anionic divalents if the $\text{NaCl}/\text{Na}_2\text{SO}_4$ or $\text{CaCl}_2/\text{CaSO}_4$ mixture were to be used.

When studying the rejection of the cations in the presence of a divalent anion for the binary system $\text{Na}_2\text{SO}_4/\text{Ca}_2\text{SO}_4$, the rejections for both calcium and sodium are slightly higher (substantially higher for TFC-SR) than those observed for the $\text{NaCl}/\text{CaCl}_2$ mixture (Fig. 8). It was shown previously that sulphate is retained more efficiently than chloride. This implies that not only is the amount of cations retained higher, but also that this cation is divalent. Therefore, to ensure electron neutrality more anions (both calcium and sodium) are retained, which explains the improved retention of both calcium and sodium in the presence of sulphate.

While sodium rejection decreased for NF70 and NF90 with increasing sodium concentration

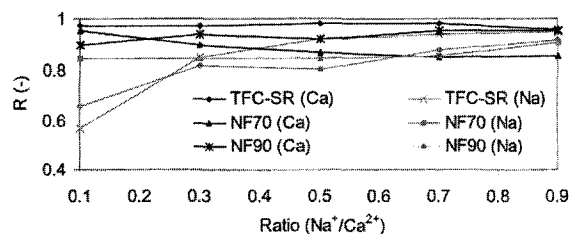


Fig. 8. Na^+ and Ca^{2+} rejections of a $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ mixture (pressure = 10 bar, total SO_4^{2-} concentration = 200 ppm).

in the presence of the monovalent chloride (Fig. 7), it increased in the presence of the divalent sulphate (Fig. 8). It was shown earlier that sodium passes the membrane easier than calcium. Similarly, it was shown that sulphate is more efficiently rejected than chloride. Therefore, in the presence of sulphate ions, more negative charged ions are retained. At low sodium content, enough divalent calcium is present to ensure electron neutrality. However, as the calcium concentration decreases (sodium increases), fewer and fewer divalent cations are present to counter-balance the sulphate. As a result, more sodium has to be retained, resulting in an increase in the retention of sodium at high sodium concentrations.

4. Conclusions

It was shown that, although all three membranes tested were able to reject sulphate, the amount of sulphate rejection is highly dependent on the counter ion and other salts in the solution. The permeability of the membranes ranged from 2.6 (NF70) to 16.5 (TFC-SR) $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. According to the uncharged rejection, NF70 and NF90 have MWCO of 60 and 200, respectively, while the TFC-SR membrane's MWCO $\gg 500$.

For the single-salt experiments all membranes effectively rejected sulphate ($R > 92\%$). While both NF70 and NF90 rejected NaCl and CaCl_2 equally well, TFC-SR rejection clearly followed

the pattern $R(1-2) \text{ salt} > R(1-1) \text{ salt} > R(2-1) \text{ salt}$, which is indicative of a negatively charged membrane. The solvent permeability in the presence of charged solutes remained approximately the same as the pure water permeability.

From the binary salt studies it was shown that sulphate rejection decreased in the presence of sodium chloride, but not in the presence of calcium chloride. The higher retention of the divalent calcium thus ensured the higher retention of the sulphate in an attempt to ensure electron neutrality. Chloride retention decreased in the presence of sulphate especially sodium sulphate. Since sodium retention is low, the chloride has to permeate with the sodium while the sulphate is retained. In terms of the cations (sodium and calcium), it was shown that sulphate improved their retention.

5. Symbols

A_w	— Water permeability ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{kPa}^{-1}$ or $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)
c_p	— Solute concentration in permeate, ppm
c_f	— Solute concentration in feed, ppm
D_i	— Diffusion coefficient in water, $\text{m}^2 \cdot \text{s}^{-1}$
J_w	— Water flux, $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ or $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$
k	— Boltzmann constant, $\text{J} \cdot \text{K}^{-1}$
R	— Rejection, - or %
r	— Pore radius, m
r_s	— Stokes radius, m
T	— Temperature, K

Greek

ΔP	— Pressure difference, kPa or bar
$\Delta \pi$	— Osmotic pressure difference, kPa or bar
Δx	— Membrane thickness, m
ϵ	— Porosity
η	— Viscosity, Pa.s
σ	— Reflection coefficient
τ	— Tortuosity

References

- [1] M. Pahwa and R.C. Maheshwari, Potential of membrane separation technology fluoride removal from underground water. <http://envisjnu.tripod.com/newslet/v8nl/model.html>, 2002.
- [2] S. Chellam and R. Sharma, Quality and membrane treatability of the lake Houston Water Supply (final report). Texas Water Resources Institute, Technical Report 186, 2001.
- [3] K. Madireddi, B. Levine, J.H. Kim and M.K. Stenstrom, Dual membrane separation for removal of organics and dissolved solids during municipal wastewater reclamation for indirect potable reuse. <http://www.seas.ucla.edu/stenstro/>.
- [4] J.A. Redondo and F. Lanari, Desalination, 113 (197) 309–323.
- [5] M. Nyström, J. Tanninen and M. Mänttari, Membr. Technol., 117 (2000) 5–9.
- [6] J.N. Cevaal, W.B. Suratt and J.E. Burke, Desalination, 103 (1995) 101–112.
- [7] B.T. Croll and R. Squires, Proc. Membr. Technol. Conf., 1993, pp. 553–567.
- [8] L. Paugam, S. Taha, J. Cabon and G. Dorange, Desalination, 152 (2003) 271–274.
- [9] W.R. Bowen, A.W. Mohammad and N. Hilal, J. Membr. Sci., 126 (1997) 91–105.
- [10] M.D. Afonso and N.M. de Pinho, J. Membr. Sci., 179 (2000) 137–154.
- [11] K. Kosutic and B. Kunst, Desalination, 142 (2002) 47–56.
- [12] Y. Kiso, Y. Sugiura, K. Kitao and K. Nishimura, J. Membr. Sci., 192 (2001) 1–10.
- [13] M. Mulder, ed., Basic Principles of Membrane Technology, 2nd ed., Kluwer Academic, Dordrecht, 1997.
- [14] J.M.M. Peeters, Characterization of nanofiltration membranes. PhD Thesis, Twente University, Enschede, the Netherlands, 1997.
- [15] P. Eriksson, Environ. Prog., 7 (1988) 58–62.
- [16] S.J. Modise, South African rural water. Analysis and treatment of inorganic salts using nanofiltration and adsorption. PhD Thesis, Potchefstroom University, South Africa, 2003.
- [17] T.J.K. Visser, S.J. Modise, H.M. Krieg and K. Keizer, Desalination, 140 (2001) 79–86.
- [18] K. Mehiguene, S. Taha, N. Gondrexon, J. Cabon and G. Dorange, Desalination, 127 (2000) 135–143.

- [19] B. Van der Bruggen, J. Shaep, D. Wilms and C. Vandecasteele, *J. Membr. Sci.*, 156 (1999) 29–41.
- [20] B. Van der Bruggen and C. Vandecasteele, *Environ. Poll.*, 122 (2003) 435–445.
- [21] I. Koyuncu and d. Topacik, *Sep. Purif. Technol.*, 33 (2003) 283–294.
- [22] B. Van der Bruggen, K. Everaert, D. Wilms and C. Vandecasteele, *J. Membr. Sci.*, 193 (2001) 239–248.
- [23] R. Liikanen, I. Miettinen and R. Laukkanen, *Water Res.*, 37 (2003) 864–872.
- [24] A. Hafiane, D. Lemordant and M. Dhahbi, *Desalination*, 130 (2000) 305–312.
- [25] X.-L. Wang, W.-N. Wang and D.-X. Wang, *Desalination*, 145 (2002) 115–122.
- [26] S. Choi, Z. Yun, S. Hong and K. Ahn, *Desalination*, 133 (2001) 53–64.