Accumulation of $GdCl_3$ in the feed of a reverse osmosis system during desalination as determined by neutron absorption

D. Schwahn[1] , V. Pipich[2], R. Kasher[3], and Y. Oren[3]

[1] Technische Universität München, Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II), D-85748 Garching, Germany.
[2] Jülich Centre for Neutron Science JCNS-FRM II, Outstation at FRM II, D-85747 Garching, Germany.
[3] Zuckerberg Institute for Water Research, Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sede Boqer Campus 84990, Israel.

E-mail: d.schwahn@fz-juelich.de, yoramo@bgu.ac.il

Abstract. This article deals with the application of *in-situ* small-angle neutron scattering to investigate wastewater desalination by reverse osmosis. In a first series of experiments we take advantage of the strong neutron absorption of gadolinium (Gd) and use 0.50 g/L $GdCl_3$ in the feed as an indicator for concentration polarization and scaling at the membrane surface. The continuous decline of scattering during the process of desalination indicates an increase of $GdCl_3$ salt concentration which after 15 hours has achieved nearly 100% enhancement with respect to its initial concentration.

1. Introduction

It is well known that the availability of potable water is a serious worldwide problem. There is large effort to further develop technology and to install plants in order to produce potable water from seawater and reclaimed wastewater [1]. An increasing number of desalination plants using reverse osmosis (RO) and nanofiltration (NF) technologies accomplish the strong demand for potable water particularly in arid areas [2]. For those countries that are remote from the sea, recycling of impaired water such as municipal wastewater to a level of unlimited application is a reasonable solution as is done today in several locations. Membrane-based technologies play an essential role in these respects. An ensemble of RO membranes in an operating plant is shown from the photos in Figure 1. Such a plant produces of the order of 500,000 m^3 potable water per day.

A serious problem in RO/NF desalination of municipal wastewater is biofouling and scaling at the membranes, limiting the membrane efficiency and lifetime [3, 4]. Calcium phosphate and organic matter were observed to accumulate on RO-membranes, suggesting that nanoparticles or smaller colloids pass through microfiltration and ultrafiltration membranes, ending up on RO-membranes as a cake-layer fouling [5]. Calcium phosphate scaling in municipal wastewater treatment systems is a severe problem as no efficient antiscalants are currently available [6]. In this respect, scaling is associated to bio-mineralization [7] as biomolecules such as proteins and polysaccharides play an important role in this process . The importance of the interactions of biomolecules and inorganic salts in water treatment processes was shown in recent small-angle neutron scattering (SANS) experiments

by the authors [8-10]. It was shown that bio-organic molecules strongly influence mineralization in a model synthetic salt solution. Proteins such as BSA and lysozyme added to a synthetic salt solution

Figure 1. Views of a desalination reverse osmosis plant such as the Ashkelon Desalination Plant in Israel showing stacks of RO-membranes. Such a plant produces of the order of 500,000 m^3 potable water per day.

induced within a few seconds strong precipitation of nearly μm large composite particles composed of organic components as well as calcium phosphate and carbonate, observed by the variation of scattering contrast of the aqueous solution. In another SANS study, gold-nanoparticles were used as templates for studying surface mineralization in the same model solution; it was found that BSA coated gold nanoparticles induces fast formation of precipitates of 0.2 μm size that are composed of 50% - 80% volume fraction of minerals, identified as calcium phosphate and calcium carbonate [9].

This article deals with *in-situ* SANS studies on the accumulation of Gd^{3+} on the membrane surface. This may be caused together with the other salts of the feed by concentration polarization followed by precipitation at the surface of thin film composite (TFC) RO/NF membranes. A special flow-cell was built for these experiments simulating under most realistic conditions as reported in more detail in [11]. In this manuscript we introduce a technique utilizing the strong neutron absorption cross-section of $GdCl_3$ added as an indicator to the synthetic salt solution.

2. Theoretical and experimental background

Gadolinium is a rare-earth element with a strong neutron absorption cross-section as tabulated in [12]. We utilize this property in order to sensitively detect small amounts of Gadolinium (III) chloride ($GdCl_3$) dissolved in a model salt solution simulating a secondary effluent (SSE). The SSE solution represents an aqueous solution for the mineral components of a secondary-treated domestic wastewater in desalination with 80 - 85% recovery of a Shafdan prospective desalination plant in Israel [13].

The corresponding relevant parameters of $GdCl_3$ are compiled in Table 1. The total macroscopic cross-section Σ_{abs} of $GdCl_3$ of thickness D_S determines its absorption neutron transmission T_{abs} according to

$$T_{abs} = \exp\{-\Sigma_{abs} D_s\}. \qquad (1)$$

A general discussion on neutron transmission is found in ref [14]. We added $GdCl_3$ to the SSE solution which corresponds to a volume fraction of $\Phi = 1.1\times10^{-4}$, which according to Eq.(1) corresponds to

Molecule	Molar mass	Mass density	Molar volume	σ_{abs} (λ=1.789Å)	Σ_{abs} (λ=12.8 Å)
Gadolinium (III) chloride	263.61 g/mol	4.52 g/cm^3	58.32 cm^3/mol	49.8×10^3 barn	3.68×10^3 cm^{-1}

Table 1. Neutron relevant parameters of gadolinium (III) chloride ($GdCl_3$)

a transmission of $T_{abs} \cong 0.945$ considering the thickness of $D_s \cong 0.14$ cm of the feed and membrane in the cell. The absorption cross-section is determined as $\Sigma_{abs} = \Phi_{GdCl_3} \times \Sigma_{GdCl_3}$ .Considering the system parameters the volume fraction Φ_{GdCl_3} of $GdCl_3$ is determined according to

$$\Phi_{GdCl_3} = -\ln(T_{abs})/(D_S \Sigma_{abs}) = -1.94\times10^{-3}\times\ln(T_{abs}). \quad (2)$$

The experiments were performed at the VSANS diffractometer KWS3 at the FRM II of the Technical University Munich (TUM) in Garching (Germany) using a specially designed flow-cell [11]. The membrane was a RO thin film composite membrane (TFC) XLE-440 of 140 µm thickness from Dow Filmtech (Minneapolis, MN, USA). Typically, TFC RO-membranes are composed of three layers. An aromatic polyamide layer of 100 to 250 nm thickness is on top of a ~ 40 µm thick micro porous polysulfone layer, both are supported by a third layer – either polypropylene or polyester – consisting of a ~ 100 µm thick non-woven fabric.

Figures 2a to c show views of the cell. Figure 2a shows the feed side of the cell. The lower

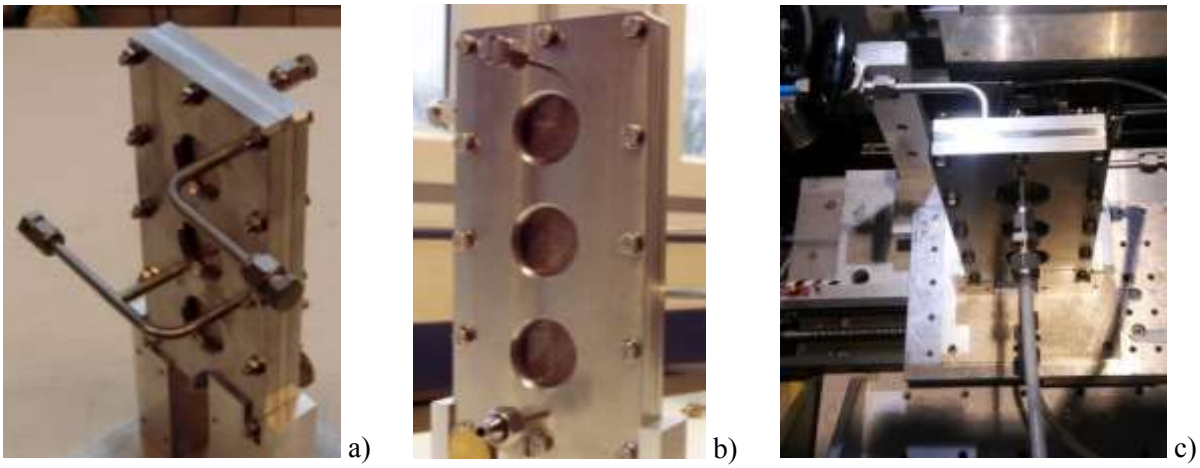

Figure 2. RO flow-cell for SANS at the (a) feed and (b) permeate side. Figure 2c shows the cell at the sample position of KWS 3. Three sapphire windows of 3 cm diameter are designed for neutrons in order to measure the membrane at three different distances from the inlet of the feed.

and upper capillary tubes are inlet for the feed (i.e. the SSE solution) and outlet for the concentrate (i.e. the concentrated feed), respectively. Figure 2b shows the permeate side with the lower capillary tube as the outlet for the cleaned water which usually has the quality of potable water. The potable water was weighted by a balance as a function of time in order to determine the permeability of the membrane in parallel to the neutron experiment. Figure 2c shows the flow-cell in operation at the sample position of the VSANS instrument KWS3.

3. Experimental Results

The upper Figure 3 shows the time evolution of neutron transmission of the cell during the process of desalination, i.e. of the SSE feed, the TFC membrane and spacer, measured at 6 bar for nearly 20 hours. The permeability and permeate flux measured in parallel are depicted in the lower Figure 3. The SSE feed was prepared on basis of 40% and 60% volume fractions of D_2O and H_2O, respectively, in order to minimize scattering from the membrane. The cavities of the polysulfone and polyester membrane layers are matched under these circumstances, i.e. they do not contribute to scattering [11]. Besides the added salts we added 0.50 g/L $GdCl_3$ to the SSE feed as already mentioned.

An overall decline of permeate flux by more than a factor of 2 is observed which is accompanied by a continuous decrease of neutron transmission. A surprising observation was made after about 10 hours when a minimum of transmission is accompanied by a small hump of permeate flux. Such a

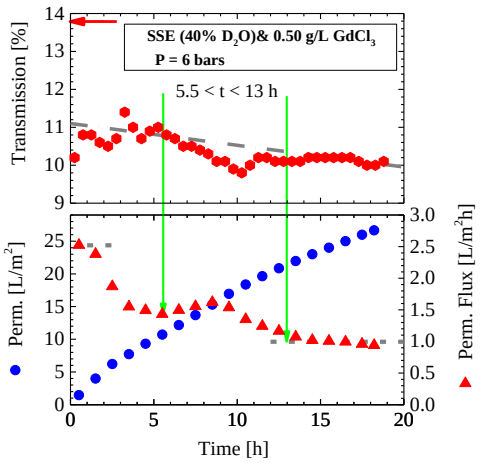

Figure 3. Neutron transmission and permeate flux during RO desalination of a SSE salt solution added with 0.50 g/L of $GdCl_3$.

phenomenon was also observed in a similar experimental without $GdCl_3$ and was interpreted as partial cleaning of the membrane from larger mineral entities [11]. The red arrow in the upper figure represents the transmission coefficient at ambient pressure measured just before starting the RO desalination. Scattering patterns measured at ambient pressure are systematically weaker. The larger intensity, i.e. lower transmission at 6 bar stems from the elasticity of the membrane in particular from the polyester non-woven fabric with its large volume fraction of about 70% [11]. Pressure induced compression of the polyester layer leads to a decline of cavity volume fraction. A decline from 70% down to 50% leads to an enhanced scattering as seen from the prefactor of $d\Sigma/d\Omega(0)$ below in Eq.(4). This effect is quantitatively outlined in ref [11]. The scattering of the new membrane at ambient pressure was always taken as the reference for the 6 bar measurements we will discuss now.

Figure 4a shows scattering patterns measured at the given times during the desalination experiment already presented in context with the transmission data in Figure 3. The scattering data were measured in the Q regime of 10^{-4} $Å^{-1}$ and represent the enhancement of $d\Sigma/d\Omega(Q)$ with respect to the scattering at ambient pressure just before starting the 6 bar experiments. The difference of enhanced scattering, $\Delta d\Sigma/d\Omega(Q)$, was fitted with the Beaucage equation in Eq.(3) function as depicted by the solid lines. Eq.(3) is a function of

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{d\Sigma}{d\Omega}(0)\,\exp(-u^2/3) + P_\alpha\left[\left(\mathrm{erf}\left(u/\sqrt{6}\right)\right)^3/Q\right]^\alpha \qquad (3)$$

the parameter u which is the product of momentum transfer Q and radius of gyration R_g. The momentum transfer is defined according to $Q=(4\pi/\lambda)\sin(\delta/2)$ from the neutron wave length λ and the scattering angle δ. Beaucage's equation represents an approximated scattering law [15]. At small

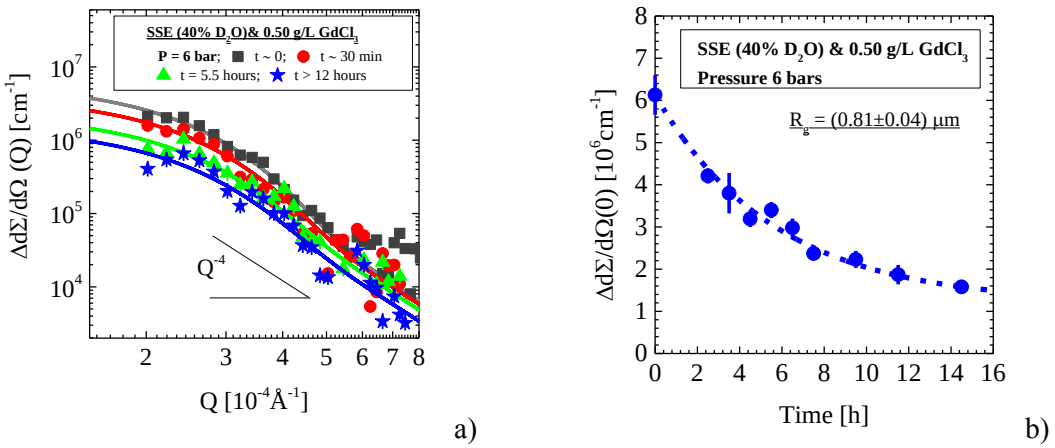

Figure 4. a) Enhanced scattering due to applied pressure which reduces during desalination because of accumulation of $GdCl_3$ concentration in the feed. b) Decline of $d\Sigma/d\Omega(0)$ versus time as derived from fitting scattering law delivering a constant R_g of 0.81±0.04 μm.

Q (< $1/R_g$) the macroscopic cross-section $d\Sigma/d\Omega$ is determined by the first term of Eq.(3) corresponding to Guinier's approximation, whereas at larger Q (> $1/R_g$) the scattering usually follows a power law. In many cases one finds a Porod law with an exponent of α=4 valid for 3 dimensional particles with a smooth surface. The parameters $d\Sigma/d\Omega(0)$ and P_4 are expressed as

$$\frac{d\Sigma}{d\Omega}(Q=0)=\Phi_P(1-\Phi_P)V_P\left[\rho_P-\rho_S\right]^2 \text{ and } P_4=2\pi N_P S_P\left[\rho_P-\rho_S\right]^2 \qquad (4)$$

Both parameters deliver quantitative structural description of the objects such as mean particle number density N_P, surface S_P, volume V_P, and volume fraction Φ_P [16].

The analysis of the scattering curves in Figure 4a deliver over the time interval a constant radius of gyration R_g of 0.81 μm whereas the enhanced extrapolated scattering cross-section at Q=0, $\Delta d\Sigma/d\Omega(0)$, is declining with time as depicted in Figure 4b. $\Delta d\Sigma/d\Omega(0)$ is following an exponential decline depicted as dashed line as guide for the eye. The constant R_g supports our interpretation that the decline of scattered intensity is due to accumulation of $GdCl_3$ concentration in the feed in front of or at the membrane.

The transmission due to $GdCl_3$ accumulation is evaluated from the ratio of $d\Sigma/d\Omega(0)$ of SSE with and without $GdCl_3$ showing values in the interval from 0.97 to 0.90 as depicted in the upper Figure 5. The change of transmission due to accumulation of $GdCl_3$ in the feed is 7%. Such decline of transmission is not visible in the transmission of the total system which is around 10% thereby inducing a change of only 0.7% over 18 hours. Such change of T is visualized as grey dashed-dotted line in the upper Figure 3.

The volume fraction Φ of $GdCl_3$ is derived from the transmission on basis of Eq.(2) and is plotted as weighted fraction w_{GdCl3} in the lower Figure 5. At the beginning of the desalination process the concentration of $GdCl_3$ is with 0.3 g/L fairly well in agreement with the initially weighted one of 0.5 g/L and approaches a value of about 0.88 g/L after about 14 hours of desalination. This enhancement

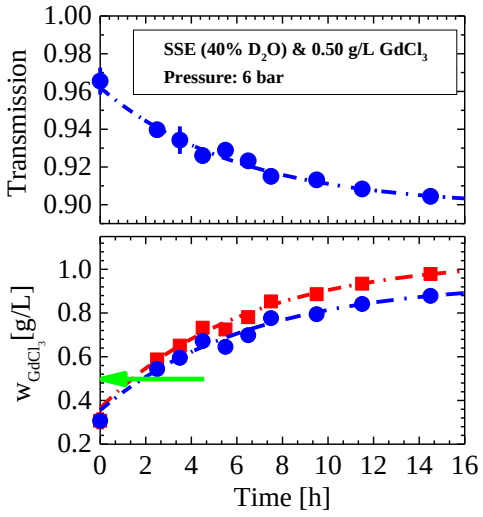

Figure 5. Decline of transmission derived from scattering and the corresponding concentration of $GdCl_3$ versus time (blue symbols). The red symbols show the corrected concentration of $GdCl_3$ in case of a factor 2 increase of scattering due to scaling. The green arrow shows the initially weighted concentration of $GdCl_3$.

corresponds to an increase of about 80% of $GdCl_3$ concentration with respect to the initial value The decay of transmission and the corresponding increase of $GdCl_3$ concentration follow an exponential behavior with a time constant of nearly 6 hours. This statement has only phenomenological character as there is no theoretical basis known at present and is mending as a guide for the eye.

In the analysis so far we assumed that the scattering in Figure 4a is declining only by enhancement of $GdCl_3$ salt. However, from former similar studies in [11] without the strong neutron absorbing salt we know that there is developing enhanced scattering by about a factor of 2 due to scaling and possibly other effects such as concentration polarization. This means that our analysis might underestimate the degree of accumulated $GdCl_3$ content. Assuming enhanced scattering by a factor of 2 over the total time due to scaling mean a slightly larger salt concentration of about 100% $GdCl_3$.

4. Conclusion

We present here one aspect of a larger project on SANS studies on scaling and fouling of RO membranes during desalination. SANS is a new and promising tool in this field as it allows *in-operando* experiments following the process of mineralization on a level of microscopic length scale and distinguishes between inorganic and organic molecules via contrast variation. Results of this work have already been reported in [8-10]. The present experiments are difficult to interpret as neutrons have to pass through several sections of the cell such as feed and the three layers of the membrane. We have to find experimental as well measuring techniques to separate and identify scattering from the different sources. One possible procedure is demonstrated in the present article, namely the determination of the amount of $GdCl_3$ being dissolved together with other salts in the feed forming a concentrated salt solution layer in front of the membrane (concentration polarization) and mineral particles forming a scaling layer at the surface of the membrane. However, from the present experiment we only know the average concentration of $GdCl_3$ at the feed side of the flow-cell. A determination of the amount of $GdCl_3$ of the scaling layer at the surface of the membrane is possible after finishing the desalination experiment and performing the measurement after filling the cell with fresh salt-free water. Another effect needs precaution, namely the enhancement of scattering from the membrane due to scaling. This effect appears much weaker as we have seen from the data in Figure 4b and 5 and can be made even more negligible by slightly increasing the $GdCl_3$ salt concentration.

Acknowledgement
We would like to thank Thomas Starc from Forschungszentrum Jülich for his engaged preparation and participation of the neutron experiments, which were performed at the KWS 3 instrument operated by JCNS at the Heinz Maier-Leibnitz Zentrum (MLZ), Garching, Germany. This work was funded by the German-Israeli Foundation for Scientific Research and Development (GIF), grant no. I-101-307.4-2013.

References

[1] Lattemann S, Kennedy M D, Schippers J C, Amy G, Chapter 2 of *Sustainable Science and Engineering*, Vome 2 (Elsevier, Amsterdam 2010).
[2] Gullinkala T, Digman B, Gorey C, Hausman R, Escobar I C, Chapter 4 of *Sustainable Science and Engineering*, Vome 2 (Elsevier, Amsterdam 2010).
[3] Lee S and Elimelech M, 2006 *Environmental Science & Technology* 40(3), 980-987.
[4] Herzberg M and Elimelech M, 2006 *J. Membr. Sci.* 295(1-2), 11-20.
[5] Ning R Y and Troyer T L, 2007 *Desalination* 208(1-3), 232-237.
[6] Greenberg G, Hasson D and Semiat R, 2005 *Desalination* 183, 273-288.
[7] Mann S, 2001 Biomineralization, Oxford University Press, Oxford 2001.
[8] Pipich V, Dahdal Y, Rapaport H, Kasher R, Oren Y and Schwahn D, 2013 *Langmuir* 29 7607 - 7617.
[9] Dahdal Y, Pipich V, Rapaport H, Oren Y, Kasher R and Schwahn D, 2014 *Langmuir* 30, 15072 - 15082.
[10] Dahdal YN, Pipich V, Rapaport H, Oren Y, Kasher R, Schwahn D, 2016 *Polymer* 85, 77-88.
[11] Schwahn D, Feilbach H, Starc T, Pipich V, Kasher R and Yoram Oren 2016 *J. Membr. Sci*. (submitted).
[12] 1992 *Neutron News* 3 29–37.
[13] Steiner Z, Rapaport H, Oren Y, and Kasher R, 2010 *Environmental Science & Technology* 44 7937–7943.
[14] Palacios J, Schwahn D, Rauch H, 1981 *NDT International* 14, 189-193.
[15] Beaucage G, 1995 *Journal of Applied Crystallography* 28, 717-728.
[16] Roe R J, *Methods of X-Ray and Neutron Scattering in Polymer Science*, University Press, Oxford, 2000.