



Ceramic nanofiltration membrane for ions separation from ion exchange brine: effect of ionic strength and salts on ionic rejection

CIE5050-09 Additional Graduation Work

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Abstract

Nanofiltration has been reported as a potential and effective technique in the treatment of desalination brines. In this study, the feasibility of ion exchange (IEX) brine treatment using TiO₂ ceramic nanofiltration membranes (CNF) was preliminarily tested in a laboratory scale. Two flat disc CNFs with different molecular weight cut-offs (MWCOs) were used to filtrate the artificial brines containing various concentrations of single salt or the mixture of NaCl/Na₂SO₄. The results showed relatively low rejections of target ions ($R(\text{SO}_4^{2-}) = 5.8\% \sim 18.2\%$; $R(\text{Cl}^-) = -0.8\% \sim 5.6\%$; $R(\text{Na}^+) = -7\% \sim 15.9\%$) at pH around 5.80. It was found that the sulfate rejection increased with decreased ionic strength and could be promoted by the addition of NaCl due to Donnan effect and co-ion competition. The change of membrane MWCO before and after salt solution filtration, as well as the water permeability drop, indicated the exist of fouling problem during experiment. Although the ionic rejection performance of the studied membranes is not good enough for the application in real IEX brine treatment, this study provides a reminder of some practical issues during filtration process, e.g., membrane fouling.

1. Introduction

1.1 Ion exchange(IEX) brine

Natural organic matter (NOM) is a complex matrix of organic compounds and a major contaminant in surface water. It can lead to undesirable color, taste, and odor problems in drinking water and has been found to be a major contributor to the formation of disinfection by-product [1]. Anion exchange is proved to be one of the efficient techniques for NOM removal, in this case negatively charged NOM. It removes also anions that are present in the water source, such as sulfate [1].

During anion exchange, negatively charged NOM and anions load to a higher concentration on resins by exchanging with negatively charged ions on the resin surface, typically chloride, because sulfate ions have a stronger affinity to the functional group than chloride [2]. However, the capacity of ion exchange resins decreases. When the resins are exhausted, the leakage of the undesired ions (sulfate) in treated water increases and the regeneration is needed. Sodium chloride is the most common regenerant used in drinking water applications of ion exchange [2]. During regeneration, high concentration of NaCl solution, normally 10 wt% [3,4], is added to convert the exhausted resin back to the its proper ionic form for service. Therefore, the IEX brine contains the anions (in this case mainly SO_4^{2-}) removed by the resin, NOM and the excess regeneration ions, i.e. Cl^- and Na^+ .

The traditional alternatives to dispose such saline and NOM rich brine, e.g. surface water discharge, are limited due to high cost of transportation and environmental impact [5]. On the other hand, it is desirable to recover the large amount of NaCl in the brine for reuse in regeneration of IEX resins. For this purpose, the waste brine treatment is recommended to separate the NOM and sulfate presented in the brine from NaCl. Pressure and electrically driven membrane processes, such as electrodialysis, ultrafiltration and nanofiltration, are efficient in treatment of organic rich ion exchange brine [6,7]. According to the study of Kabsch-Korbutowicz et al., the electrodialysis of the simulated brine i.e. the mixture of NaCl and humic substances can achieve an almost 100% recovery of NaCl and the retention of NOM particles is 91% when the feed to receiver volume ratio is 5:3. Nanofiltration process has also been applied to treat this model brine and reach a NOM removal of 99% [6]. Nevertheless, the

separation between sulfate and chloride ions may not be as easy as the NOM rejection because of their similar sizes [8,9].

1.2 Ceramic nanofiltration membranes

Nanofiltration (NF) is widely used in drinking and wastewater treatment [8-13]. Charged Nanofiltration membranes with average pore radius in the nanometer range, can reject ions of the opposite charge, due to the charge carried on membrane surface in aqueous environment and the small pore size as well [14]. In the study of Liu et al., the prepared thin-film composite NF membrane showed a high performance for sulfate removal (>95%) from the concentrated sodium chloride aqueous (200gL^{-1} NaCl, 20gL^{-1} Na_2SO_4) with the permeate flux of around $23\text{Lm}^{-2}\text{h}^{-1}$ at 15 bar, while the rejection of NaCl was only about 0.5% [9]. In another research [8], two thin-film polyamide nanofiltration membranes NF270 with a large fraction of pores of approximately 0.85nm were used to treat the sulfate-containing natural water (128mgL^{-1} SO_4^{2-} , 26.6mgL^{-1} Cl⁻) for drinking purpose. These membranes exhibited very high retentions of sulfate (>99%) and much lower retention rates of chloride (~40%) under operating pressure of 10 bar. However, the permeate flux rates during experiments were not mentioned in the paper. Not only polymeric NF membranes, but also ceramic nanofiltration (CNF) membranes have been extensively investigated in recent years. CNF membranes are increasingly preferred due to their high chemical stability and adaptability of extreme pH, temperature and operating pressures. Robust backwashing and chemical cleaning can be applied to these membranes to control fouling [15]. The salt rejection behavior of a tubular ceramic TiO_2 NF membrane with the molecular weight cut-off (MWCO) of 500~600 Dalton and the ultrapure water permeability of $20\text{Lh}^{-1}\text{m}^{-2}\text{bar}^{-1}$ was tested by Van Gestel et al. For the 0.01molL^{-1} NaCl solution, the rejection rate of NaCl was 43% at pH 10 but lower than 5% at pH 6. While for the 0.01molL^{-1} Na_2SO_4 solution, the sulfate rejection was higher than 95% at pH 10 but around 10% when pH was lower than 6 [12]. It has been found that the ionic rejection of NF membranes is highly influenced by factors such as pH, trans-membrane pressure and salt concentration of feed water [9,10,12].

1.3 Study objectives

As was mentioned before, TiO₂ CNF membranes exhibit different rejection performances for different ions, indicating their potential to separate SO₄²⁻ from concentrated NaCl solution.

In this work, the feasibility of IEX brine treatment using ceramic NF membranes was primarily examined with two disk TiO₂ CNF membranes (U30, U01). The experiments and analysis were based on the simplified artificial brine with only NaCl or/and Na₂SO₄ in it. The aim of this study was to understand the effect of ionic strength, salt compositions, and pore size on the rejection performance of specific membranes. Efforts were made to answer the following research questions:

- What is the effect of ionic strength on ionic rejection?
- What is the effect of mixing different salts on ionic rejection?
- What is the effect of pore size on ionic rejection?

2. Theoretical background

2.1 Mechanisms of ionic rejection by CNF

Rejection of charged solutes by nanofiltration membranes is rather complicated because various mechanisms are involved, such as steric exclusion, electrostatic repulsion between the membrane and ions, dielectric exclusion [16], and differences in diffusivity of ions [8]. In this chapter we will focus on the contribution of steric exclusion and electrostatic repulsion.

2.1.1 Steric exclusion

Steric exclusion is similar to sieving and relatively easy to understand: the molecules or hydrated ions that are larger than the diameter of the pores will be retained by the membranes, while the smaller ones go through the membrane to the permeate side. In order to characterize the pore size of membranes, it is necessary to determine the molecular weight cut-off (MWCO). In this research, the MWCO is the molecular weight in Daltons at which 90% of the solute (polyethylene glycols, PEG) is retained by the membrane [17]. The mean pore radius (r_p in nm) of the NF membranes can be calculated based on the MWCO (in Da) using the following equation [18]:

$$r_p = 0.065 \cdot MWCO^{0.438} \cdot 0.5 \quad (1)$$

2.1.2 Electrostatic effect

Isoelectric point (IEP) is the pH at which a particular molecule carries no net electrical charge in the statistical mean [19]. According to previous studies, TiO₂-based ceramic membranes exhibit an IEP in the pH range of 3.5~6.5 [20, 21]. In an aqueous electrolyte environment with the pH that is different from the IEP, the surface as well as the pores of the membrane are charged and form an electrical double layer (EDL). It has been widely accepted that the electrical double layer theory plays an important role in controlling the salt rejection behavior of NF membranes [20-24]. As shown in figure 1, in the Stern layer, the electric potential decreases almost linearly from the surface potential; while in the diffuse layer, it decreases roughly exponentially due to the gradual change of counter-ion concentration over the distance from the wall [20,25,26].

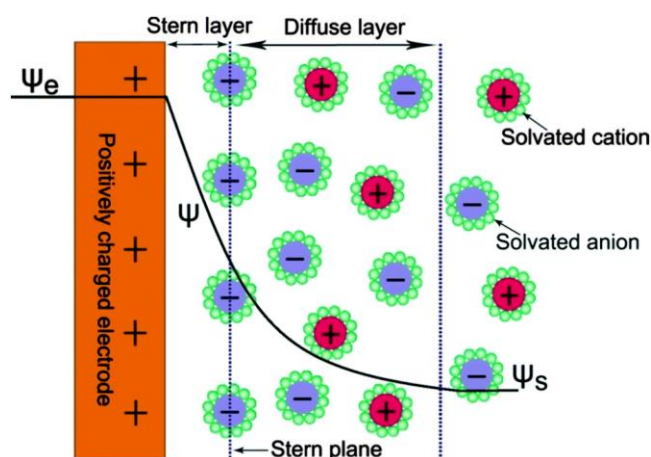


Figure 1 Stern model of the electrical double layer at a positively charged electrode in an aqueous electrolyte. ψ_e , ψ , ψ_s are the electrical potential at the electrode surface, the electrode/electrolyte interface and the bulk electrolyte, respectively [26].

The Debye length (denoted as κ^{-1} , m), characterizes the thickness of this electrical double layer, and can be calculated using equation (2) and (3) [20]. The calculation of ionic strength should take all major ions into account. The author thinks that the membrane can be considered electroneutral when the distance from the surface is larger than the Debye length.

$$\kappa^{-1} = \left(\frac{\epsilon_0 \cdot \epsilon_r \cdot K_B \cdot T}{2000 \cdot N_A \cdot e^2 \cdot I} \right)^{1/2} \quad (2)$$

$$I = \frac{1}{2} \sum m_i \times z_i^2 \quad (3)$$

Where

ϵ_0 — vacuum permeability, $8.85 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$;

ϵ_r —— relative permittivity of the background solution (80 for water at 20°C);

K_B —— Boltzmann constant, $1.38 \times 10^{-23} \text{ J K}^{-1}$;

T —— absolute temperature, K;

N_A —— Avogadro number, $6.0 \times 10^{23} \text{ mol}^{-1}$;

e —— elementary charge, $1.6 \times 10^{-19} \text{ C}$;

I —— ionic strength, mol L^{-1} ;

m_i —— molality of ion i , mol L^{-1} ;

z_i —— charge number of ion i .

If the pore size of the membrane is small enough compared to the Debye length, the electrical double layer can overlap inside the pores. In this case, the counter-ions (i.e. ions carrying opposite charge to the membrane) are likely to occupy the whole pore space, leading to an increase of the membrane repulsive forces on co-ions (i.e. ions carrying similar charge to the membrane) [20]. The Debye ratio, defined as the ratio of the Debye length to the pore radius, can indicate the degree of electrical potential overlap in the pore space [20]. Therefore, a higher rejection rate of co-ions is expected with an increased Debye ratio.

When only the electrostatic repulsion is taken into account, the co-ion is likely to be dominant in the salt rejection process by nanofiltration membranes, resulting in an unbalanced electroneutrality at both sides of the membrane. According to Donnan's research [27,28], if the co-ion of a certain salt is rejected by the membrane because of electrostatic exclusion, then the counter-ion will also be rejected so as to counteract the potential difference between different sides of the membrane and maintain electroneutrality [20,29]. On the other hand, the counter-ions in the permeate side can also draw the co-ions through the membrane leading to a low rejection of certain co-ions.

In the case of the membrane without a fixed charge, the dielectric expulsion theory is applied to explain the interactions between ions and the polarized membrane-solvent interfaces [30-32]. However, some authors concluded that the effect of dielectric exclusion could be ignored when working with simple solutions, e.g., mixed NaCl/Na₂SO₄ solution [11,22], so this effect was not studied in this report.

3. Materials and methods

3.1 Feed water

In order to study the effect of ionic strength on salt rejection behavior of the CNF membranes, feed water with various ionic strengths (IS=0.001, 0.02, 0.0367, 0.1 mol L⁻¹) was used in this work. Three different salt compositions were used for each ionic strength: single NaCl, single Na₂SO₄ and the mixture of the two salts (mass ratio NaCl:Na₂SO₄ ≈ 2.5:1) to study the effect of salt compositions. The solutes were dissolved in ultrapure water without artificial pH adjustment to avoid the change of ionic strength. As no other chemicals were added into the water, the major ions in feed water were Na⁺, Cl⁻ and SO₄²⁻. The concentrations of two salts in each test are shown in Table 1.

Table 1 Salt composition of feed water

Membrane	MWCO (Dalton)	IS (mol L ⁻¹)	NaCl (g L ⁻¹)	Na ₂ SO ₄ (g L ⁻¹)
U30	610	0.001	-	0.05
			1.17	-
		0.02	-	0.95
			0.78	0.32
		0.0367	2.14	-
			-	1.74
			1.43	0.58
		0.1	5.85	-
			-	4.73
			3.90	1.58
U01	325	0.001	-	0.05
			2.14	-
		0.0367	-	1.74
			1.43	0.58

3.2 Ceramic nanofiltration membrane

Two flat disc TiO₂ ceramic NF membranes (Inopor[®], Germany) with pristine MWCOs of 610Da (U30) and 325 Da (U01) were used in this study. Both membranes have an effective filtration area of 56.3 cm² with a diameter of 8.47cm. During operation, each membrane was put in the membrane disc holder (TAMI Industries, France) shown in figure 2. The feed water

was pumped to the middle of the upper surface of the membrane (effective layer), while the concentrate came out from the upper edge of the membrane and then recycled to the feed water tank. Inside the membrane holder, the feed flow traveled tangentially across the membrane surface, along the spiral trail. The permeate passing through the membranes was collected from the bottom outlet of the membrane holder. When not being in use, the membranes were conserved in ultrapure water at 4°C.

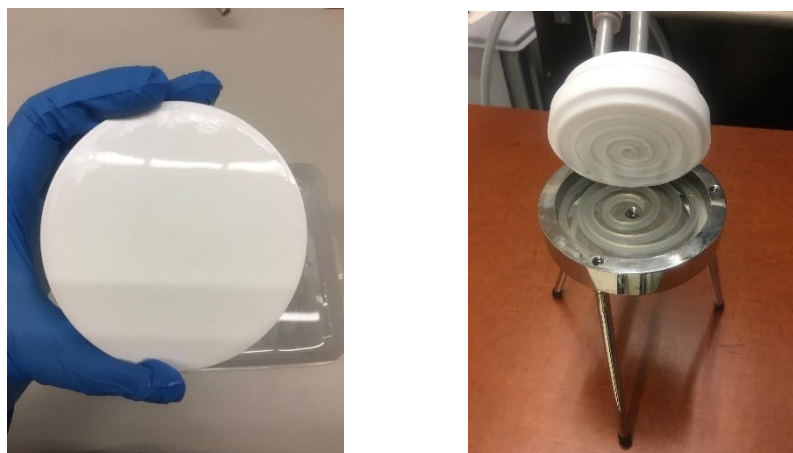


Figure 2 Flat disc TiO₂ CNF (left) and membrane holder (right)

3.3 Filtration set-up and experiment procedure

All experiments were carried out in a laboratory scale using a cross-flow filtration unit. The outline of the experimental setup is shown in figure 3. The feed water had a volume of 7 liters and was pumped from a feed tank into the membrane holder by a ceramic pump. The concentrate was recycled back to the feed tank. The pH, feed temperature, feed pressure, concentrate pressure, and cross flow rate were monitored continuously throughout the experiment. The permeate flow rate was $2.72 \pm 0.2 \text{ Lmin}^{-1}$ during filtration process and the membrane cross flow velocity was then calculated to be around 6.53 ms^{-1} . The pressure of the system and cross flow and the was controlled by the regulating valve and the pump speed (RPM), in order to obtain a constant permeate flux for all experiments with the same membrane (U30: $\sim 20 \text{ Lm}^{-2}\cdot\text{h}^{-1}$; U01: $\sim 11 \text{ Lm}^{-2}\cdot\text{h}^{-1}$). The experiments where performed in a temperature range of 17 to 23°C, and the temperature of the water in the feed tank increased during each test because of the heat transfer from the working pump. The pH was measured and had a stable level at around 5.80. Samples of permeate and feed were taken every 30 minutes (including 10-minute permeate collection) at least 1-hour after the start-up of the filtration system. For each

experiment, six samples (3 permeate + 3 feed) were collected, and then filtered by 0.45µm filter before measurement.

The permeability of the membranes was measured before and after each salt test using ultra-pure water. When the permeability dropped too much to achieve the constant permeate flux, even when the highest possible feed pressure (4.0 bar) was applied, a 10-minute chemical cleaning with 0.2% Cl₂ was performed on the membrane. In this study, the cross flow velocity was relatively high (~6.53 ms⁻¹) so that the effect of concentration polarization was not considered.

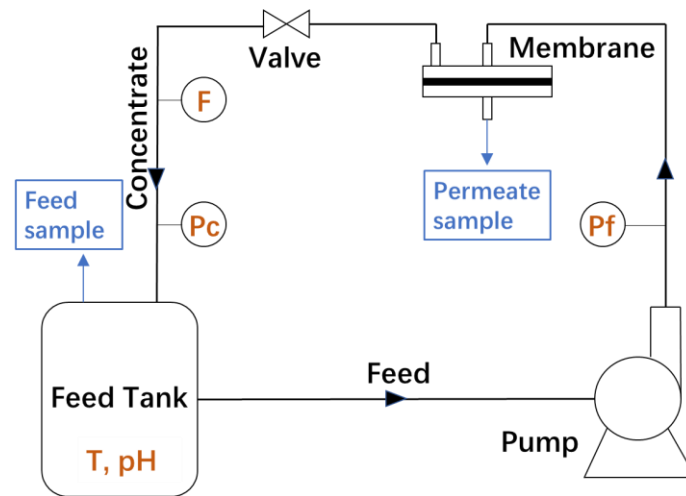


Figure 3 Outline of experimental setup

3.4 Analytical methods

3.4.1 Salt rejection

The concentrations of three ions (Na⁺, Cl⁻ and SO₄²⁻) in both permeate samples and feed samples were mainly determined by the ionic chromatography (IC, ©Metrohm, Swiss) measurement. Part of SO₄²⁻ concentrations in the following tests were also measured by Sulfate Cell Test with NOVA 60 Spectroquant Merck.

- Single Na₂SO₄ solutions with IS of 0.001mol/L and 0.02molL⁻¹(Cell Test only);
- Mixed salt solutions (NaCl + Na₂SO₄) with IS of 0.02, 0.0367 and 0.1 mol/L (IC + Cell Test).

The measurement ranges of the methods were 0 ~ 50 mgL⁻¹ for the IC, and 5 ~ 250 mgL⁻¹ for the cell test. Therefore, most of the samples were diluted before measurement. The ion rejection was indicated by rejection rate R_e , which was calculated by equation (4). For the samples

measured with both IC and Cell test method, the final rejection result was calculated by taking the average of both measurements.

$$\text{Re}(\%) = 100 \times \left(1 - \frac{c_p}{c_f}\right) \quad (4)$$

Where

c_p —— ion concentration in permeate water, gL^{-1} ;

c_f —— ion concentration in feed water, gL^{-1} .

3.4.2 Membrane permeability

The membrane performance was also evaluated by the water permeability. The permeability can, to some extent, reflect the pore size and fouling process of the membrane, and it can be calculated using equation (5) [18]:

$$L_{p,20^\circ\text{C}} = \frac{J}{\text{TMP}} \cdot \frac{\eta_T}{\eta_{20}} = \frac{J \cdot e^{-0.0239(T-20)}}{\text{TMP}} \quad (5)$$

Where

$L_{p,20^\circ\text{C}}$ —— permeability at 20°C , $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$;

J —— permeate flux, $\text{Lm}^{-2}\text{h}^{-1}$;

T —— measured water temperature, $^\circ\text{C}$;

TMP —— trans membrane pressure, bar;

η_T, η_{20} —— the permeate viscosity at $T^\circ\text{C}$, 20°C .

The TMP and J used in equation (5) were defined by equation (6) and (7), respectively.

$$J = \frac{Q_p}{\text{Area}_{\text{mem}}} = \frac{\left(\frac{\Delta m}{\Delta t}\right)/\rho}{\text{Area}_{\text{mem}}} \quad (6)$$

$$\text{TMP} = \frac{1}{2}(P_f + P_c) - P_p \approx \frac{1}{2}(P_f + P_c) \quad (7)$$

Where

Q_p —— permeate volume flow, Lh^{-1} ;

P_f, P_c, P_p —— pressure of feed water, concentrate and permeate, bar.

4. Results

4.1 Sulfate rejection

Figure 4 depicts the result of sulfate rejection by membrane U30 as a function of ionic strength. The pore sizes of the two membranes used in this study are calculated using equation (1) and the effective radii of ions in aqueous environment are shown in table 3. As can be seen in table 2, the pore sizes of the two membranes measured after the experiments are different from the pristine pore sizes. The hydrated radius of SO_4^{2-} ion (0.38nm) is larger than Na^+ (0.36nm) and Cl^- (0.33nm) [8,9] but smaller than the pore sizes of both U30 (0.501nm) and U01 (0.533nm) measured after the experiment. It can therefore be concluded that the steric exclusion might play a less role in the filtration process in this study. The ions rejection by these two membranes is mainly controlled by electrostatic repulsion between the membrane and the target ions.

Table 2 Membrane characteristics

Membrane	Pristine membrane		After experiment	
	MWCO (Da)	pore radius (nm)	MWCO (Da)	pore radius (nm)
U30	610	0.539	516	0.501
U01	325	0.409	595	0.533

Table 3 Dimension and mobility of ions [8,9]

Ion	Hydrated radius(nm)	Diffusion coefficient at infinite dilution ($10^{-9} \text{ m}^2\text{s}^{-1}$)
SO_4^{2-}	0.38	1.06
Cl^-	0.33	2.03
Na^+	0.36	1.33

According to figure 4, the sulfate rejection rate decreases from 15.6% to 5.6% as the ionic strength increases from 0.001 molL^{-1} to 0.1 molL^{-1} in the single Na_2SO_4 solution. As mentioned in chapter 2.1, this change of rejection behavior is mainly caused by the variation of Debye ratio. The increase in ionic strength leads to a decreased Debye ratio, meaning less double layer overlap in the membrane pores [20]. Consequently, the repulsive force of the membrane on co-ions such as sulfate becomes weaker and the ion permeate flux increases accordingly. This trend as a function of ionic strength provides evidence of the negative charge of the studied membrane and is also in line with many results reported in previous studies [20,11,23,33]. Furthermore, it can be observed that the sulfate rejection rate decayed more rapidly when the ionic strength is

below 0.0367 molL^{-1} . This might be due to the dramatic decline of Debye ratio under low ionic strength shown in figure 5.

To study the effect of salt compositions, the ions rejection in single and multi-salt ($\text{NaCl} + \text{Na}_2\text{SO}_4$) solutions with identical ionic strength were compared to each other. The results of $\text{IS} = 0.0367 \text{ molL}^{-1}$ and 0.1 molL^{-1} indicate that the addition of Cl^- promotes the SO_4^{2-} rejection at the expense of a reduction of Cl^- rejection, which will be illustrated in section 4.2. This phenomenon of selective ionic rejection can be explained by the difference in size, valence and mobility of the studied ions. The major mechanisms of ion transport through membrane include diffusion (due to concentration gradient), convection (pressure gradient) and electromigration (electric potential gradient). Pérez-González et al. [11] studied the contribution of these mechanisms and found that diffusion was always the dominant one for sulfate and chloride in the mixed $\text{NaCl}/\text{Na}_2\text{SO}_4$ solutions with chloride concentration of $0.2 \sim 1.2 \text{ molL}^{-1}$ under the pressure of $5 \sim 20$ bars. It can be seen from table 3 that the diffusion coefficient of Cl^- is almost twice as that of SO_4^{2-} , suggesting that Cl^- has a higher mobility or transport rate in the membrane [9]. Given the fact that membrane U30 is slightly negatively charged, the counter-ion Na^+ are well transmitted by the membrane. Based on Donnan effect, Cl^- and SO_4^{2-} are prone to be dragged into the permeate solution by Na^+ in order to maintain the electroneutrality condition. Since Cl^- has less negative charge (less electrostatic repulsion) and higher mobility, more Cl^- ions permeate through the membrane resulting in a higher rejection of SO_4^{2-} . Besides, this result is in good agreement with the findings of Szoke et al. [13] and Déon et al. [14] in whose studies with different fractions of NaCl in the $\text{NaCl}/\text{Na}_2\text{SO}_4$ solution. This phenomenon is also referred to as co-ion competition by Luo et al. [22] and is used to explain the increment of H_2PO_4^- rejection with the addition of NaCl [20].

However, the result at IS of 0.02 molL^{-1} shows a lower SO_4^{2-} rejection in the multi-salt solution contradicting this principle of co-ion competition and no similar recording is found in the literature. Thus, a duplicate experiment is recommended.

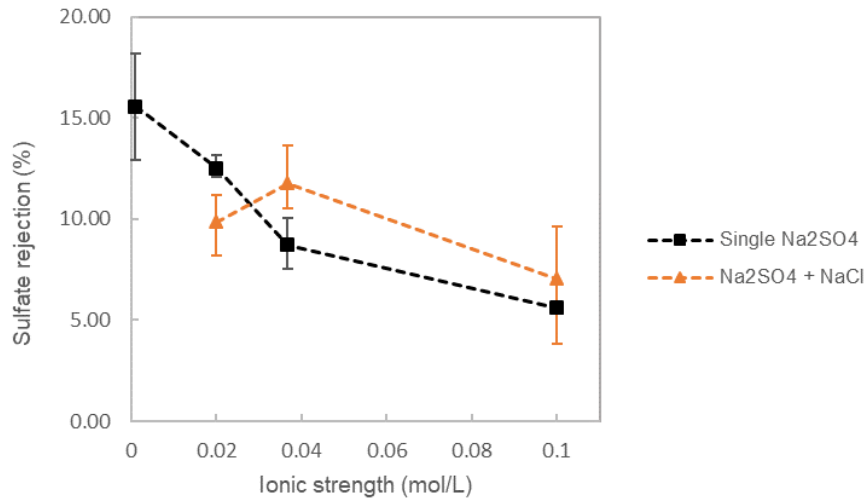


Figure 4 Sulfate rejection by U30 as a function of ionic strength

(Error bars of each data point indicate the maximum and minimum measurement results of the test, the same below.)

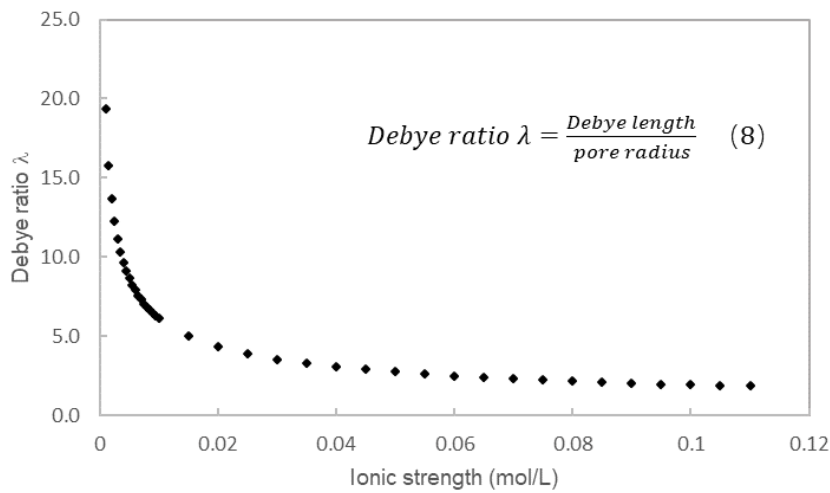


Figure 5 Debye ratio (U30) as a function of ionic strength (calculated using equation (2), (3), (8))

4.2 Rejection of chloride and sodium

With regard of single salt solutions, the rejection rates of chloride and sodium are rather low with the range of 0.5% ~ 5.6% and 0.7% ~15.9%, respectively. Based on previous findings [22,33], a decrease of rejection was expected with increasing salt concentration, whereas contradictory results were achieved in this study. The effect of ionic strength on the retention of chloride and sodium is hard to interpret by the electric double layer overlap.

In the case of single NaCl solution, the retention of both Cl⁻ and Na⁺ get their maximums at IS of 0.0367 molL⁻¹(green dashed line). An increasing trend of Na⁺ rejection is shown in figure 7 when there's only Na₂SO₄ in the feed solution (black dashed line). Comparing the black dashed

lines in both figure 4 and figure 7, it can be found that, in the single Na_2SO_4 case, the SO_4^{2-} rejections are quite different from the Na^+ rejections, indicating an unbalanced charge in solution. This result might have something to do with the measurement and calculation method: for the concentrations of Na^+ and Cl^- , only IC measurement was used; while for the SO_4^{2-} concentrations, the average result of IC and Cell test measurement was used to make figure 4. Thus, repeated experiments should be done in the future to verify the results.

As for the chloride rejection in multi-salt solutions, the percentage of Cl^- rejected by the membrane is lower than that in the single NaCl case (figure 6). This observation matches the increment of SO_4^{2-} retention discussed in section 4.1. Significant decrease (30%) of Cl^- rejection in multi-salt solution at neutral pH has been reported in previous research [13]. Even negative Cl^- rejection rates are often observed when the NF process is used to treat mixed monovalent-multivalent salt solutions [11,13,14,34].

The sodium rejection in single Na_2SO_4 solution is higher than that in the single NaCl and mixed $\text{NaCl}/\text{Na}_2\text{SO}_4$ solutions, however, the difference of Na^+ rejection between single NaCl and $\text{NaCl}/\text{Na}_2\text{SO}_4$ mixtures is not quite obvious (figure 7). In addition, negative Na^+ rejection was observed in the multi-salt solutions. The relatively high Na^+ rejection in Na_2SO_4 solution is contributed to Donnan effect, i.e. more counter-ion Na^+ needs to be retained to counteract the unbalanced charge due to high rejection of SO_4^{2-} . Besides, the concentration of Na^+ is the lowest in single Na_2SO_4 solution among the three cases, leading to less concentration gradient at the different sides of membrane, therefore, less cations tend to permeate through membrane by diffusion [11]. Déon et al. [14] investigated the ions rejection in $\text{NaCl}/\text{Na}_2\text{SO}_4$ mixtures with various proportions of the divalent ion, and they found that the rejection of Na^+ increased with increasing SO_4^{2-} proportion, from pure NaCl to pure Na_2SO_4 concentrations. However, Déon et al.'s experiments are conducted with a constant sodium concentration while the comparison in this study is based on constant ionic strengths. This might be one of the reasons that the Na^+ rejection shows little difference between the multi-salt solution case and the single NaCl case. Moreover, negative Na^+ rejection has also been found by Hagemeyer and Gimbel [33] for low salt concentration ($\text{NaCl}: 1\text{mmolL}^{-1}$) at low permeate flux ($\sim 3.6\text{ Lm}^{-2}\text{h}^{-1}$).

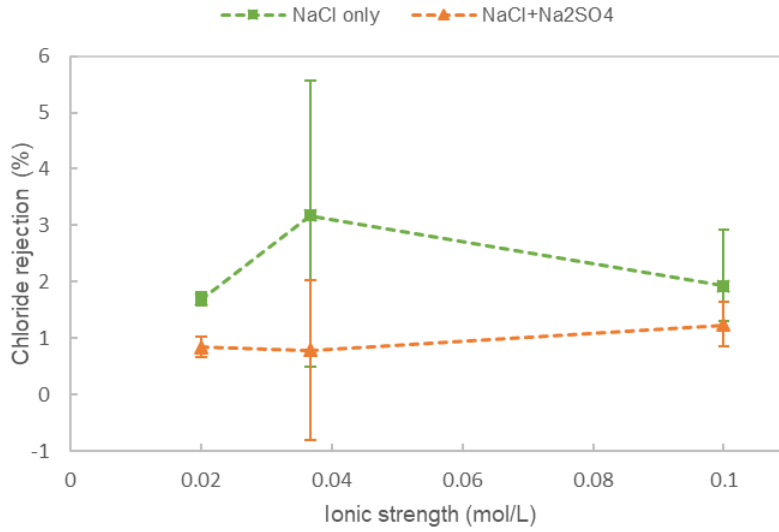


Figure 6 Chloride rejection by U30 as a function of ionic strength

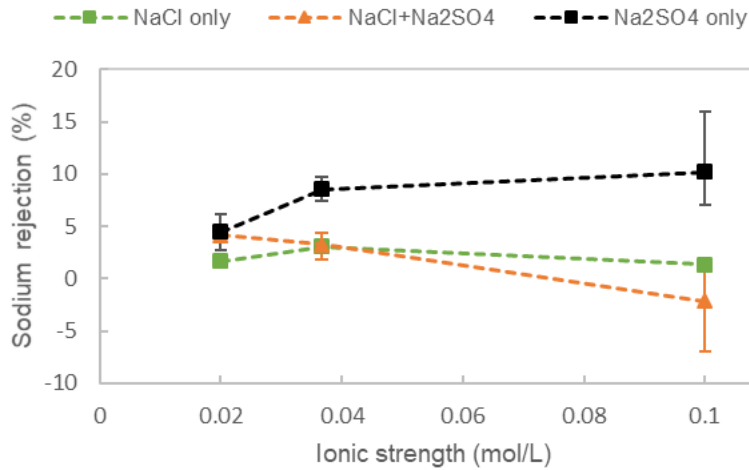


Figure 7 Sodium rejection by U30 as a function of ionic strength

4.3 Filtration and MWCO of the membranes

It is noteworthy that the pristine MWCO values of U30 and U01 are different from the MWCOs after the salt experiments. As listed in table 2, the MWCOs of the two membranes after the experiments are 516Da (U30) and 595Da (U01), respectively. The similar MWCO might explain the similar rejection performance for sodium and chloride shown in figure 8(b, c). For the sulfate rejection, the performance of U30 is higher than U01. This might be due to the difference in permeate flux (U30: $\sim 20 \text{ Lm}^{-2}\cdot\text{h}^{-1}$, U01: $\sim 11 \text{ Lm}^{-2}\cdot\text{h}^{-1}$). Because the ion permeate flux is not proportional to the water flux through membranes, a higher flux can dilute the ions in permeate side resulting in a lower permeate concentration and higher rejection rate [11,14,20]. However, the reason why this dilution effect didn't appear in the chloride and sodium rejection

in this work has not been found yet.

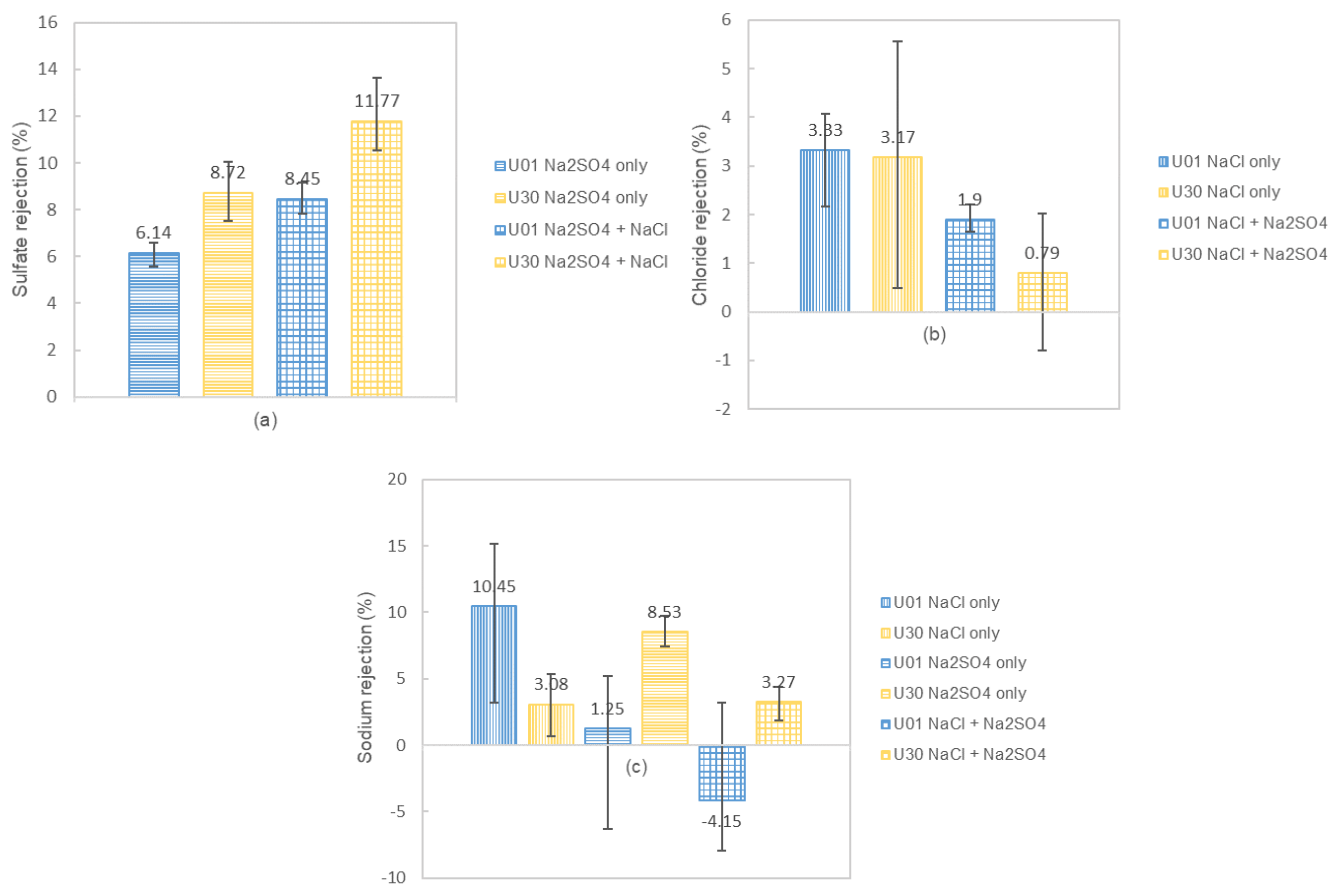


Figure 8 Comparison of ion rejection by two membranes with the IS of 0.0367molL^{-1} (at pH 5.80)

(a) SO_4^{2-} rejection; (b) Cl^- rejection; (c) Na^+ rejection

5. Discussion

Relatively low ions rejection rates were achieved in this experiment. Sulfate rejection was between 5.8% and 18.2%, while chloride rejection was between -0.8% and ~ 5.6%, and sodium rejection was between -7% and 15.9%. The difference in rejection among sulfate, sodium and chloride ions is too low to achieve the separation of sulfate from solutions. Sulfate rejections higher than 95% have been reported in several studies [8,9,12], though under different conditions. In one previous peer study conducted with another disc CNF membrane from the same production batch, the sulfate rejection of 66% for single Na_2SO_4 solution (1mmolL^{-1}) is achieved at pH 6 with the permeate flux of $37.6\text{Lm}^{-2}\text{h}^{-1}$.

In view of these high rejections in literatures and the previous peer study, higher sulfate rejection rates in this study can be expected. Although the ion rejection performance depends on the specific membrane studied, on the solution treated, and on the operating conditions, there are still some points worthwhile to think about.

5.1 Effect of Membrane fouling

Fouling has always been a tough problem in the application of membrane techniques. It is defined as the deposition of suspended and dissolved substances on the membrane surface, in front of or in the membrane pores [35]. In this work, there was rapid fouling, even with the filtration of only ultrapure water or salts in ultrapure water. Measurement of permeability provides insight into the amount of fouling. Figure 9 shows the change of water permeability of U01 during a series of experiments, where blue dots represent the permeability for ultrapure water, and orange dots represent the permeability for salt solutions. A significant increase of permeability (from 5 to 10.5 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) was obtained at 260 min right after the chemical cleaning, after that, however, the permeability dropped again to only 6 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$. This finding might suggest that almost half of the membrane pore surface is blocked, which is partly verified by the MWCO analysis of this membrane. It can be seen from figure 10 that the membrane has an almost 100% retention on the PEG particles larger than 1000Da both for the pristine membrane and after salt solution experiments. However, the rejection for smaller molecules is lower after the salt tests, indicating a blockage of the smaller pores of the membrane. This might have influenced the salt rejection of this study in three ways. First, according to the dilution effect mentioned before, a membrane at lower water flux is expected to have a more concentrated permeate. Second, if the smaller pores are blocked, the water in the permeate can flow only through the larger pores; thus, the effective pore size of the membrane increases. Third, according to the literature, membrane fouling can alter the membrane surface charge, leading to a significant change on the retention behavior [36,37].

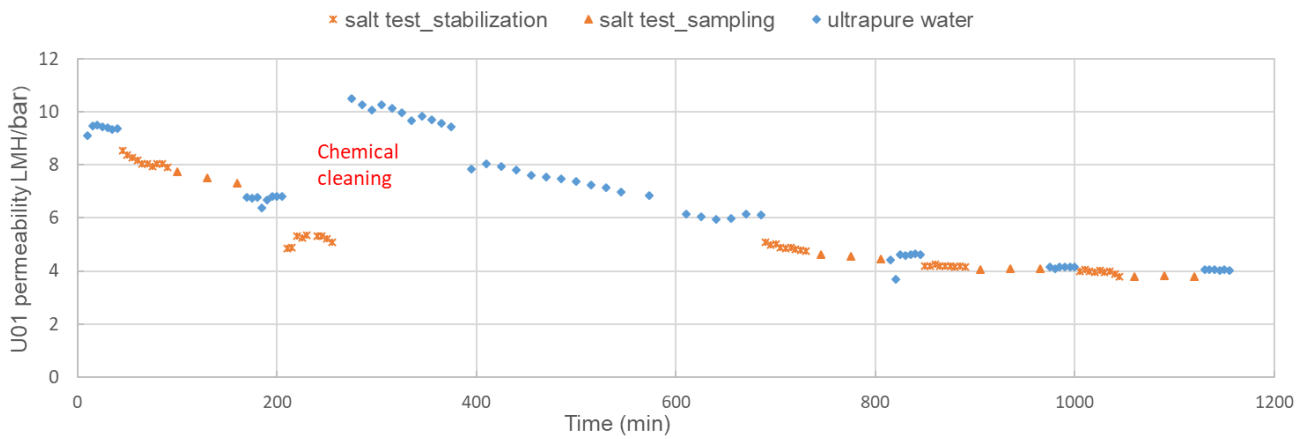


Figure 9 Water permeability of U01

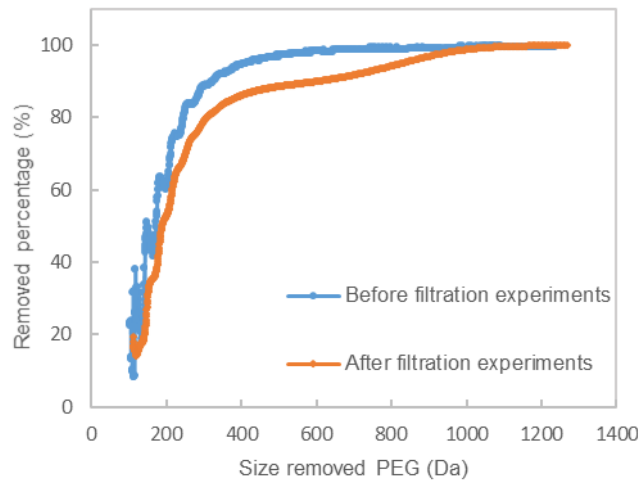
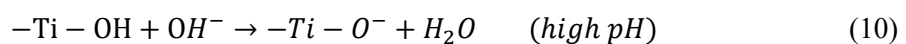
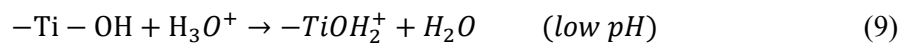


Figure 10 MWCO of U01 before and after filtration experiments

5.2 Effect of membrane surface charge

The experiment results in this work show that both U30 and U01 might only have slightly negative charges at pH 5.80. In the work of Ran et al. [12, 20], the membrane material, TiO_2 , shows an amphoteric behavior in water solution, meaning that it carries no net electrical charge at neutral pH.



Therefore, it can be inferred that the pH 5.80 might be one reason causing the low ionic rejections. Van Gestel et al. [12] investigated the effect of pH on TiO_2 membrane performance, finding that the minimum rejection rate of both Na_2SO_4 and NaCl was at around pH 6: below

5% for NaCl and 10% for Na₂SO₄. Similar results are also reported in the study of Szoke et al. [13]. In further experiments, adjusting pH is highly recommended to obtain denser membrane surface charge and optimize ion separation.

5.3 Ion concentration measurement

Measurement errors might also have contributed to the unexplained results in this study, e.g. the rejection rate of Cl⁻ and Na⁺ in the single salt solutions. The ion charge of the rejection experiments showed some unbalance, of maximum of 10%. In following experiments, further attention should be paid on the dilution factor (currently up to 100 for the highest salt concentration tests), accuracy of pipettes, and IC data reprocessing.

6. Conclusions and recommendations

6.1 Conclusions

The studied disc ceramic TiO₂ nanofiltration membranes were found to be slightly negative charged at pH around 5.80. They were able to achieve a sulfate rejection between 5.8% to 18.2%, with the decreasing ionic strength from 0.1molL⁻¹ to 0.001molL⁻¹. Higher ionic strength led to lower sulfate rejections. Compared with single salt solutions, sulfate rejection was mostly higher in the NaCl/Na₂SO₄ mixture, while the chloride rejection decreased due to Donnan exclusion and co-ion competition. The rejection of Cl⁻ was low in all the experiments (-0.8% ~ 5.6%). The effect of changing pore size from 600 to 300 Da of molecular weight cut off could not be studied, because the effective pore size of the 300 Da membrane was probably larger than the pore size of the pristine membrane. The suspected cause for this was membrane fouling. Ions separation by CNF membrane depends on the specific conditions of the certain membrane. For the purpose of application in the treatment of IEX brine, further study regarding membrane fouling and surface charge in various pH should be carried out.

6.2 Recommendations

Based on the discussion above, some recommendations are given for following studies:

- Investigating the isoelectric point (IEP) of the studied membrane by Zeta potential

measurement, in order to optimize the salt rejection by pH adjustment.

- Performing chemical cleaning more frequently, in order to keep a high permeability of the membrane, and thus reduce the effect of fouling on salt rejection.
- Paying more attention on the ion concentration measurements.
- Verifying the results of these tests by repeating the experiments.

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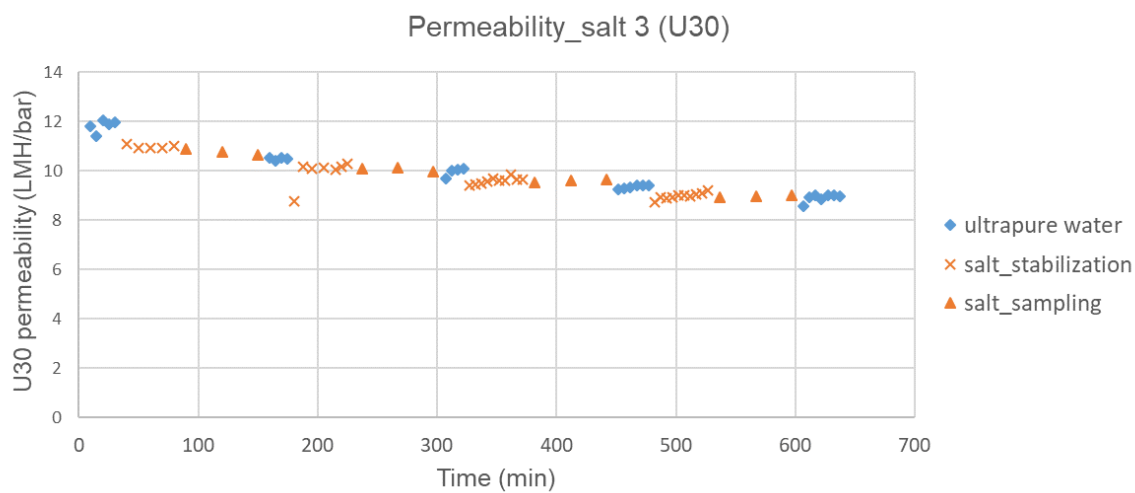
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Appendix

The specific experiment procedures on each membrane and the water permeability data is shown below:

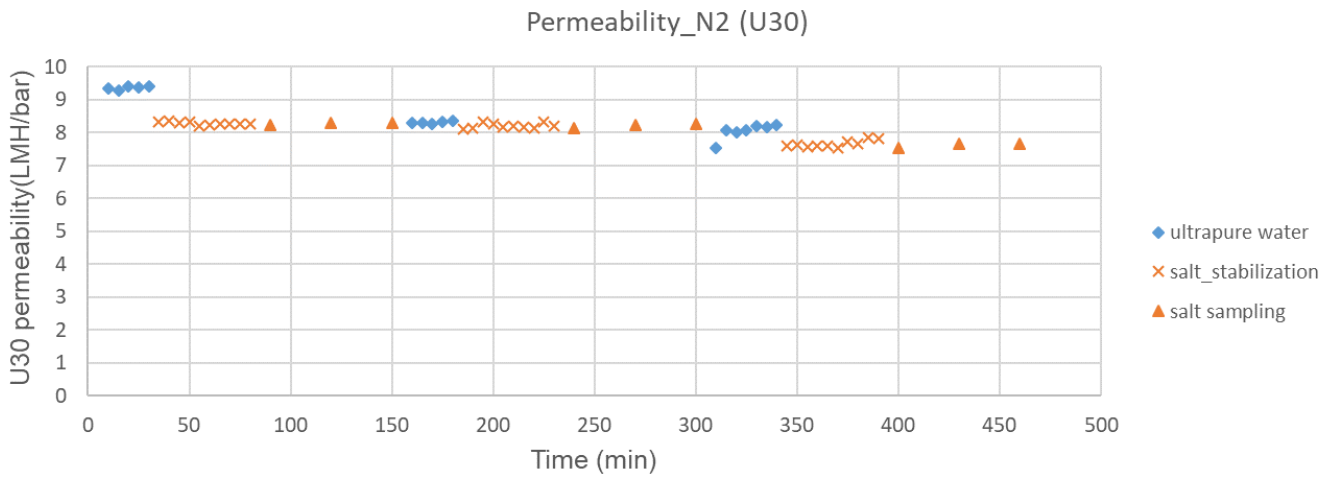
A1. U30 IS=0.02molL⁻¹

Salt3 U30 IS=0.02mol/L				
date	operation	permeability(L/hm ² bar)	flux(L/hm ²)	data sheet
2018/2/6	UP permeability test 90min	~11.9		up 0
2018/2/7	salt test with only NaCl (pipe explosion)			salt3_1(burst)
	salt test with only NaCl	11.08-->10.65	20.5	salt3_1
	up permeability test	~10.5		up 1
2018/2/8	salt test with only Na ₂ SO ₄	~10.0	20.3	salt3_2
	up permeability test	~10.0		up 2
2018/2/9	salt test with NaCl + Na ₂ SO ₄ (more)	~9.6	20.5	salt3_3
	up permeability test	~9.4		up 3
2018/2/10	salt test with NaCl(more) + Na ₂ SO ₄	~8.9	20.6	salt3_4
	up permeability test	~9.0		up 4
2018/2/12	up permeability test	~9.3		up 5
	Summary			sum N1



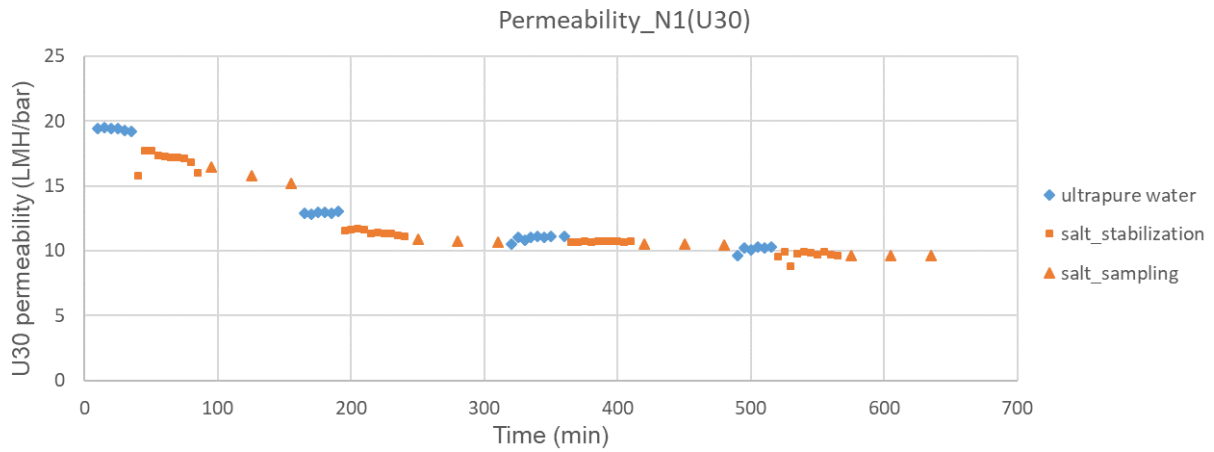
A2. U30 IS=0.0367molL⁻¹

N2 U30 IS=0.0367				
date	operation	permeability(LMH/ bar)	flux(LMH)	data sheet
2018/2/19	UP permeability test	~9.4		up 0
	salt test with only NaCl	~8.28	21.2	N2_1
2018/2/20	up permeability test	~8.3		up 1
	salt test with only Na2SO4	~8.2	20.6	N2_2
	up permeability test	~8.20		up 2
	salt test with NaCl(more) + Na2SO4	~7.60	19.5	N2_3
	Summary			sum N2



A3. U30 IS=0.1molL⁻¹

N1 U30 IS=0.1mol/L					
	date	operation	permeability(LMH/bar)	flux(LMH)	data sheet
	2018/2/13	10min cleaning (0.2%Cl2)			
		UP permeability test 90min	23.8-->20.5		up 0
leave it for one night	2018/2/14	UP permeability test	~19.2		up 0 (2)
		salt test with only NaCl	17.7-->15.2	19.1	N1_1
		up permeability test	~12.9		up 1
		salt test with only Na2SO4	11.6-->10.7	20.3	N1_2
	2018/2/15	up permeability test	~11.1		up 2
		salt test with NaCl(more) + Na2SO4	10.7-->10.4	20.5	N1_3
	2018/2/16	up permeability test	~10.2		up 3
		salt test with only NaCl	9.8-->9.6	20.9	N1_1(2)
		Summary			sum N1



A4. U01 IS=0.0367molL⁻¹

N3 U01 IS=0.0367				
date	operation	permeability(LMH/bar)	flux(LMH)	data sheet
2018/2/13	10 min cleaning with 0.2% Cl2			
2018/2/21	UP permeability test	~9.3		up 0
	salt test with only NaCl	8.5-->7.3	18.3	N3_1
	up permeability test	~6.8		up 1
2018/2/22	salt test with only Na2SO4(pipe explosion, no samples)	~5		N3_2
	10 min cleaning with 0.2% Cl2			
	110min up permeability test	10.5-->9.4		up 0 (2)
2018/2/23	310min up permeability test	8.0-->6.0		up 0 (3)
2018/2/24	salt test with only Na2SO4	5.0-->4.5	12.6	N3_2(2)
	up permeability test	~4.6		up 2
	salt test with NaCl(more) + Na2SO4	4.2-->4.1	11.8	N3_3
	up permeability test	~4.15		up 3
2018/2/26	salt test with only NaCl	4.0-->3.8	10.7	N3_1(2)
	up permeability test	~4.05		up 4
	Summary			sum N2

