

HOW CAKE ENHANCED CONCENTRATION POLARIZATION CAN DECREASE THE MEMBRANE RESISTANCE

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ABSTRACT

Colloidal fouling (cake layer formation) and the related increase in the hydraulic resistance is, besides biofouling, one of the main causes of energetic performance loss in membrane based desalination processes. Although this loss is economically highly relevant, physicochemical mechanisms behind the fouling related increase of hydraulic resistance are still poorly understood. Relevant interactions between simultaneously occurring membrane phenomena like concentration polarization (CP), surface charge screening, and coupled fluxes through membranes are insufficiently investigated. This particularly applies to membranes with only partial salt retention like nanofiltration (NF) or in parts brackish water reverse osmosis (BWRO) membranes as the salt can intrude into and interact with the membrane material which potentially affects mass transfer across the membrane.

One important reason for the knowledge gap is the lack of differentiated experimental methods by means of which contributions of specific types of resistances to the overall resistance could be explicitly determined. The derivation of such relationships is highly complex since the formation of a cake layer, with its associated fouling layer resistance (R_F), also influences the resistance of the concentration polarization layer (R_{CP}) and the resistance of the membrane (R_M) by a variety of potentially unknown coupling mechanisms. Therefore, the measured fouling related increase of the overall hydraulic resistance (OHR) is not necessarily equivalent to R_F but may also be due to co-existing variations of R_{CP} and/or R_M .

Within the performed study a combination of dead-end and cross-flow filtration experiments was applied to achieve a differentiated quantitative assessment of the cake layer related resistance mechanisms. Unexpectedly it was found that the simultaneous determination of R_M , R_F and R_{CP} resulted in an OHR smaller than the sum of the individually measured values although, according to conductivity measurements, the cake obviously increases CP and should thus also increase feed side osmotic pressure. Moreover, dead-end experiments revealed that R_F of a fully consolidated colloidal cake either stays constant or increases with CP. Consequently the most likely explanation for the reduced OHR at simultaneous measurement is a significant decrease in R_M when CP exceeds a certain level as a result of cake formation. However, when changes in CP were induced by performing flux variations, parallel determination of apparent retention showed that the complex salt retention mechanism of the applied NF membrane is largely independent of the membrane fouling status.

KEYWORDS

Nanofiltration, colloidal fouling, hydraulic resistance, solute retention mechanism, cake-enhanced concentration polarization

1. THEORY

Hydraulic resistances in membrane filtration

The hydraulic resistance of any type of water permeable layer is defined as:

$$R = \frac{\Delta p}{\eta_w \cdot J_w} \quad [1-1]$$

in which J_w is the volumetric water flux, η_w the dynamic viscosity of water, and Δp the pressure loss across the layer. Thus, for (partially) salt retaining membranes the hydraulic resistances is given by

$$R_M = \frac{\Delta p_m}{\eta_w \cdot J_w} - R_\pi \quad [1-2]$$

in which Δp_m is the transmembrane pressure difference and R_π is the hydraulic resistance related to the osmotic pressure difference between bulk and permeate ($\Delta\pi$). When the molar solute concentrations of bulk, $c_{s,B}$, and permeate, $c_{s,P}$, are known R_π can be calculated by using van't Hoff's equation for low-concentration solutions. For a single solute feed R_π becomes

$$R_\pi = \frac{\Delta\pi}{\eta_w \cdot J_w} = \frac{(c_{s,B} - c_{s,P}) \cdot RT}{\eta_w \cdot J_w} \quad [1-3]$$

in which R is the universal gas constant and T the thermodynamic temperature.

This approach however, does not consider the effect of concentration polarization (CP) on the solute concentration at the feed side membrane surface, $c_{s,M}$. In case the intrinsic salt retention of the membrane, $\mathfrak{R}_s^{\text{int}}$, is known $c_{s,M}$ can be derived from measured $c_{s,P}$ using

$$c_{s,M} = \frac{c_{s,P}}{1 - \mathfrak{R}_s^{\text{int}}} \quad [1-4]$$

Therewith, the hydraulic resistance of the CP layer of retained solutes becomes

$$R_{CP} = \frac{(c_{s,M} - c_{s,B}) \cdot RT}{\eta \cdot J_w} = \frac{\left(\frac{c_{s,P}}{1 - \mathfrak{R}_s^{\text{int}}} - c_{s,B}\right) \cdot RT}{\eta \cdot J_w} \quad [1-5]$$

When additionally a cake layer is present at the feed side membrane surface, its hydraulic resistance, R_F , has to be considered. With Δp_F being the trans-cake layer pressure difference R_F is given by

$$R_F = \frac{\Delta p_F}{\eta_w \cdot J_w} \quad [1-6]$$

Effect of flux, CP and fouling on membrane solute retention

According to the well-known solution diffusion model (SDM) for decoupled water and salt fluxes $\mathfrak{R}_s^{\text{int,SDM}}$ is

$$\mathfrak{R}_s^{\text{int,SDM}} = 1 / \left(1 + \frac{P_s}{J_w} \right) \quad [1-7]$$

in which P_s is the membranes permeability coefficient for the salt given by

$$P_s = J_{M,s} / (c_{s,M} - c_{s,P}) \quad [1-8]$$

with $J_{M,s}$ as the total salt flux through the membrane. P_s is commonly considered constant and independent of J_w , thus $\mathfrak{R}_s^{\text{int,SDM}}$ necessarily increases with J_w . For coupled water and salt transfer in less dense membranes intrinsic retention, $\mathfrak{R}_s^{\text{int,SDM,co}}$, becomes

$$\mathfrak{R}_s^{\text{int,SDM,co}} = \mathfrak{R}_s^{\text{int,SDM}} \cdot \left(1 - \kappa \cdot \frac{\lambda_s}{\lambda_w} \right) = \mathfrak{R}_s^{\text{int,SDM}} \cdot (1 - \kappa \cdot D^*) \quad [1-9]$$

The coupling coefficient, κ , is assumed to be constant and can have values between 0 and 1. It indicates the ratio of salt velocity to water velocity in the porous part of the membrane where salt is only transported by convection. The partitioning coefficient, λ_i , is defined as the ratio of the concentration of substance “i” in the membrane to its respective concentration at the membrane surface. In case either κ and/or the partitioning ratio, D^* , is dependent on J_w or $c_{s,M}$, a decrease in $\mathfrak{R}_s^{\text{int,SDM,co}}$ is potentially possible also at an increasing flux.

The membranes apparent salt retention for coupled fluxes, $\mathfrak{R}_s^{\text{app,SDM,co}}$, further considers the effect of CP by implementing the CP-coefficient, β , yielding

$$\mathfrak{R}_s^{\text{app,SDM,co}} = 1 - \frac{c_{s,P}}{c_{s,B}} = 1 - \frac{\beta \cdot (P_s + J_w \cdot \kappa \cdot D^*)}{P_s + J_w} = \mathfrak{R}_s^{\text{int,SDM}} \cdot \frac{P_s \cdot (\beta - 1) + \kappa \cdot D^* \cdot \beta \cdot J_w}{P_s + J_w} \quad [1-10]$$

According to film theory β is given by

$$\beta = \frac{c_{s,M} - c_{s,P}}{c_{s,B} - c_{s,P}} = \exp\left(\frac{J_w}{k_s}\right) \quad [1-11]$$

The solute mass transfer coefficient k_s was found to be strongly depending on the fouling situation within the feed flow channel. According to the well-known cake enhanced concentration polarization (CECP) model k_s decreases in presence of a porous cake layer as it hinders back-diffusion of solutes into the bulk phase [1]. At the same time mixing due to viscous shear forces originating from the cross-flow stream is strongly reduced within the cake layer structure. However, other studies imply that CP can also be reduced by cake formation when the cake layer itself retains salt to some extent [2].

2. MATERIAL AND METHODS

Reagents and model foulants

All feed solutions were prepared from deionized tap water (DI), subsequently filtered through a 0.2 μm cartridge filter (Sartopure® 0.2 μm , Sartorius Stedim Biotech GmbH, Goettingen, DE). All added salts are of analytical grade. In cross-flow experiments monodisperse spherical silica particles (Ludox TMA, Sigma Aldrich Co., St. Louis, US) were applied as model foulant. While the manufacturer indicates the particle size with 22 nm, own measurements using Zetasizer Nano ZS (Malvern Instruments Ltd., Worcestershire, UK) revealed a mean particle size of 42 nm and a zeta potential of -50 mV. At 25°C and pH 4.9 particle size as well as zeta potential readings of a 0.5 g/l silica dispersion were stable over extended periods of time (stirred and not stirred) and did not change significantly when the NaCl concentration changes between 0 and 10 g/l. Dead-end fouling experiments were performed using 28 nm and 280 nm monodisperse polystyrene (PS) particle size standards (Bangs Laboratories Inc., Fishers, IN, US) as model foulant. In deionized water the respective dispersion was stable for at least 24 h. No significant effect on dispersion stability was observed when up to 10 g/l NaCl were added. Further DE-experiments were performed by using sodium-alginate (Carl Roth GmbH + Co. KG, Karlsruhe, DE).

Membrane

All experiments were performed using thin film composite membrane DOW™ FILMTEC™ NF270 (Dow Water & Process Solutions, Minneapolis, MN, US). Membrane sheets were taken from a commercially available 2.5" membrane element (NF270-2540). Extracted flat sheets were cut into shape and stored at 4°C in the dark to avoid drying and oxidation. Each experiment is performed using a new membrane sheet, which was stored in 0.2 μm filtered deionized water for at least 24 hours and rinsed thoroughly for 5 minutes from both sides immediately before usage. NF270 is known to have a limited NaCl retention ranging between 15% and 60% depending on the filtration conditions [3]. Before each filtration experiment the applied membrane was compacted and conditioned by filtering 0.2 μm filtered DI until a stable TMP was achieved.

Experimental set-up and procedure

Membrane setup for cross-flow experiments

Cross-flow (CF) filtration experiments were carried out using a custom-made membrane filtration unit (Convergence Industry B.V., Enschede, NL) which is schematically represented in Fig. 1. The fully automated system comprises two identical water recirculation systems, which merge before and separate immediately after the test cell. Each line is connected to an individual feed tank. In long-term operation, retentate and permeate are fully recycled to the respective feed tank in use. The two separate circuits allow a quick change of the feed water source without interruption of the filtration process or mixing of the different quality streams. Feed tanks and permeate line are equipped with conductivity sensors that continuously measure the salinity of the recycled water. Cross-flow velocity as well as permeation rate (flux) are independently controlled by a synchronized adjustment of the feed pump capacity and the dosing valve in the retentate line. All process parameters are constantly monitored and recorded on a variable temporal basis.

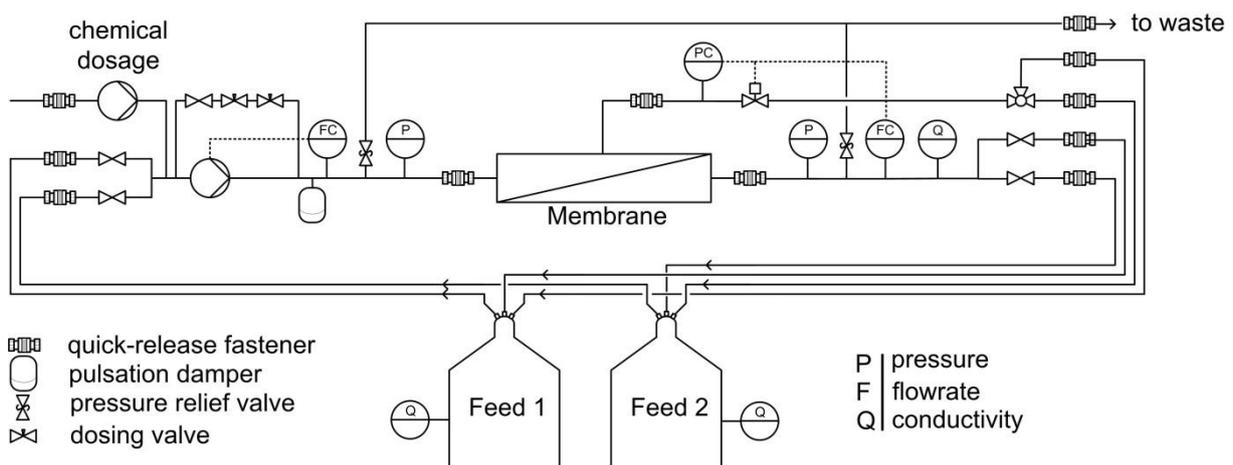


Fig. 1 Schematic diagram of the experimental setup

The applied membrane test cell encloses a cross flow channel of 200 mm x 70 mm x 0.7 mm and an effective membrane area of 140 cm². Massive stainless steel cell design ensures high mechanical stability and stable geometric properties of the flow channel even under changing pressure conditions. In order to achieve a homogeneous flow field within the flow channel no feed spacers were applied within the present study.

Unless specified otherwise, flux was maintained constant at 50 LMH while the cross-flow velocity was adjusted to 22 cm/s. Experiments were performed in an air-conditioned laboratory at a stable ambient temperature of 25°C. All experiments were performed in triplicate repetition to ensure reproducibility.

Cake layer generation in cross-flow mode

Cake layer formation was induced by a simultaneous temporal adaption of flux and ionic composition of the foulant containing feed. For the given experimental setup a relevant fouling rate, represented by steady increase of TMP, was achieved by filtering a 25 mM Ca^{2+} solution containing 0.5 g/l silica particles at an over-critical flux of 80 LMH (fouling conditions). As shown in Fig. 2 a sub-critical flux of 50 LMH was not sufficient to achieve any visible fouling in terms of a fouling related TMP increase. The continuity of the TMP curve, achieved after restoring over-critical flux after an intermediate phase of sub-critical flux, indicates that the generated cake layer remains at the membrane surface also under usual experimental (no fouling) conditions and is not affected or removed by the lateral shear forces occurring at a constant cross flow rate of 22 cm/s. To provide cake layers with similar dimension and morphology all cake layers were built within a fixed time frame of 160 min, during that fouling conditions were applied. No visible agglomeration of silica particle was obtained in the feed tank during cake layer build up.

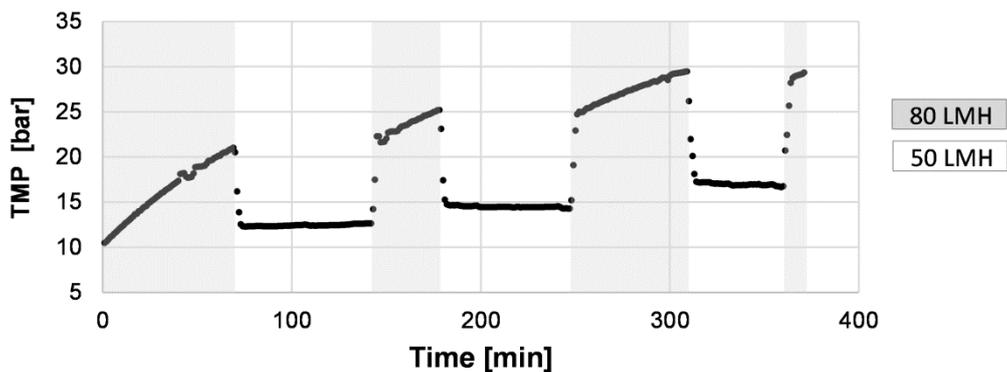


Fig. 2: Development of TMP during cake layer build-up at different applied fluxes. Feed water is 25 mM Ca^{2+} with 0.5 g/l Ludox® TMA colloidal silica particles.

Membrane setup for dead-end experiments

Dead-end (DE) filtration experiments were carried out using a membrane filtration unit comprising a cylindrical DE-filtration cell with an inner diameter of 34 mm and an active membrane area of 9.08 cm^2 . Flux is automatically maintained by a PID controlled micro gear pump coupled online to a coriolis mass-flow meter. Two separate feed tanks allow a change of the feed water source while filtration is in progress. A dosing point for model foulants is located directly upstream of the pressure generating gear pump. A hydrodynamic optimized DE-cell geometry ensures that the foulant mass contained in the feed is uniformly deposited on the membrane surface. A more detailed description of the DE-plant can be found in respective publications [4, 5].

All DE experiments were performed at a constant flux of 50 LMH. Temperature, measured within the filtration cell, was maintained at $25 \pm 0.1^\circ\text{C}$ by using a flow through tempering unit wrapped around the flow cell which was connected to a thermostat.

Cake layer generation in dead-end mode

In DE mode cake layers were generated by injecting a defined amount of foulant directly into the feed water stream. Since the applied foulant was fully retained by the membrane, loading of the membrane could be easily calculated by simple mass balancing and did not change throughout the experiment. A more detailed description of the fouling procedure can be found elsewhere [4, 5].

Differentiated measurement of individual resistances in dead-end and cross-flow mode

Individual filtration conditions are known to be associated with the occurrence of specific types of resistances. An obvious example is the presence of salt in the feed and the generation of a CP layer contributing an associated resistance R_{CP} . When such filtration conditions are selectively changed the respectively measured change in overall hydraulic OHR can be directly attributed to the occurrence of the corresponding type of resistance including coupled processes. Thus, by selectively changing specific filtration conditions, associated types of resistances can be determined singularly or simultaneously by just considering the respective change in total pressure difference Δp_{tot} or OHR. For a layer of type "i" OHR is given by

$$OHR_i = \sum_n R_n = \frac{\Delta p_{tot}}{\eta_w \cdot J_w} \quad [2-1]$$

In present case variability in the filtration conditions was restricted to the presence or absence of a cake layer at the feed side membrane surface and the presence or absence of NaCl in the feed water. All other filtration conditions (flux, CF-velocity, temperature, etc.) were maintained. In Table 1 the relation between the applied filtration conditions, the respectively measured Δp_{tot} and OHR as well as the potentially associated resistances that are contributing to OHR is provided.

Table 1 Resistances contributing to overall hydraulic pressure (OHR) for variable feed salt concentration and fouling status of the membrane. Indices written in parenthesis are indicating the filtration conditions applied during measurement of the respective parameter.

Filtration Conditions		Measured pressure difference	Related measured OHR	Contributing resistances
Feed water	Cake layer			
DI	No	Δp_M	OHR_M	$R_{M(DI)}$
SW	No	$\Delta p_{M,CP}$	$OHR_{M,CP}$	$R_{M(SW)} + R_{\pi} + R_{CP}$
DI	Yes	$\Delta p_{M,F}$	$OHR_{M,F}$	$R_{M(F)} + R_{F(DI)}$
SW	Yes	$\Delta p_{M,CP,F}$	$OHR_{M,CP,F}$	$R_{M(SW,F)} + R_{F(SW)} + R_{\pi(F)} + R_{CP(F)}$

Indices: M = membrane; CP = CP layer; F = cake layer; DI = feed is deionized water; SW = feed is salt water; parameters provided in parenthesis indicate presence during measurement

When the respective OHR values are measured at steady-state conditions specific relations between the contributing resistances exists that are depending on the applied filtration mode (DE or CF). These relations can be utilized for further interpretation of the results. Further on the high index “•” is used to indicate steady-state conditions established in DE-mode while high index “x” refers to CF-mode.

Cross-flow filtration mode

In CF filtration mode $c_{s,p}$ freely changes with CP and therefore provides a well accessible measure for the extent of CP in the system. Assuming $R_{M(DI)} \approx R_{M(SW)}$, R_{CP}^x can be easily obtained by a simple subtraction operation from measured OHR values like:

$$R_{CP}^x = OHR_{M,CP}^x - OHR_M^x - R_\pi \quad [2-2]$$

Inserting into [1-5] and solving for \mathfrak{R}_s^{int} yields:

$$\mathfrak{R}_s^{int} = 1 - c_{s,p} / \left(\frac{\eta_w J_w (OHR_{M,CP}^x - OHR_M^x - R_\pi)}{RT} + c_{s,B} \right) \quad [2-3]$$

As for applied NaCl solutions the concentration-conductivity relationship was found to be linear over the range of ionic strengths used, $c_{s,p}$ and $c_{s,B}$ can be easily obtained by conductivity measurement. Providing validity of van't Hoff's equation R_π can be calculated using [1-3].

If \mathfrak{R}_s^{int} is an intrinsic property of the membrane, it should not change in presence of a cake layer. Thus, $R_{CP,F}^x$ can be anticipated from [1-5] by inserting \mathfrak{R}_s^{int} measured with no cake layer present at the membrane surface together with $c_{s,p}^x$ determined when a cake layer is present at the membrane surface.

Dead-end filtration mode

In DE filtration mode retained salt ions continuously concentrate at the feed side membrane surface. According to equations [1-4] and [1-8] the related increase in $c_{s,M}$ leads to an increase in $c_{s,p}$ and $J_{M,s}$ respectively. The enrichment process proceeds until $c_{s,M}$ either reaches the solubility limit and salt starts precipitating or it approaches an equilibrium concentration, $c_{s,M}^\bullet$, where $J_{M,s}$ is equivalent to the feed salt flux $J_{F,s}$ and $c_{s,B}$ equals $c_{s,p}$. Any further, e.g. fouling related, increase of $c_{s,M}^\bullet$ would automatically increase $J_{M,s}$ by enhancing diffusive salt transport through the membrane, thus leading to the physically impossible condition $J_{M,s} > J_{F,s}$.

Because $J_{F,s} \sim J_w$ the equilibrium state $J_{M,s}$ is strictly proportional to J_w . Thus, at constant $c_{s,B}$ and J_w , $c_{s,M}^*$ represents a limiting concentration that depends on the specific retention mechanism of the applied membrane.

Considering $\mathfrak{R}_s^{\text{int}}$ as depending on $c_{s,M}$ but as independent of the presence of any cake layer at the membrane surface, for a fouling independent $c_{s,M}^*$, limiting CP layer resistance R_{CP}^* is always (for all fouling conditions) correctly determined by

$$R_{CP}^* = R_{CP(F)}^* = \frac{(c_{s,M}^* - c_{s,P}^*) \cdot RT}{\eta_w \cdot J_w} = \frac{(c_{s,M}^* - c_{s,B}^*) \cdot RT}{\eta_w \cdot J_w}. \quad [2-4]$$

By further considering $R_{M(SW)}^* \approx R_{M(SW,F)}^*$ as well as the validity of van't Hoff's equation, $R_{F(SW)}^*$ can be determined by simple pressure measurements yielding

$$R_{F(SW)}^* = OHR_{M,CP,F}^* - OHR_{M,CP}^*. \quad [2-5]$$

Considering R_M as a function of ionic strength, assumption $R_{M(SW)}^* \approx R_{M(SW,F)}^*$ seems plausible as in DE steady-state the water matrix at the membrane surface is not affected by cake formation.

To avoid precipitation in DE-filtration experiments $c_{s,B}$ has to be adjusted to the applicable J_w and $\mathfrak{R}_s^{\text{int}}$ of the applied type of membrane. Obviously, due to their lower salt retention, NF membranes are more suitable for carrying out this kind of DE experiments.

3. RESULTS AND DISCUSSION

Cross-flow experiments

Following the experimental concept described in the previous chapter CF filtration experiments were performed at a constant flux of 50, 80 and 110 LMH. In Fig. 3 the sum of the separately determined resistances R_F^x , R_M^x , R_{CP}^x , and R_τ^x is compared to the result of a simultaneous measurement of the respective parameters ($OHR_{M,CP,F}^x$). In each of the depicted cases the simultaneously measured resistance is lower than the sum of the individual measured ones. This unexpected finding contradicts existing model theory, according to which the CECP should increase R_{CP}^x , and therefore OHR, in presence of a cake layer.

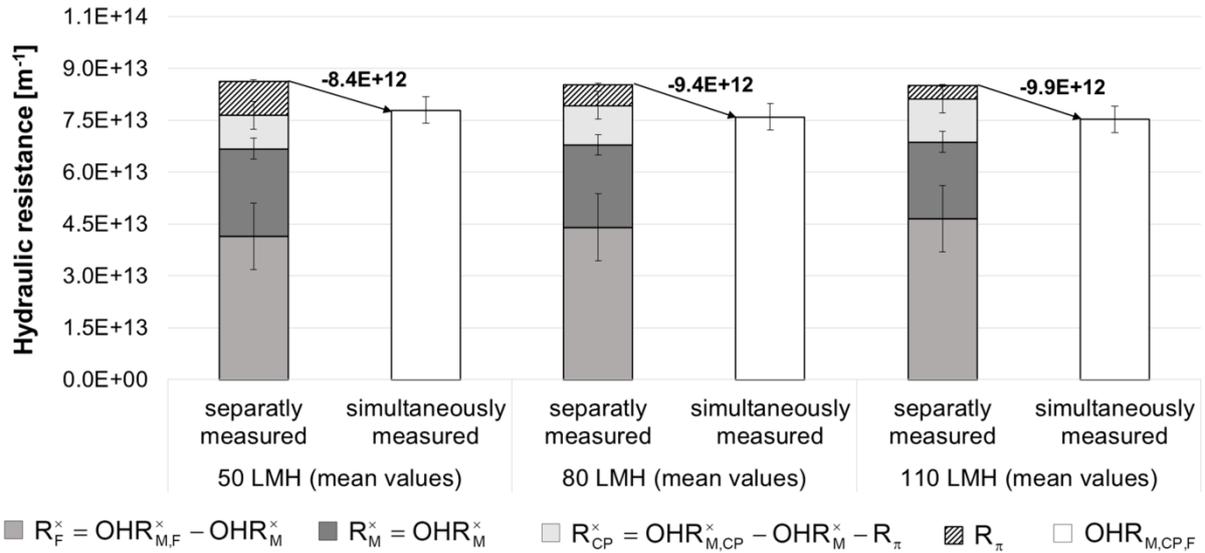


Fig. 3: Comparison of steady-state resistances measured separately or simultaneously for three different fluxes. Filtration parameters: feed salt content 5 g NaCl /l, cross flow velocity 22 cm/s, temperature 25°C.

In order to further assess this finding, flux dependency of salt retention and measured pressure difference are considered separately. Based on measured feed and permeate salt concentrations it was found that $\mathfrak{R}_{NaCl}^{app,SDM}$ of the applied membrane NF270 decreases with flux by a constant rate of -0.06% / LMH as shown in Fig. 4 (left). As according to [1-11] CP-coefficient β increases with increasing flux J_w , determined reduction of $\mathfrak{R}_{NaCl}^{app}$ is in accordance with [1-10] while contribution of other potentially flux dependent parameters like κ , D^* and P_s is generally possible.

A strong increase in CP, potentially caused by CECP, might also be the reason for the significant decrease in $\mathfrak{R}_{NaCl}^{app}$ that is associated with the formation of a cake layer at the membrane surface. Moreover, nearly identical flux dependencies (-0.06% / LMH) for virgin and fouled membranes suggest that the relevant mechanisms of salt retention are largely independent of the fouling state of the membrane as well as of the associated change in $c_{s,M}$. In this case it is likely to assume that D^* and P_s are intrinsic constants of the applied type of NF membrane and $\mathfrak{R}_s^{int,SDM,co}$ is only depending on κ .

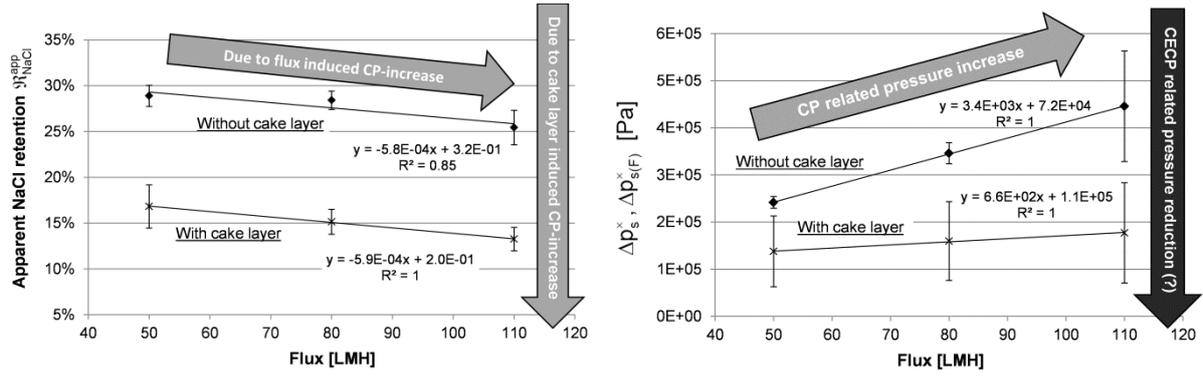


Fig. 4: Influence of flux and presence of a cake layer development on apparent NaCl retention and trans-membrane osmotic pressure of membrane NF270. Filtration parameters: feed salt content 5 g NaCl/l, cross flow velocity 22 cm/s, temperature 25°C.

In contrast to $\mathfrak{R}_{\text{NaCl}}^{\text{app}}$, Fig. 4 (right) shows that salt related pressure difference Δp_s^x , with $\Delta p_s^x = \Delta p_{\text{M,CP}}^x - \Delta p_{\text{M}}^x$, or $\Delta p_{\text{s(F)}}^x = \Delta p_{\text{M,CP,F}}^x - \Delta p_{\text{M,F}}^x$ respectively, increases with flux, whereas the rate of increase seems to be lower in case of the presence of a cake layer. This finding can also be explained by flux depended CP whereas Δp_s^x increases with R_{CP}^x . This, however, implies that a further increase of CP due to a potential CECP effect, as it was postulated from the interpretation of retention data, should result in an additional increase of Δp_s^x . Instead Fig. 4 shows that Δp_s^x is actually lower in presence of a cake layer.

This contradiction becomes even more evident when measured pressure differences are combined with concentration data for the determination of $\mathfrak{R}_{\text{NaCl}}^{\text{int}}$ using [2-3] and assuming $R_{\text{M(DI)}} \approx R_{\text{M(SW)}}$. Results depicted in Fig. 5 show that, in case no cake layer is present at the membrane surface, $\mathfrak{R}_{\text{NaCl}}^{\text{int}}$ increases with J_w . This development is in agreement with equation [1-7], thus showing that, in likely case of coupled water and salt transport in NF membranes (cf. [1-9]), D^* , κ , and P_s are either constant, or their dependency on J_w is of such kind that the combined effect is contributing to a general positive dependency between J_w and $\mathfrak{R}_{\text{NaCl}}^{\text{int}}$. Considering $\mathfrak{R}_s^{\text{int}}$ as a constant property of the membrane, $R_{\text{CP,F}}^x$ can be anticipated from [1-5] by inserting $\mathfrak{R}_s^{\text{int}}$, measured with a clean membrane, together with $c_{\text{s,P}}$ determined when a cake layer is present at the membrane surface. Results, provided in Fig. 5 (right), show that anticipated $R_{\text{CP,F}}^x$ strongly increases in presence of a cake layer. This finding is inconsistent with previously reported results, according to which OHR significantly reduces when contributing resistances occur simultaneously. Thus, considering $R_{\text{CP(F)}}^x > R_{\text{CP}}^x$ as proven by conductivity measurements, the only possible explanation for reduced OHR in simultaneous measurement is that the cake related increase in R_{CP}^x is overcompensated by a concurrent reduction of R_{F}^x and/or R_{M}^x , whereas $R_{\text{F(SW)}}^x < R_{\text{F(DI)}}^x$ and/or $R_{\text{M}}^x < R_{\text{M(CP,F)}}^x$ applies.

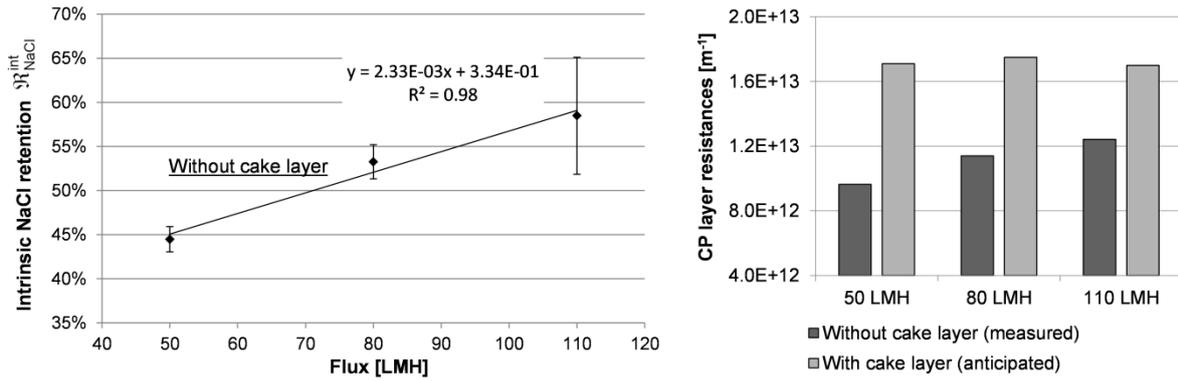


Fig. 5: Influence of flux changes on intrinsic NaCl retention of membrane NF270 and related hydraulic resistance of the CP layer for different fouling status. Filtration parameters: feed salt content 5 g NaCl/l, cross flow velocity 22 cm/s, temperature 25°C.

Dead-end experiments

By using the DE-measuring approach described in chapter 2 it can be determined how R_F reacts to changes in the feed water composition and the associated change in CP. In Fig. 6 steady-state hydraulic resistances of different types of colloidal cake layers are shown. All cake layers were formed in 0.2 μm filtered deionized water (DI) until steady-state was achieved. Then feed was changed to 4 g NaCl / l and the associated change in R_F^* was registered. In each of the depicted cases determined R_F^* is increased when NaCl is present in the feed water. This effect is particularly high for cake layers solely composed of small (28 nm) polystyrene (PS) particles or layers containing alginate. In case of alginate, it is possible that this effect is caused by a material specific molecular mechanism that transfers the alginate molecule in presence of NaCl into a condensed form of higher hydraulic resistance [6]. In case of PS, however, particle shape will not change in presence of NaCl. Therefore, the obtained resistance increase must be caused either by a change in layer porosity or the applied DE-measuring approach is corrupted by an unknown cake related effect, other than CECP, causing $R_{CP(F)}^* > R_{CP}^*$.

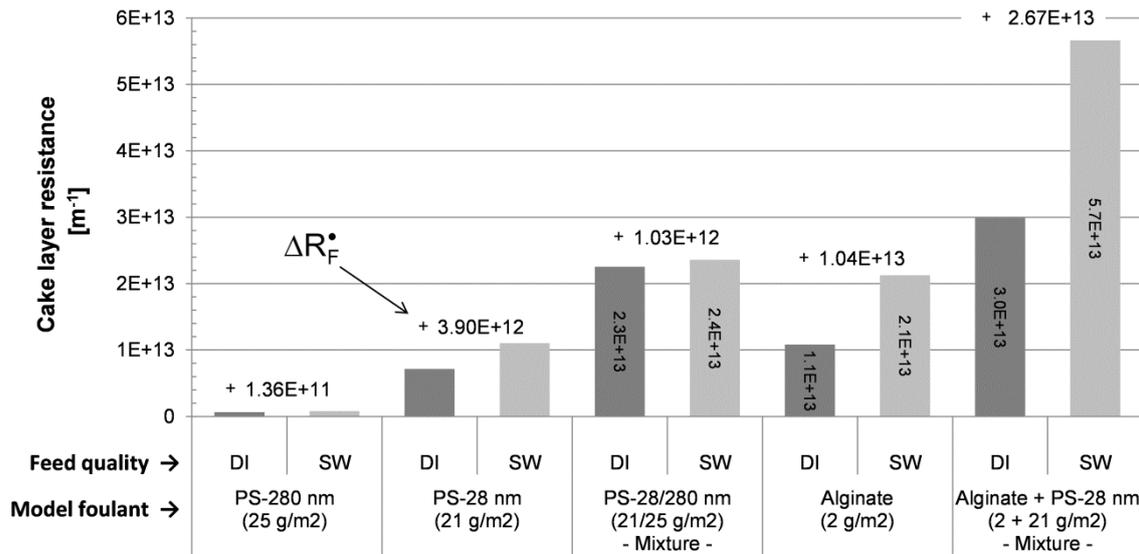


Fig. 6 Effect of feed water quality on the hydraulic resistance of cake layers formed in 0.2 μm filtered deionized water from different size polystyrene particles (PS) and alginate. Deionized water (DI) contains no salt or fouling particles, salt water (SW) contains 4 g NaCl / l. Filtration parameters: flux 50 LMH, temperature 25°C

Since the effect of NaCl addition on R_F^* was found to be completely reversible, a causative change in layer porosity is rather unlikely as a complete restoration of the resistance determining layer morphology after a change in NaCl concentration appears implausible. A potential mechanisms explaining $R_{CP(F)}^* > R_{CP}^*$ is based on partial clogging (inactivation) of the membrane surface by the initially deposited colloidal particles, which are in direct contact with the membrane surface [5]. By that effect J_w is locally increased even if the volumetric flow rate of the feed remains constant. Thus, when salt is present in the feed water $c_{s,M}^*$ and related $R_{CP,F}^*$ increase proportional to J_w while the resistance of the readily developed cake layer R_F^* remains constant. In case of 28 nm PS the measured reversible effect of ionic strength on R_F^* can be quantitatively explained by this mechanism when inactivation rates of $\sim 10\%$ of the effective membrane area are assumed [5].

However, the effect of ionic strength on R_F^* is considerably more significant when the feed salt content is changed during the cake formation phase. In Fig. 7 the development of R_F^* is provided for different membrane loading status. Loading with 28 nm PS particles was carried out with and without NaCl present in the feed by the stepwise addition of identical amounts of PS to the feed. A new loading step was started after steady-state was achieved. In both depicted cases linear dependency between loading and R_F^* implies a Darcy-type resistance mechanism. Moreover, results show that the extent of R_F^* is strongly depending on the ionic strength of the feed prevailing during layer formation. In contrast, a change in water quality performed after the cake layer formation is completed has significantly less effect on

the level of R_F^\bullet . Therefore, two different mechanisms can be distinguished: A strong irreversible mechanism that determines R_F^\bullet while the cake layer is formed and a minor reversible mechanism, which appears to be independent of initial R_F^\bullet . While a possible explanation for the reversible effect was presented earlier, the irreversible effect on R_F^\bullet might be due to changes in the cake layer morphology, taking place during the dynamic cake formation phase in which the cake layer exists in a semi-fluidic condition [5]. It is likely to assume that during that consolidation phase the cake layer adapts to shear forces originating from the permeating fluid by adopting a hydrodynamic favorable configuration. As ionic shielding of electrostatic repulsion forces will increase adhesion probability between particles, reorganization of particles in the cake layer is less probable at higher ionic strength. Thus, it is concluded that the dynamic adaption process that leads to the formation of a hydrodynamic optimized layer morphology is less pronounced when salt is present in the feed. Consequently resulting R_F^\bullet is increased.

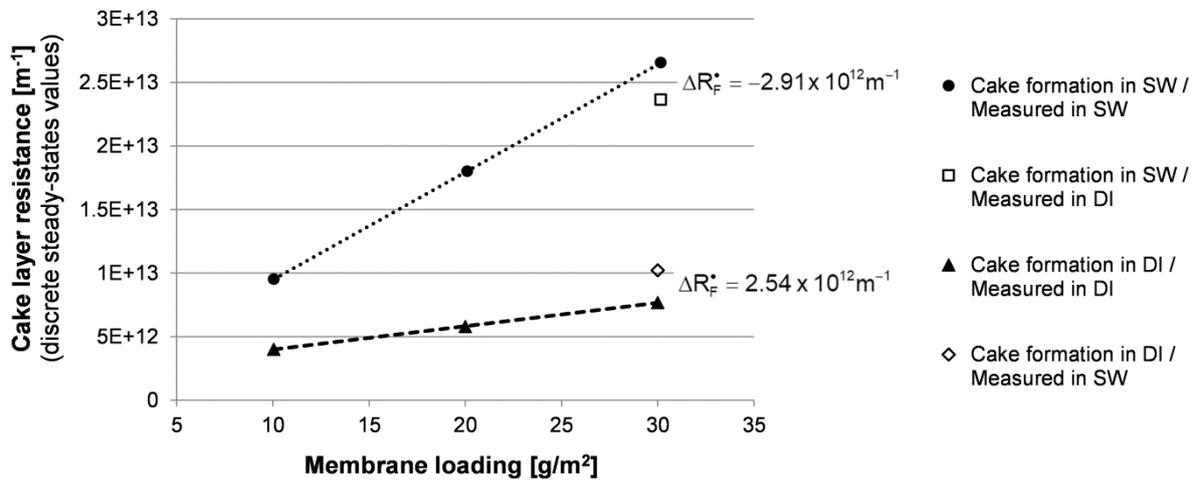


Fig. 7 Influence of ionic strength on the equilibrium resistance of cake layers composed of 28 nm PS particles. Deionized water (DI) contains no salt or fouling particles, salt water (SW) contains 4 g NaCl / l. Filtration parameters: flux 50 LMH, temperature 25°C

Conclusions

By performing cross-flow experiments it could be shown that $R_{CP(F)}^x > R_{CP}^x$. In parallel $R_{\pi(F)}^x < R_{\pi}^x$ was observed, whereas a quantitative comparison of the respective changes in resistances revealed $(R_{CP(F)}^x - R_{CP}^x) > (R_{\pi}^x - R_{\pi(F)}^x)$. Moreover, when considered cake layers are formed and consolidated from rigid spherical colloids in an identical ionic strength environment $R_{F(SW)}^\bullet \geq R_{F(DI)}^\bullet$ was demonstrated by DE-experiments. Both results suggest that measured $OHR_{M,CP,F}$ should be higher than the sum of the contributing resistances obtained in individual measurement. This conclusion, however, does not correspond to the experimental observation depicted in Fig. 3. Thus, the only explanation for the determined reduction of OHR, in case of

simultaneous measurement, can be a significant reduction of R_M^x in presence of a cake layer that overcompensates the predicted increase of R_{CP}^x .

4. REFERENCES

- [1] E.M.V. Hoek, M. Elimelech, Cake-enhanced concentration polarization: A new fouling mechanism for salt-rejecting membranes, *Environmental Science & Technology*, 37 (2003) 5581-5588.
- [2] S. Kim, S. Lee, E. Lee, S. Sarper, C.H. Kim, J. Cho, Enhanced or reduced concentration polarization by membrane fouling in seawater reverse osmosis (SWRO) processes, *Desalination*, 247 (2009) 162-168.
- [3] J. Wang, Y. Mo, S. Mahendra, E.M.V. Hoek, Effects of water chemistry on structure and performance of polyamide composite membranes, *Journal of Membrane Science*, 452 (2014) 415-425.
- [4] M. Keller, S. Panglisch, R. Gimbel, Measuring hydraulic layer resistance and correlated effects in colloidal fouling of salt-retaining membranes, *Water Science and Technology: Water Supply*, 17 (2017) 985 - 997.
- [5] M. Keller, Zur Bedeutung hydraulisch bedingter Deckschichtwiderstände beim Fouling salzrückhaltender Membranen unter besonderer Berücksichtigung von Kopplungseffekten, in: Fakultät für Ingenieurwissenschaften, Abteilung Maschinenbau und Verfahrenstechnik, Universität Duisburg-Essen, Duisburg, 2016.
- [6] X. Jin, X. Huang, E.M.V. Hoek, Role of specific ion interactions in seawater RO membrane fouling by alginic acid, *Environmental Science and Technology*, 43 (2009) 3580-3587.

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