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TNO report**TNO 2014 R11030****NoWaste (Membrane)**

*A combined Membrane distillation-crystallization process
for the production of solid salts and pure water out of
brines.*

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Samenvatting

Doel van het NoWaste project is de ontwikkeling van een gecombineerd membraandestillatie-kristallisatieproces voor de behandeling van brijn stromen bijvoorbeeld afkomstig uit de procesindustrie of uit de ontzouting van water met behulp van omgekeerde osmose, waarbij een schone waterstroom en vast zout wordt geproduceerd. Belangrijke onderzoeksvraag in het project is hoe kristallisatie te laten plaatsvinden zonder het membraan te vervuilen. Zowel modeloplossingen als zeewater zijn gebruikt als brijn stroom.

Gestart is met het onderzoek naar membraandestillatie (MD) op laboratoriumschaal gebruikmakend van een modeloplossing van NaCl in water. Het blijkt mogelijk om deze oplossing te concentreren tot NaCl verzadiging met behulp van hydrofobe PTFE membranen bij een voedingstemperatuur van 73 °C en een temperatuurverschil over het membraan van 13 °C. zonder dat zich problemen van vervuiling voordoen. Echter op het moment dat er kristallisatie optreedt door waterverwijdering, daalt de flux door het membraan drastisch. Dit duidt op kristallisatie op het membraan.

Om dit te voorkomen is de mogelijkheid van het toevoegen van enten onderzocht. Idee hierachter is dat door het aanbieden van een groot kristallisatieoppervlak via deze enten, kristallisatie op deze enten i.p.v. op het membraan kan plaatsvinden. Vele type enten zijn getest, van zowel verschillende grootte als verschillende lading, maar het is niet mogelijk gebleken het kristallisatiegedrag van NaCl via deze enten te beïnvloeden en lijkt dan ook geen geschikte methode.

Een andere optie om kristallisatie op het membraan te voorkomen is de toepassing van osmotische destillatie (OD) i.p.v. MD. Bij OD wordt aan de destillaatzijde van het membraan een 'trekvloeistof' gebruikt. Als trekvloeistof is een geconcentreerde CaCl_2 oplossing gebruikt. Door gebruik van een dergelijk geconcentreerde oplossing kan een waterdampdruk verschil over het membraan ingesteld worden, terwijl de temperatuur aan de destillaatzijde hoger kan zijn dan aan de voedingszijde van het membraan. De verwachting is dat als gevolg hiervan de temperatuur aan het membraan hoger zal zijn dan in de bulk van de vloeistof. Hypothese is dat daardoor NaCl kristallisatie eerder op zal treden in de bulk dan aan het membraan (waar de oplosbaarheid hoger is door de hogere temperatuur). OD experimenten zijn uitgevoerd met zowel modeloplossing als zeewater en alhoewel de fluxafname na kristallisatie langzamer lijkt te gaan, daalt de flux tot een laag niveau, wat wijst op vervuiling (kristallisatie) van het membraan.

In de voorgaande experimenten kristalliseert veel zout uit bij waterverwijdering. Mogelijk dat de hoeveelheid zou van invloed is op het vervuilingsgedrag van het membraan.

Om de hoeveelheid zout te verminderen wordt aan de voeding na voorconcentrerend met MD een geconcentreerde CaCl_2 of MgCl_2 oplossing toegevoegd. Hierdoor wordt de wateractiviteit verlaagd en kristalliseert een groot deel van het NaCl uit (antisolvent behandeling).

Een afgescheiden vloeistof (met een veel lagere NaCl concentratie) wordt vervolgens als voeding voor het OD proces gebruikt. Diverse experimenten gebaseerd op dit principe hebben niet geleid tot voorkoming van precipitatie op het membraan. Dit probleem is nog niet opgelost. Spoelen van het systeem met een geringe hoeveelheid water leidt wel tot een sterke fluxtoename, maar deze methodiek is nog niet geoptimaliseerd.

Niet alleen de kristallisatie van NaCl is een aandachtspunt. In een brijn waarin Ca-zouten aanwezig zijn, kan scaling een probleem zijn. Toevoeging van enten om Ca-scaling te voorkomen lijkt wel succesvol, zeker waar het het voorkomen van scaling van CaCO_3 betreft. CaSO_4 zouten kunnen nog steeds een probleem vormen, maar kristallisatie hiervan vindt vooral op de warmtewisselaar plaats en niet op het membraan. Dit is ook vastgesteld in experimenten in 2 verschillende pilotsystemen. Een van deze systemen is een Memstill systeem met vlakke membranen. Er zijn in dit systeem enten toegevoegd, maar het bleek niet mogelijk deze in suspensie te houden. Desondanks is met zeewater een concentratiefactor 5 bereikt. Op dit niveau bleek het mogelijk de flux redelijk constant te houden, terwijl bij deze concentratiefactor Ca scaling verwacht kan worden. Een tweede pilot systeem is een direct contact membraan systeem. Hier zijn geen enten toegevoegd, omdat de membraanmodules (spiraalgewonden) zouden verstopten. Bij deze experimenten is het heel duidelijk dat de warmtewisselaars vervuilen t.g.v. Ca scaling.

Alhoewel de kristallisatieproblematiek voor met name het OD gedeelte nog niet opgelost is, is er wel nagegaan hoe een proces eruit zou kunnen zien, wanneer zowel MD als OD stabiel zouden werken. Een proces kan bestaan uit een MD gedeelte (met enten), waarin de brijn geconcentreerd wordt tot NaCl verzadiging en een OD gedeelte, waarin de kristallisatie plaatsvindt. Een antisolvent behandeling tussen MD en OD is optioneel. Omdat het OD gedeelte nog niet naar behoren werkt, kan deze stap ook vervangen worden door een conventionele verdampingsstap, waarbij de warmte herbruikbaar is in de MD stap.

Voor dit MD/OD proces is een eerste economische evaluatie gemaakt, uitgaande van de concentrering van zeewater en een stabiele MD/OD werking. In Tabel 1 zijn de resultaten van deze evaluatie weergegeven.

Tabel 1: Economische evaluatie van MD/OD proces

<i>Proces stap</i>	<i>Water productie (ton/uur)</i>	<i>Membraan oppervlak (. 1000 m²)</i>	<i>Investering Modules (M€)</i>	<i>Investering Hardware (M€)</i>	<i>Capex (€/m³ zeewater)</i>	<i>Warmte kosten (€/m³ zeewater)</i>	<i>Capex + warmte+ elektriciteit (€/m³ zeewater)</i>
MD1	1585	396	13,9	21,2	0,461	0,026	0,73
MD2	1640	273	9,6	14,6	0,318	0,080	0,40
OD	340	68	2,4	3,7	0,080	0,327	0,40
TOTAAL	3565	737	25,8	39,5	0,859	0,43	1,53
DOEL						1,50	4,00

Criteria:

- 8000 productie uren / jaar (behandeling van 28.8 Mm³/jaar zeewater)
- Module prijs: € 100 /m² (schatting voor 2015); vervanging in 4 jaar
- Extra hardware: geschat op € 500,- per m³/dag zeewater (3 x de Memstill schatting voor zeewater, rekening houdend met extra extra componenten voor kristallisatie, vaste stof handling, trekvloeistof regeneratie etc.).
- Rente/afschrijving extra hardware: Annuïteit = 16%.
- Elektriciteit: totaal 3 kWh per m³ zeewater (4 x Memstill), bij € 0,08 = € 0,24 / m³ zeewater.
- Restwarmte kosten: € 1.00 per GJ (363 K) resp. € 1,50 per GJ (393 K) stoom.
- Onderhoud, arbeid: 5% van Hardware investeringen (niet inbegrepen in tabel 1.).

Samenvattend kan het volgende geconcludeerd worden:

- Het blijkt in principe mogelijk om brijnen te concentreren met een gecombineerd MD/OD proces, waarbij schoon water en vast zout wordt verkregen.
- Een groot deel van het NaCl kan vóór de OD stap al verwijderd worden via precipitatie door toevoeging van een antisolvent zoals een geconcentreerde CaCl₂ of MgCl₂ oplossing.
- Het blijkt mogelijk om scaling op het membraan in de vorm van CaCO₃ te voorkomen door toevoeging van enten. CaSO₄ precipitatie blijkt vooral plaats te vinden in de warmtewisselaar.
- Het OD proces is toegepast om NaCl precipitatie op het membraan te voorkomen. Dit blijkt vooralsnog onvoldoende te werken. Regelmatige spoeling van het membraan is nodig om neergeslagen NaCl opnieuw op te lossen en de flux te herstellen. Dit spoelproces is nog niet geoptimaliseerd.
- Eerste economische schattingen voor het MD/OD proces zijn gunstig, in het bijzonder bij continue bedrijfsvoering en grote capaciteit. Voor kleine capaciteiten of beperkte bedrijfstijd is de situatie duidelijk ongunstiger, maar aantrekkelijkheid zal nog altijd afhangen van lokale lozingskosten.

Summary

Aim of the NoWaste project is the development of a combined membrane distillation-crystallization process to treat brines originating from industrial processes or the desalination of water by reverse osmosis and producing clean water and solid salts. Challenge in the project is the crystallization of salts in the membrane module without plugging the membrane.

Both model solutions and real seawater have been used as brines.

First approach was the application of membrane distillation (MD) on laboratory scale on a model solution of NaCl in water. It is possible to concentrate this model solution with MD up to saturation of NaCl by the use of hydrophobic PTFE membranes at a temperature of 73 °C and a temperature difference across the membrane of 13 °C, without problems of clogging by crystallization. However, as soon as crystallization occurs due to water removal (super saturation), the flux drops immediately. This indicates crystallization on the membrane surface.

Second approach was the addition of seeds to the brine in the expectation that crystallization of NaCl occurs on the seeds instead on top of the membrane.

Experiments with many different seeds of different size and charge have been executed, but it turned out to be impossible to crystallize NaCl on the seeds. So, seeds are no option to prevent crystallization of NaCl on the membrane in MD operation above saturation of NaCl.

Third approach was the application of osmotic distillation (OD) instead of MD. In OD a draw liquid is used at the distillate side to lower the vapour pressure. In this way it is possible to maintain a driving force across the membrane while the temperature at the distillate side is even higher than the temperature at the feed side. By doing this it is expected that the temperature near the membrane at the feed side is higher than the temperature in the bulk. It is expected that the solubility of NaCl near the membrane is higher than in the bulk and therefore crystallisation will start in the bulk instead of on the membrane surface (assuming a limited concentration polarization effect). Experiments have been carried out with both model solutions and seawater, but although the flux decline after crystallization was slower, the final flux level was very low, still indicating crystallization on the membrane surface.

The last approach within the project to prevent formation of NaCl crystals on the membrane surface was the combination of an antisolvent step, followed by OD. The diluted brine is concentrated to near saturation by MD. Consequently a salt like CaCl_2 or MgCl_2 is added to precipitate a large part of the NaCl in the solution. Due to addition of the salt the water activity decreases with salting-out effect of NaCl as a result. The remaining supernatant is used as feed for the OD process. Based on the analysis of the components and the visual observation solid NaCl is produced. Despite the good start of the OD experiment the flux suddenly drops after some time. The solution becomes also clear at that moment. Apparently small crystals are formed that plug the membrane. This problem is not solved yet.

Not only the crystallization of NaCl is important. If in a mixture e.g. Ca salts are present, scaling of the membranes may occur. Although the addition of seeds to prevent NaCl crystallization was not successful, this is different for seeds to prevent Ca scaling. Initial laboratory experiments showed a good performance by adding seeds to prevent CaCO_3 scaling. By adding these seeds in a solution both containing NaCl and Ca salts with potential scaling, it seems possible to concentrate the NaCl solution up to saturation while controlling the crystallization of Ca-salts.

This is tested in 2 pilot systems with seawater. One pilot system is a Memstill system with flat sheet membranes. The addition of the seeds is not optimal, and settling of seeds occurs in the feed tank. After a short period of time, no more seeds were added, nevertheless the flux at a concentration factor of 5 is rather constant. This is at a concentration level where Ca scaling is expected. In a second pilot installation with a direct contact membrane distillation system a seawater concentration experiment is executed without the addition of seeds. Here plugging of the external stainless steel heat exchanger due to scaling is observed. Given these results a process configuration consisting partly out of a MD system (with seeds) up to saturation of NaCl and partly out of an OD system for crystallizing NaCl is an option. Because the possibility of the OD system for NaCl crystallization is not proven yet, the crystallization step can also be performed by a conventional evaporation system where the waste heat can be re-used in the MD part. A preliminary economic evaluation has been made for the MD/OD system for concentrating a very high flow of seawater assuming a stable operation of the MD/OD process.. In Table 1 the results from this evaluation are shown.

Table 1: Results preliminary economic evaluation of MD/OD

<i>Process step</i>	<i>Water production (ton/h)</i>	<i>Membrane surface (. 1000 m²)</i>	<i>Investment Modules (M€)</i>	<i>Investment Hardware (M€)</i>	<i>Capex (€/m³ sea water)</i>	<i>Heat costs (€/m³ sea water)</i>	<i>Capex + heat + electricity (€/m³ sea water)</i>
MD1	1585	396	13.9	21.2	0.461	0.026	0.73
MD2	1640	273	9.6	14.6	0.318	0.080	0.40
OD	340	68	2.4	3.7	0.080	0.327	0.40
TOTAL	3565	737	25.8	39.5	0.859	0.43	1.53
TARGET						1.50	4.00
<p><i>Criteria:</i></p> <ul style="list-style-type: none"> - 8000 production hours / year (treatment of 28.8 Mm³/year sea water) - Module price: € 100 /m² (estimation for 2015); replacement in 4 years - Additional hardware: estimated at € 500,- per m³/day of sea water (3 x the Memstill estimation for sea water desalination, to account for the extra components for crystallization, solids handling, draw liquid regeneration etc.). - Interest /depreciation auxiliary hardware: Annuity = 16%. - Electricity: total 3 kWh per m³ sea water (4 x Memstill), ad € 0,08 = € 0,24 / m³ sea water. - Waste heat costs: € 1.00 per GJ (90 °C) resp. € 1,50 per GJ (120 °C) steam. - Maintenance, labor: 5% of Hardware investment (not included in table 1). 							

Summarizing, the following can be concluded:

- In principle it is possible to concentrate brines and precipitate salts by a combined MD/OD process.
- A large part of NaCl can be precipitated by adding an antisolvent like CaCl₂ or MgCl₂ after the MD steps, but before the OD step.

- In the MD process Ca scaling as CaCO_3 can be prevented by addition of seeds, CaSO_4 precipitation occurs mainly in the heat exchanger part.
- The OD process is designed for the prevention of NaCl precipitation on the membrane, but stable operation is not possible yet. Frequent rinsing is necessary to dissolve precipitated NaCl on the membrane and restore the flux through the membrane. The frequency of rinsing is not optimized yet.

Assuming a stable operation of the MD/OD process, preliminary economic calculations look promising, especially for large capacity and continuous operation. For small capacity and limited operation over the year, depreciation cost will be much higher per m^3 of feed water, which makes the economics less attractive, but still depending on application and current waste disposal costs.

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Introduction

Disposal of brines (concentrated salt solutions) is becoming a serious problem because of more stringent legislation. At the same time the total volume of brines produced increases due to measures for the (re)use of water (e.g. desalination technologies). The type and concentration of brine depends on the source and treatment. Possibilities for disposal also depends on the location of the brines. In general, inland disposal is more difficult than disposal on sea. To facilitate the reuse of water, the brine issue has to be solved in an economical feasible way. Existing technologies are only limitedly applied because of technical limitations (e.g. reverse osmosis, because of concentration limitations) or economical limitations (e.g. conventional evaporation technologies). Objective of the project is to develop a technology that is economical and technical feasible for treating brines. The membrane distillation-crystallisation technology is expected to meet these criteria. In order to determine the feasibility of this technology the following questions have to be answered:

- 1. How does the way of operation of membrane distillation effect the crystallization of salts onto the membrane surface?*
- 2. How does the way of operation of membrane distillation effect the energy consumption?*
- 3. Is it possible to control the crystallization process during membrane distillation-crystallization by addition of seeds?*
- 4. Is it possible to fractionate the precipitated salts during membrane distillation-crystallization out of a mixed salt solution?*
- 5. What are the economic forecasts for the process?*

The answers on these questions are obtained by a combination of theoretical work and experimental work on both laboratory bench scale and pilot scale.

1 Background

Disposal of brines is a fundamental problem in desalination processes, e.g. after reverse osmosis (RO) treatment, multistage flash (MSF) or multi-effect distillation (MED). The most frequent disposal practice is the direct discharge in the environment. However, the more and more stringent environmental regulations preclude in many cases this low cost practice, aiming to protect the aquatic environment [1]. MSF/MED and RO desalination are extensively applied with a capacity of respectively 50 million m³/day and 20 million m³/day [2]. The water recovery in seawater RO operations generally varies from 30 to 50%, being the remaining part rejected. Innovative techniques and approaches aiming to reduce the volume of wastes and to extract dissolved salts from RO reject brines can represent an interesting opportunity towards sustainability, also in terms of cost-saving [3]. Concentrating these brines with conventional methods like evaporation and crystallization is an option, but very expensive because of high energy consumption [4] and the application of expensive high quality metals in installations like Ni- or Cu-base alloys, stainless steel, or titanium and aluminium alloys [5] which are subjected to corrosion under severe operating conditions. Membrane crystallization (MCr) may offer an attractive alternative for evaporation/crystallization. MCr is a combination of membrane distillation (MD) and a separate crystallizer in which pure water is produced as permeate from the MD process while the concentrated solutes can be recovered as solids from the crystallizer [6]. It can be applied for seawater desalination and treatment of NF and RO brines to obtain high water recovery and produce valuable crystalline products, like NaCl, CaCO₃ and MgSO₄·7H₂O [1,7].

The application of MCr to the crystallization of sodium chloride has been firstly mentioned by Curcio et al. [8] by operating at moderate temperature gradient (feed and distillate inlet temperatures of 29 °C and 9 °C, respectively) to keep the trans membrane flux low ($\sim 1 \times 10^{-4} \text{ kg m}^{-2} \text{ s}^{-1}$) reducing the influence of concentration polarization on the super saturation profile and preventing eventual incrustation at the membrane surface. Gryta [9] integrated membrane distillation with a crystallization unit. He obtained a permeate flux of 400 l.m⁻².d⁻¹ with a 205–240 g/L NaCl solution as feed ($T_{\text{feed,in}} = 85 \text{ °C}$, $T_{\text{distillate,in}} = 25 \text{ °C}$). The average yield was 100 kg.m⁻².d⁻¹ of NaCl crystals. Anhydrous sodium sulphate crystals with a relatively narrow crystal size distribution have been obtained at high feed temperatures (50–60 °C) with fluxes up to 20 l.m⁻².h⁻¹ by Tun et al. [6]. The transmembrane flux gradually declined due to a high evaporation rate and relevant polarization phenomena.

MD is an emerging non-isothermal membrane separation process known for about 50 years and is being developed for its adequate industrial implementation. It refers to a thermally driven transport of vapour through non-wetted porous hydrophobic membranes, the driving force being the vapour pressure difference between the two sides of the membrane pores [10]. Benefits of MD are a low operating pressure, use of (waste) heat of modest temperatures (up to 90 °C), potentially complete retention of non-volatile solutes, and high purity of permeate water [11]. Because of these relatively low temperatures MD modules can be made from polymer material.

These corrosion-resistant materials are much cheaper than the high quality metals needed in conventional desalination processing. MD has an advantage over reverse osmosis (RO) as a concentration and water recovery process at high solute concentrations. When operating MD at high concentrations, viscosity and vapour pressure suppression are the factors influencing the flux [12,13]. However in MD, which is driven by thermally induced vapour pressure difference, the suppression of driving force caused by high concentrations is modest [12].

On the other hand, in the RO process, significantly elevated pressures are required to overcome the osmotic pressure in concentrate processing. In practice, MD can operate with reasonable fluxes at moderate temperatures with high solute concentrations.

This attribute favours the combination of MD, rather than RO, to crystallization as a means of solids recovery.

As an alternative for the current MCr process which consists of a membrane distillation unit and a separate crystallization unit, an integrated membrane distillation crystallization (MDC) process is presented.

2 Principle of Membrane Distillation Crystallization (MDC)

The principle of the membrane distillation crystallization process is schematically shown in Figure 1.

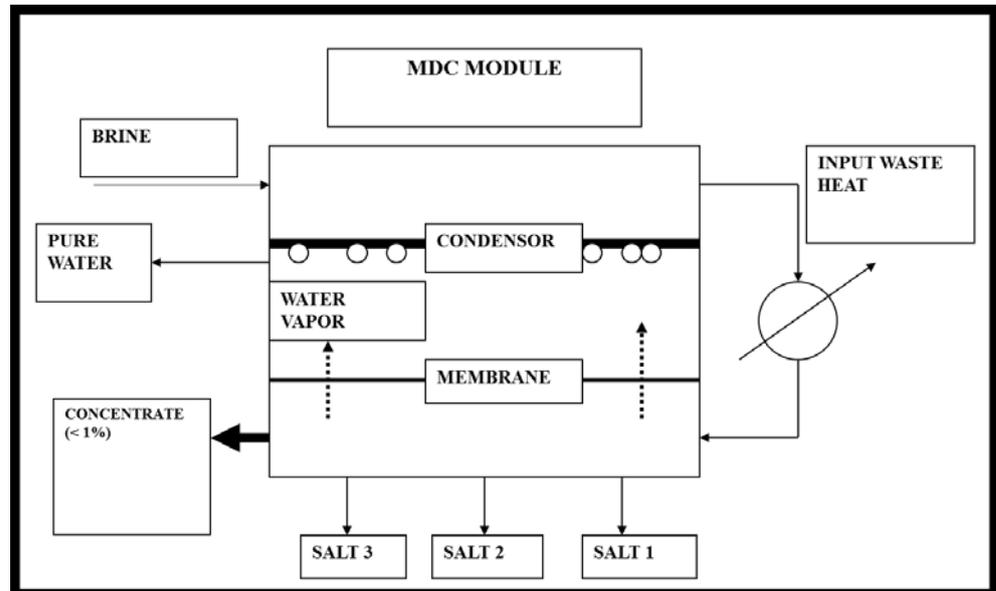


Figure 1: Principle MDC process in a liquid-gap or air-gap membrane distillation unit. The concentrate volume can be less than 1% of the original brine volume, while almost all the salts present in the brine solution are precipitated during water removal.

A brine (aqueous salt solution) is treated in a membrane distillation (MD) module. In Figure 1 a situation is depicted where both a condenser sheet and a membrane sheet are present in the module (liquid- or air-gap MD). After heating of the feed, it flows alongside a hydrophobic membrane in counter current with the brine entering the module at the condenser side. Due to the temperature difference across the membrane, water evaporates and water vapour is transported through the membrane. As a consequence the brine will be concentrated while flowing along the membrane. Depending on the solubility of the salt present in the brine, salts will become saturated during the water removal alongside the membrane and crystallization will occur. Because of the difference in solubility, the salt will precipitate at different concentrations and therefore fractionation of the salts during water removal is possible. A major challenge in this process is to crystallize as much salt as possible without fouling/scaling of the membrane.

The process described can also be executed with direct contact MD. In that situation only a membrane is present in the module where at one side of the membrane the brine is flowing and at the other side of the membrane the distillate is flowing. Heat can be recovered by an external heat exchanger. The principle of such a set-up is shown in Figure 2.

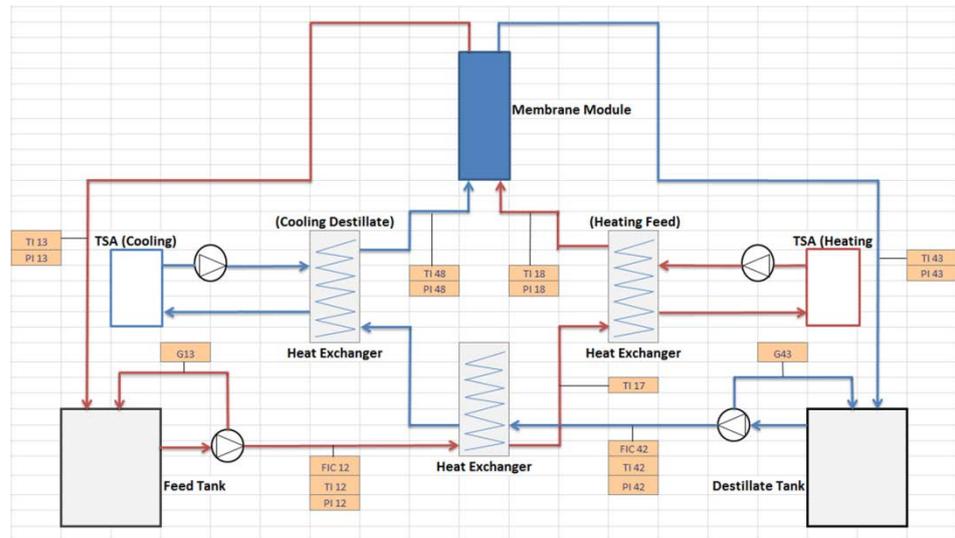


Figure 2: Direct contact membrane distillation unit with external heat recovery. TSA = external heating device.

The direct contact MD principle is applied in the laboratory tests. It is an easy set-up to characterize the membrane. Fluxes are in general higher than in air-gap or liquid-gap membrane distillation, but energy consumption is also higher.

3 Experimental set-up Membrane distillation Crystallization (MDC)

3.1 Test equipment

Experiments with MDC have been executed on laboratory scale with direct contact membrane distillation equipment. A schematic set-up is shown in Figure 3.

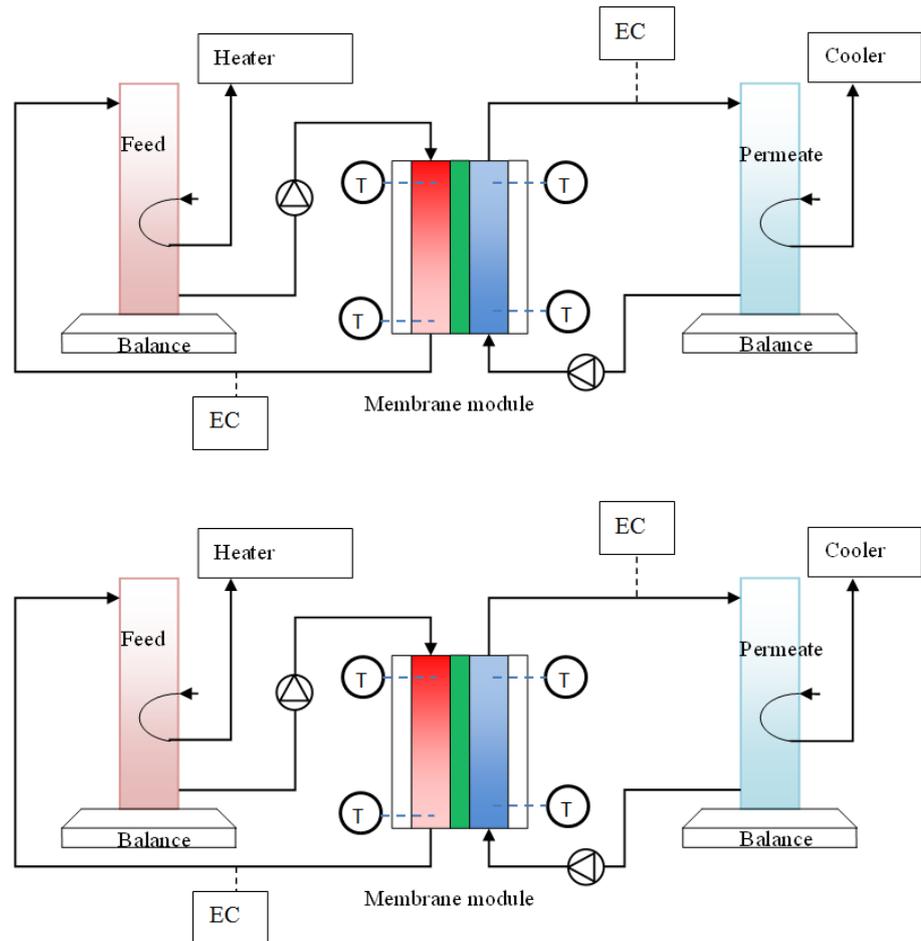


Figure 3: Experimental set-up MD and MDC experiments on laboratory scale (T = thermocouple; EC = electrical conductivity meter).

In the experimental set-up a flat MD membrane is applied with a surface area of 500-600 cm² (depending on the used lab module). The membrane module is constructed out of polycarbonate and has the possibility for additional heating or cooling in separate compartments in the module. The membrane separates a heating circuit from a cooling circuit. The temperature can be controlled between 20 and 80 °C.

The volume of the storage glass vessels in both the heating and cooling circuit is about 1 litre, and the volume of the total system is about 1.5 litre on both sides. Based on the set-up shown in

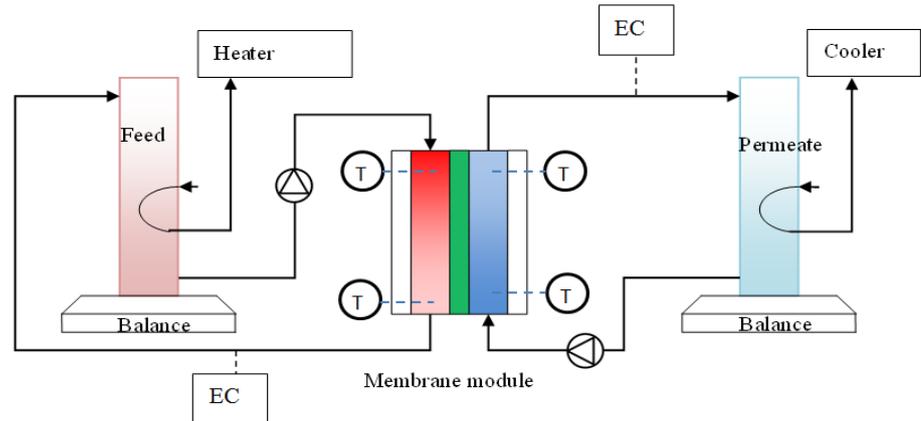


Figure 3, equipment is added depending on the requirements (e.g. settler for removing the crystals formed in the membrane setup during crystallization). In Figure 4 a photo of this equipment is shown.



Figure 4: Laboratory set-up MDC equipment.

3.2 Membrane material

For MD(C) experiments hydrophobic materials have to be applied, to make sure the membrane is not wetted. Commercial available materials tested are PTFE, HDPE and PES with a surface treatment to make it oleophobic. Table 2 shows some specifications of the membranes used.

Table 2: Membranes tested during the project.

Membrane	Material	Thickness [μm]	Pore size (av) [μm]	remarks
M-01	PTFE	100	0.08	
M-02	PTFE	150	0.08	
M-03	PTFE	50	0.05	
M-04	PP	84	N.A.	Celgrad (PP) 2400
M-05	HDPE	76	0.3	Solupor van Lydall
M-06	Oleophobic PES	N.A.	0.2	Laminate with thin active layer

3.3 Selection of brines

The experiments have been partly executed with single salt solutions (NaCl) and partly with seawater (coastal water from the North Sea water intake in Den Helder, the Netherlands, composition in Appendix D).

4 Experiments and results

4.1 Experiments with membrane Distillation (MD)

4.1.1 MD experiments with a NaCl solution

The experiments with a starting concentration near saturation of NaCl have been executed to observe the behaviour of the flux in a MD operation during crystallization. A typical result of these experiments is shown in Figure 5.

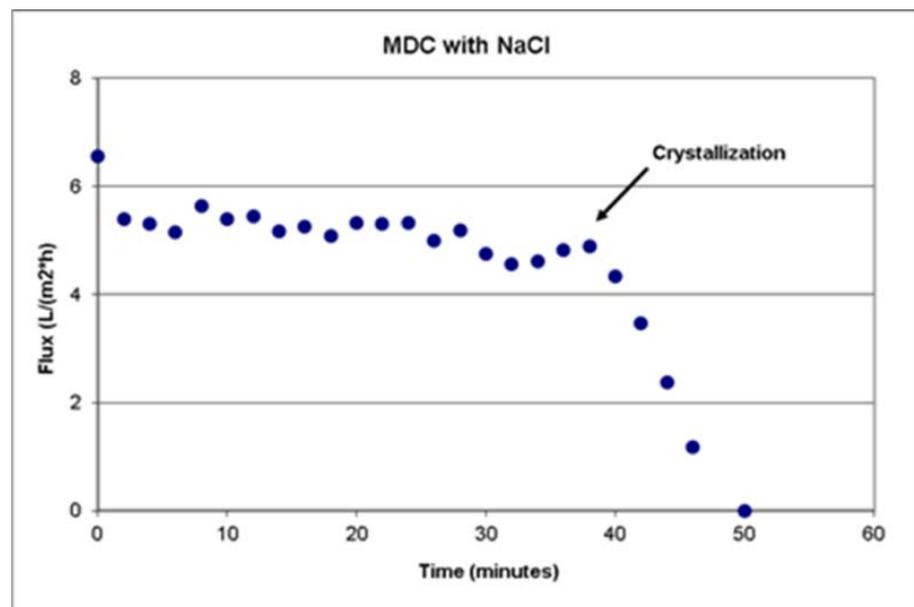


Figure 5: Flux versus time during concentration and crystallization of a NaCl solution.
Experimental conditions: Feed temperature: 73 °C Distillate temperature: 60 °C.
Membrane material: PTFE (M-02).

Figure 5 shows that a rapid flux decline occurs at the moment that crystallization is observed in the feed vessel. Probably, crystals are also formed on the membrane surface. The flux decline might be expected based on the temperature profile near the membrane. The temperature profile is shown in Figure 6.

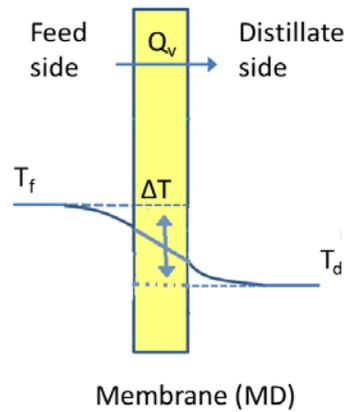


Figure 6: Typical temperature profile over the membrane in MD operation. T_f is the feed temperature in the bulk solution. Due to a stagnant fluid layer and evaporation of water near the membrane the temperature drops near the membrane. The temperature drop in the membrane is due to the thermal resistance of the membrane material. The temperature drop near the membrane at the distillate side is due to the stagnant fluid layer near the membrane. T_d is the distillate temperature in the bulk solution. Q_v is the heat of evaporation.

Figure 6 shows that the temperature at the feed side near the membrane is lower than in the bulk due to evaporation of water near the membrane. As a consequence, the solubility of the salt near the membrane will be lower than the solubility in the bulk. An additional effect is concentration polarization. Due to the evaporation of water near the membrane the concentration of NaCl near the membrane will be higher than the concentration in the bulk. Both effects near the membrane cause crystallization of NaCl near or on the membrane surface. From Figure 5 it can be concluded that this crystallization leads to a severe flux decline. As long as crystallization does not occur, a nearly saturated NaCl solution can be operated with MD at constant flux. This is shown in Figure 7, where MD is executed with a nearly saturated NaCl solution for a period of 4 days.

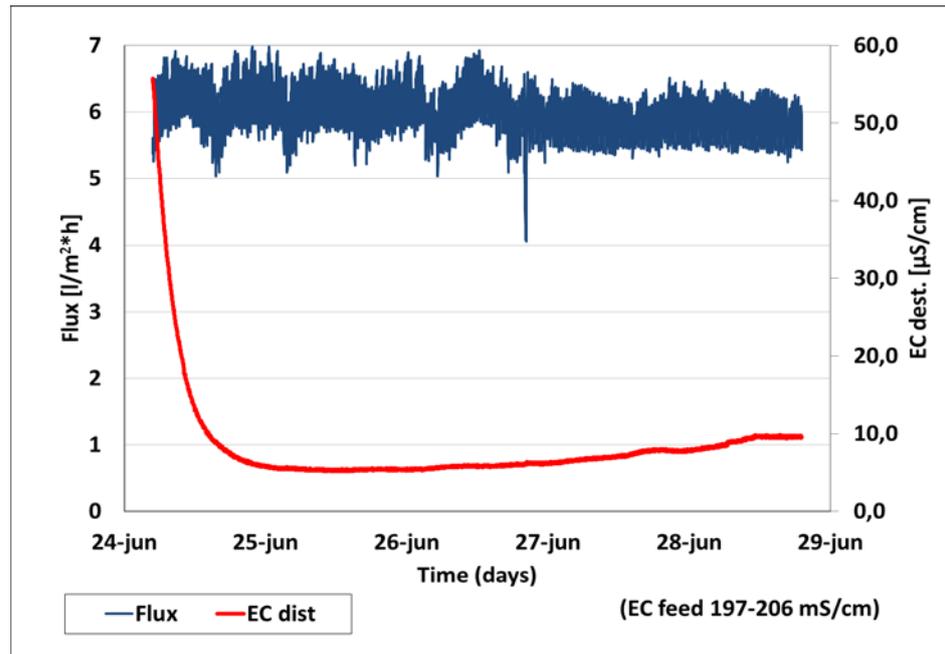


Figure 7: MD flux of a nearly saturated NaCl solution (about 95%) during a period of 4 days. Experiments have been executed with a PTFE membrane (M-02). $T_{\text{feed}} = 78 \text{ }^{\circ}\text{C}$, $T_{\text{distillate}} = 70 \text{ }^{\circ}\text{C}$.

The results shown in Figure 5 and 7 indicate that flux decline occurs at the point of crystallization of NaCl.

During the project several methods have been studied to control this crystallization in order to prevent flux decline:

- Membrane material selection
- Crystallization modifications
- Process modifications

Although the initial experiments were performed with a single salt solution, seawater treatment with MD or MDC is a potential case (or concentrate from seawater RO operation). Seawater is a mixture of different salts, which makes the MD performance more realistic, also facing possible problems like Ca-scaling. The above mentioned subjects were studied with seawater.

4.1.2 MD(C) experiments with seawater.

Seawater treatment with MD is an interesting application (e.g. treatment of concentrate from RO operation).

Coastal water from the Dutch North Sea area is used for the MD tests.

Looking at seawater we can expect a precipitation/crystallization of several salts during the removal of water. This is qualitatively shown in Figure 8.

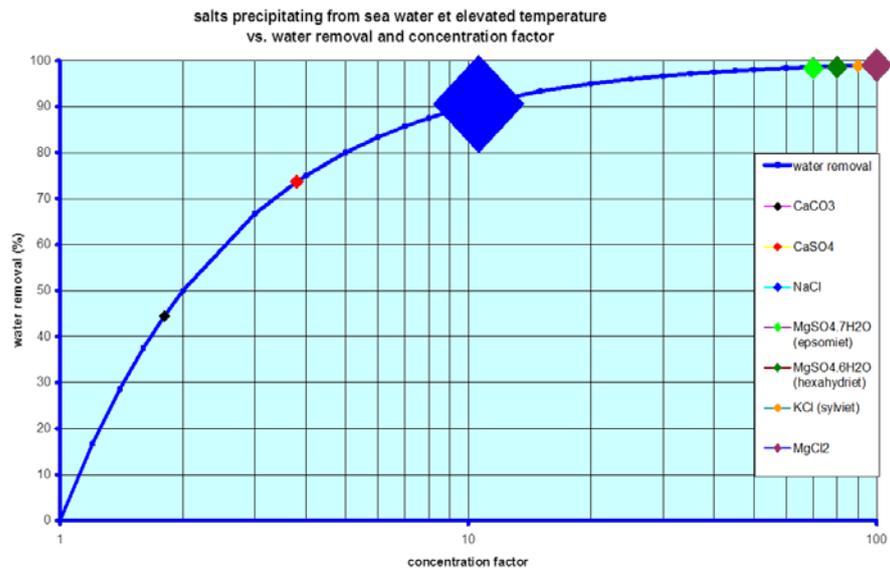


Figure 8: Types of salts precipitating during MDC of sea water as a function of water removal c.q. concentration factor. The size of the points is an indication of the amount of salt.

From Figure 8 it follows that before saturation of NaCl, CaCO₃ and CaSO₄ may precipitate.

A typical result from experiments with seawater is shown in Figure 9.

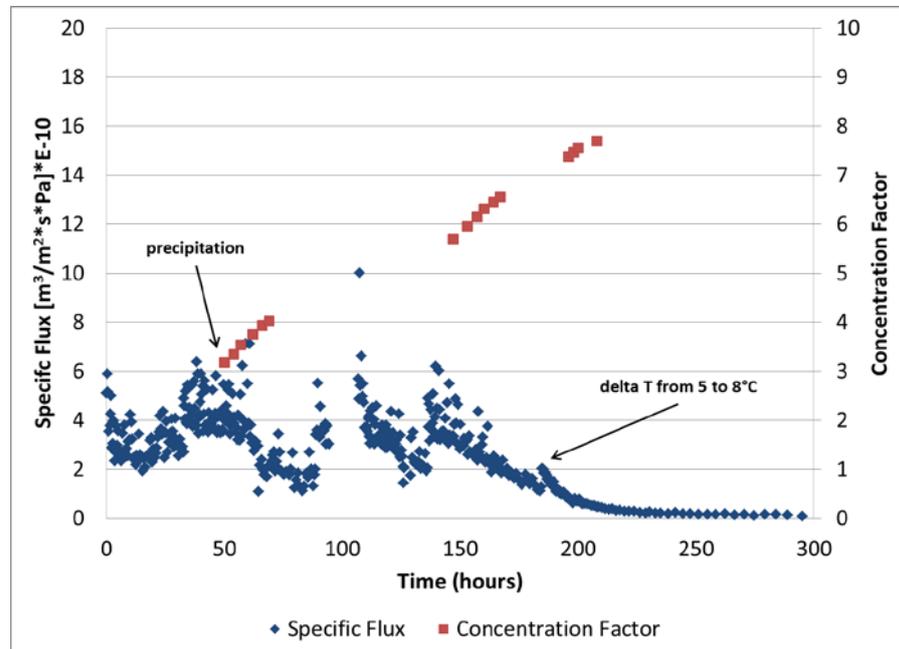


Figure 9: Specific flux (blue) and concentration factor (red) versus time during MD operation with seawater. T_{feed} = 70 °C. ΔT = 5-8 °C. Membrane M-02.

Figure 9 shows that the specific flux drops during the concentration of the sea water. At a concentration factor of about 4 ($t = 70$ h) crystallization is observed (salt particles in the system), probably CaCO_3 and/or CaSO_4 (see Figure 8). At timestamp $t = 90$ h, at a concentration factor of about 4, the temperature difference across the membrane has been increased from 5 to 8 °C and as a result the flux increases temporarily, but drops again to almost zero after some time. To remain a constant specific flux during concentration of the feed, the temperature difference across the membrane needs to be increased to compensate for the decline in vapour pressure (boiling point elevation) at the feed side due to an increasing salt level in the feed.

4.1.3 *Membrane material selection*

Membrane selection might be an option to prevent fouling of the membranes by scaling, because of difference in e.g. hydrophobicity and roughness. Membrane materials involved in this study are PTFE, HDPE and surface treated PES (Pall Supor R). Materials have to be hydrophobic to prevent wetting of the membrane pores. The pore size in the membrane also has to be quite uniform to prevent leakage. With the materials selected it was not possible to prevent flux decline on the membrane during crystallization. No study has been done to determine the difference in sensitivity of the membranes to crystallization. Another issue observed is the leakage of the membrane due to crystallization on the membrane and consequently crystal growth through the pores of the membrane.

4.1.4 *Crystallization modifications*

Different options have been studied to prevent crystallization on the membrane by crystallization modifications like:

- addition of heterogeneous templates that promote crystallization but do not dissolve in under saturated solution.
- addition of additives that change the habit of the crystal and reduce affinity with the membrane.

4.1.4.1 *Addition of (heterogeneous) templates.*

The addition of seeds to promote crystallization is a well-known option for Ca-salts. Additional advantage is that the Ca-salts are possibly more concentrated in the bulk than in the boundary layer near the membrane. This has to do with the solubility profile of the Ca-salt and as a consequence the concentration profile in the MD process (Figure 10) near the membrane wall.

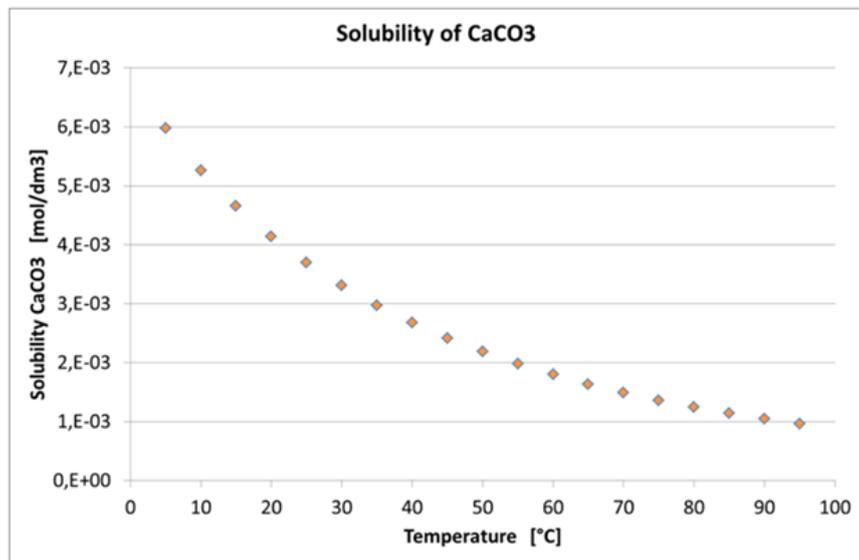
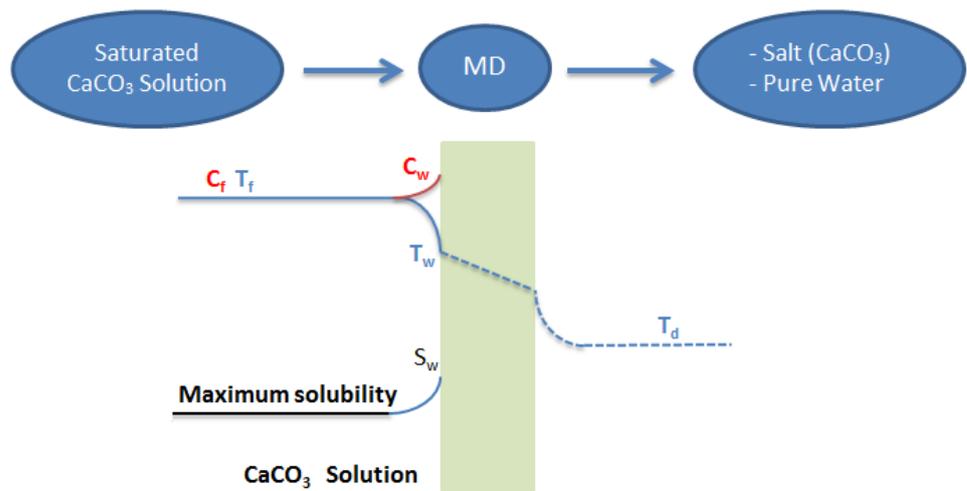


Figure 10: Solubility of CaCO₃ as function of temperature and concentration profile of CaCO₃ in MD operation.

From Figure 10, it follows that depending on the balance between concentration polarization and temperature polarization, the super saturation of CaCO₃ in the bulk phase is most likely to be higher than in the boundary layer near the membrane. As a consequence the presence of seeds in the bulk might be effective to promote crystallization in the bulk instead of near the membrane.

In Figure 11 and Figure 12 the results of a MD experiment with a CaCO₃ solution without seeds and with seeds are shown.

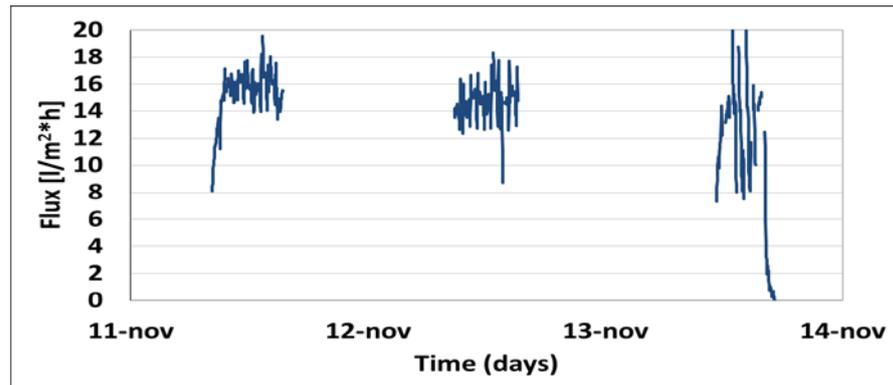


Figure 11: Flux during dewatering and crystallization of a saturated CaCO_3 solution. Trans-membrane temperature difference is 5 K. Feed temperature is 350 K. The intervals between the flux data are due to switching off the installation during night time. Membrane material: PTFE

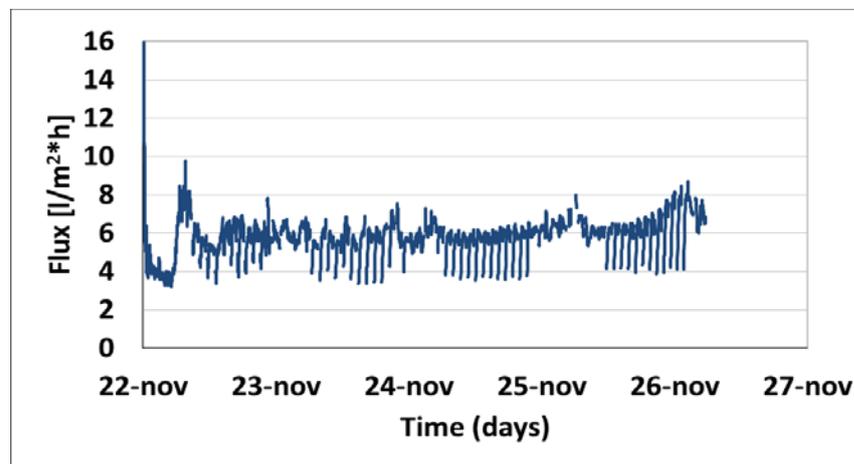


Figure 12: Flux during dewatering and crystallization of a saturated CaCO_3 solution with addition of crystallization seeds (Calflo, 1g/l). Trans-membrane temperature difference is 10 K. Feed temperature is 353 K. Membrane material is PTFE (M-02).

In the experiment shown in Figure 12, CaCO_3 seeds were added to the saturated CaCO_3 solution in order to compete with the membrane in the initiation of nucleation. The initial flux was $16 \text{ L m}^{-2} \text{ h}^{-1}$ like in the previous experiment (Figure 11). However, a sharp flux decline was observed directly at the beginning of the experiment. This is probably due to the presence of the crystallization seeds that partly block the membrane pores. The remaining flux is fluctuating around $6 \text{ L m}^{-2} \text{ h}^{-1}$ for at least 4.5 days (Figure 12). From this it can be concluded that CaCO_3 crystallization on the seeds is preferred above crystallization on the membrane.

The data in Figure 11 and Figure 12 show that the addition of seeds results in a stable flux over time.

Addition of Calflo seeds to prevent scaling of Ca-salts in a MD seawater experiment does not result in an obvious advantage (see Figure 13) compared to the experiment without seeds (Figure 9).

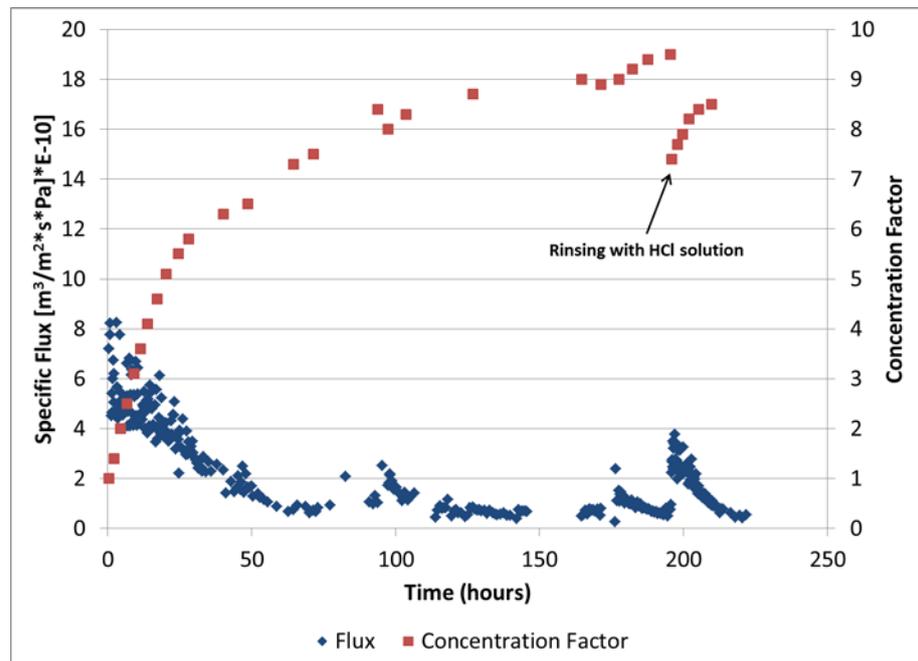


Figure 13: Specific flux (blue) versus time and concentration factor (red) during MD operation with seawater and addition of Calflo seeds (1 g/l). $T_{feed} = 343\text{K}$. $\Delta T = 5-11\text{ K}$

Rinsing with a HCl solution leads to a sharp flux increase which indicates removal of Ca-salts from the membrane. However, after rinsing the flux drops again fast. Difference between Figure 11 and 13 is the type of solution. In Figure 11 a model solution is used with only CaCO_3 present, while in Figure 13 real seawater is used. Around concentration factor 4 also precipitation of CaSO_4 is expected. Apparently this does not occur (only) on the seeds in the bulk but also on the membrane.

Seeding materials for Ca, Mg salts are well known, but this is not the case for NaCl. In first instance small NaCl crystals have been added to an almost saturated solution to force crystallization on the added crystals instead of on the membrane. Severe flux decline was still observed after crystallization. In Table 3 an overview is shown from the materials studied in order to prevent crystallization on the membrane.

Table 3: Overview of materials applied as seeds for NaCl crystallization.

Material	Type	Size (diameterxL)	External area (m ² /g)	BET surface area (m ² /g)	Costs (€/kg)	Costs (€/m ³ water)*
Sand (applied in pelletreactor)	Garnet sand	600 µm	0,005	0,005	0,30	60
Diatomaceous Earth (porous, inert/calcinated, biological origin)	Celite calflo	19 µm	1	120	3,50	3,50
Diatomaceous Earth (porous, inert, biological origin)	Celite diafil 590	4 µm	5	32	1,15	0,23
Perlite (volcanic, inert)	Harborlite H300	20 µm	1	n.a.	1,15	1,15
Bentonite (clay platelets, negatively charged)		8 µm	2	2	3,50	1,75
Sepiolite (clay needles, negatively and positively charged)	Pangel HV	4 x 2000 nm?	200	200	3,00	0,015
Palygorskite (clay needles, negatively and positively charged)	Actigel 208	3 x 1500 nm	300	300	4,60	0,015
Laponite (clay platelets, negatively and positively charged, synthetic)	Laponite RD	25 x 1 nm	600	600	12	0,020

* Assuming an material use of 1 m² external area/l water.

As shown in Table 3 many of the selected seeds are charged aiming at an interaction with salt ions. Also small particles have been selected to add as many nuclei as possible (especially Sepiolite, Palygorskite and Laponite). The structure of Actigel 208 is shown in Figure 14.

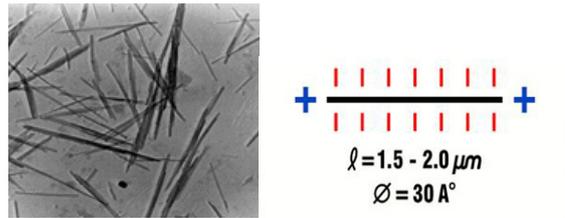


Figure 14: Structure, charge distribution and dimensions of Actigel 208.

Despite the addition of these seeds in the feed flow the flux decline was comparable to the experiments without seeds. Variation in the concentration of seeds (2-100 g/l) did not improve these results. Possible cause could be pugging of the membrane pores by the very fine seeds. However, results from experiments with pure water with these seeds did not show any flux decline. Apparently, the interaction of the saturated NaCl solution with the seeds is insufficient to prevent the formation of homogeneous crystals on the membrane surface and/or in the bulk phase.

Another possible option studied to prevent crystallization on the membrane is the application of filter aids. By applying filter aids a permeable controlled coating is formed on the membrane. Possibly the crystallization layer is formed on top of the filter aid instead on top of the membrane and is more easily removed by the flow along the membrane. Materials tested are diatomaceous earth, perlite and synthetic silicates. Experiments with these filter aids did not show an obvious improvement in flux behavior after crystallization.

4.1.4.2 Addition of additives that change the properties and structure of the crystal

A way to change the habit of the crystal is the addition of Potassium Ferro Cyanate ($K_4Fe(CN)_6$). In Figure 15 it is shown how the addition affects the crystal structure.

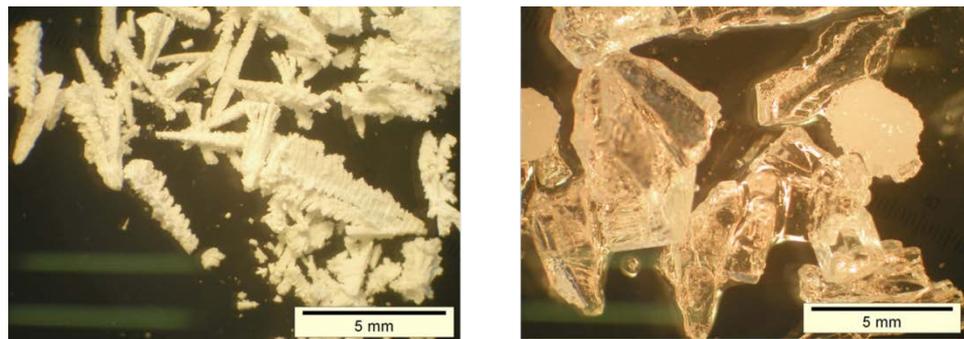


Figure 15: NaCl crystals with (left) or without (right) addition of $K_4Fe(CN)_6$

The results with MD experiment with saturated NaCl solution addition of $K_4Fe(CN)_6$ (Figure 16) show that there is still flux decline. Apparently the structure of the crystals does not affect the crystallization behaviour on the membrane.

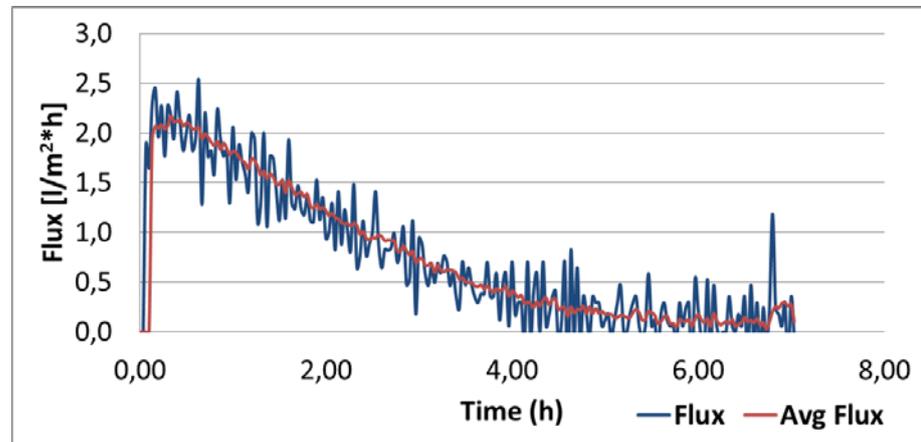


Figure 16: Flux in l/(m².h) after addition of 1wt% $K_4Fe(CN)_6$. Membrane M-02.

4.2 Process modifications

Another option to control the crystallization is by the way of operating the process.

Two options have been studied:

- Osmotic Distillation (OD)
- Anti-solvent crystallization in combination with OD

4.2.1 Osmotic Distillation (OD)

The principle of osmotic distillation is shown in Figure 17.

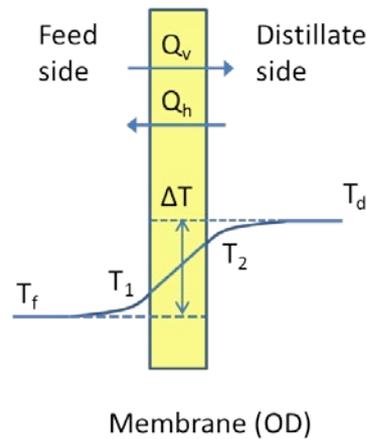


Figure 17: Principle of osmotic distillation (OD). T_f and T_d are the temperatures in the bulk of respectively the feed solution and the distillate solution. T_1 and T_2 are the temperatures near the membrane at respectively the feed side and the distillate side. Q_v is the heat flow due to evaporation, Q_h is the heat flow due to heat conduction in the membrane.

In Figure 17 the temperature at the distillate side is higher than the temperature at the feed side of the membrane. As a consequence the vapour pressure at the distillate side is higher than the vapour pressure at the feed side, causing a vapour flow from the distillate side to the feed side. Because a vapour flow from the feed side to the distillate side is required, the vapour pressure at the distillate side has to be lowered. This is realized by using a drawing liquid at the distillate side instead of pure water. This drawing liquid (e.g. a concentrated CaCl_2 solution) decreases the vapour pressure to such a level that the vapour pressure at the distillate side is lower than the vapour pressure at the feed side of the membrane. Given the temperature profile as shown in Figure 17, a concentration and temperature profile for the osmotic distillation of a NaCl solution is expected as shown in Figure 18.

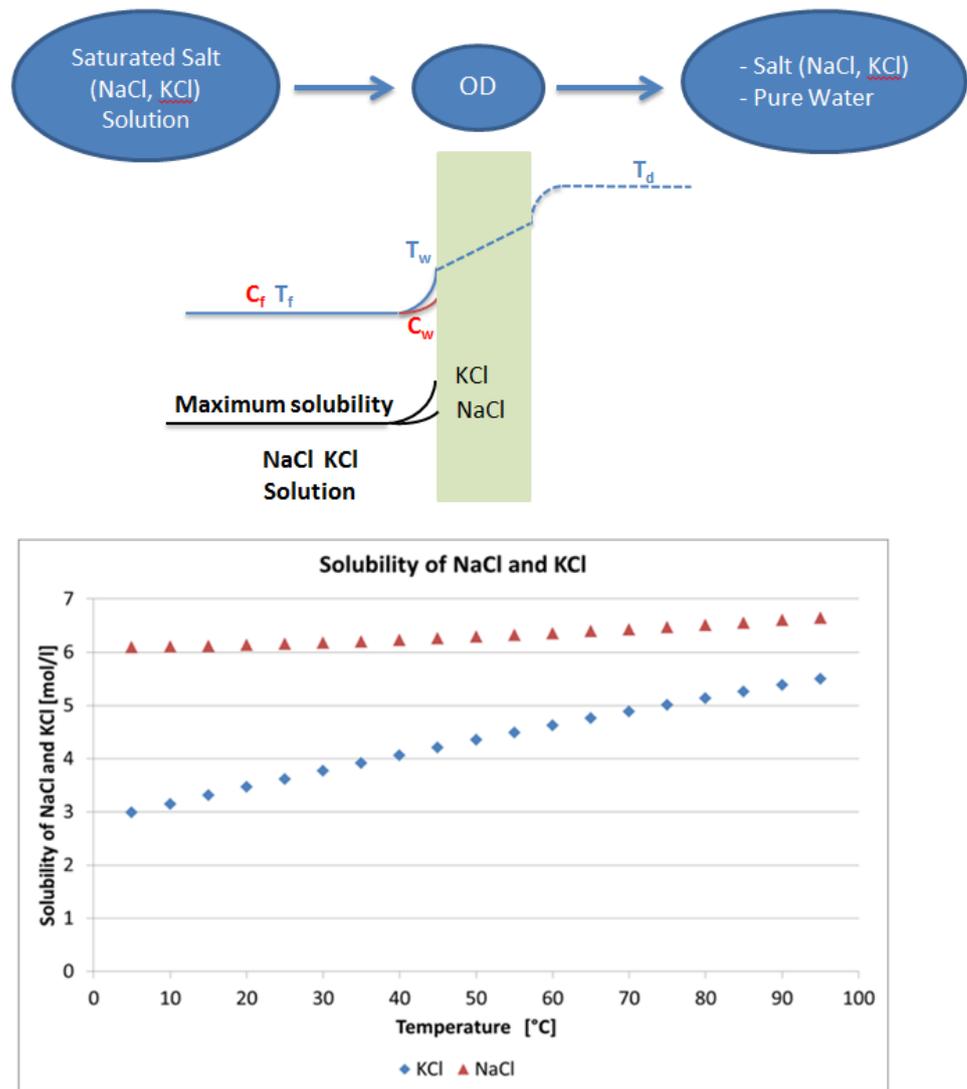


Figure 18: Expected temperature and concentration profile at operating OD at high distillate temperature level.

Considering the solubility-temperature profile of a NaCl or KCl solution, the solubility of NaCl increases in the boundary layer due to a higher temperature in the boundary layer compared to the temperature in the bulk at the feed side of the membrane. This effect in the boundary layer could be compensated by the effect of concentration polarization. Depending on the level of concentration polarization the OD principle might work or not. If the concentration polarization is too high, crystallization on the membrane will occur. Because the effect of temperature on solubility is higher in the case of KCl than in case of NaCl (see Figure 18) experiments of the OD effect on crystallization on the membrane have been started with a KCl solution. The equipment applied for the experiments is similar to the MD equipment. The setup is schematically shown in Figure 19.

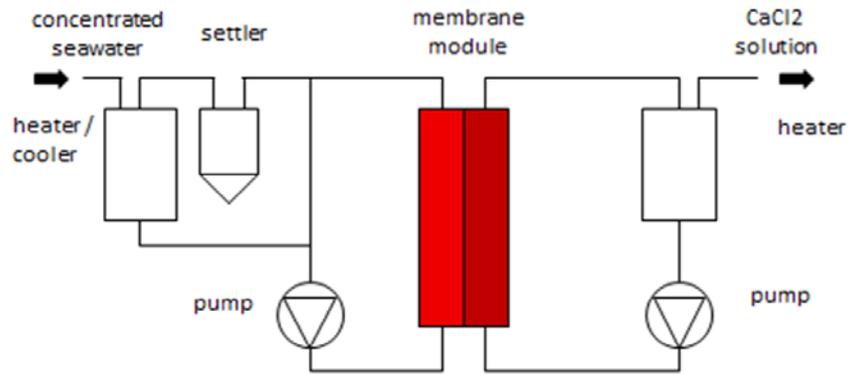


Figure 19: Laboratory setup for osmotic distillation (OD) experiments.

Both the feed solution and the draw liquid are circulated along the membrane in co-current flow.

A typical result of these experiments is shown in Figure 20.

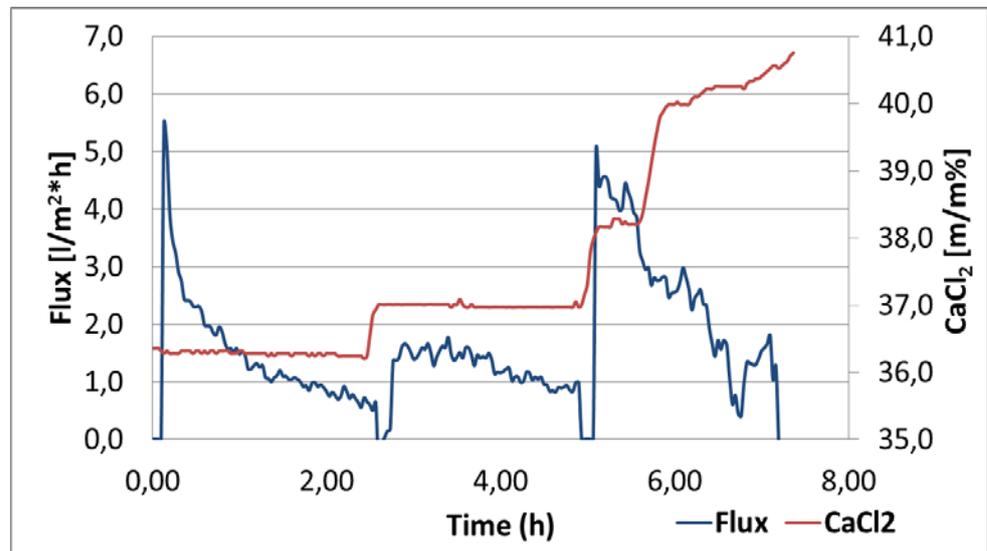


Figure 20: Flux ($l \cdot m^{-2} \cdot h^{-1}$) on the left y-axis against time during OD operation of a near saturated KCl solution with a $CaCl_2$ solution (with variable strength, see right y-axis in wt% $CaCl_2$) as drawing liquid. Temperature at distillate (344 K) side is 11 K higher than the temperature at the feed side (333 K).

Figure 20 shows a decrease in flux during time. In first instance the flux can be partly restored by increasing the strength of the drawing liquid, but after about 7 hours this is not possible anymore. Apparently the membrane is blocked by particles due to crystallization. In this experiment KCl is selected instead of NaCl, because the solubility of KCl is more dependent on the temperature and a stronger effect of OD near the membrane surface was expected. However, OD experiments with NaCl solutions gave similar results. Although addition of seeds to the NaCl solution in the MD operation was not successful, addition of seeds is also applied in the OD operation with NaCl solutions, because crystallization in the bulk phase is expected. A typical result of these experiments is shown in Figure 21.

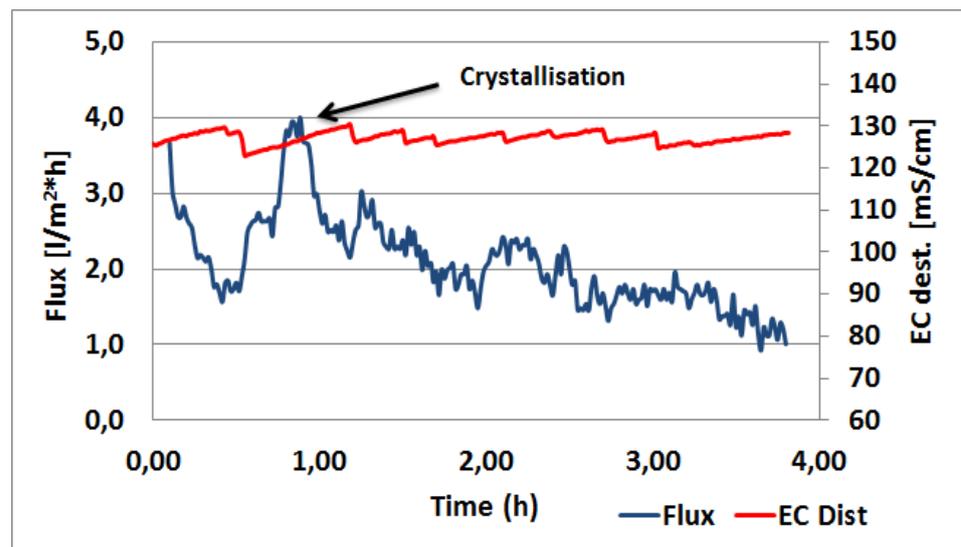


Figure 21: Addition of seeds in an OD operation with a NaCl solution.

Although the flux decline is less rapid compared to the results with MD there is still a flux decline observed. Addition of seeds seems no solution for the crystallization problem in OD operation with a nearly saturated NaCl solution.

4.2.2 *Anti-solvent crystallization in combination with MD/OD*

An alternative OD-route is explored, in which an extra anti-solvent crystallization process step is included. By addition of water-binding solvents like CaCl_2 to the nearly saturated NaCl brine, the bulk of NaCl can be precipitated in a separate mixer/separator, leaving a mother liquor which can be treated by OD to remove water and to crystallize the remaining NaCl. The CaCl_2 can be recycled.

The principle is schematically shown in Figure 22.

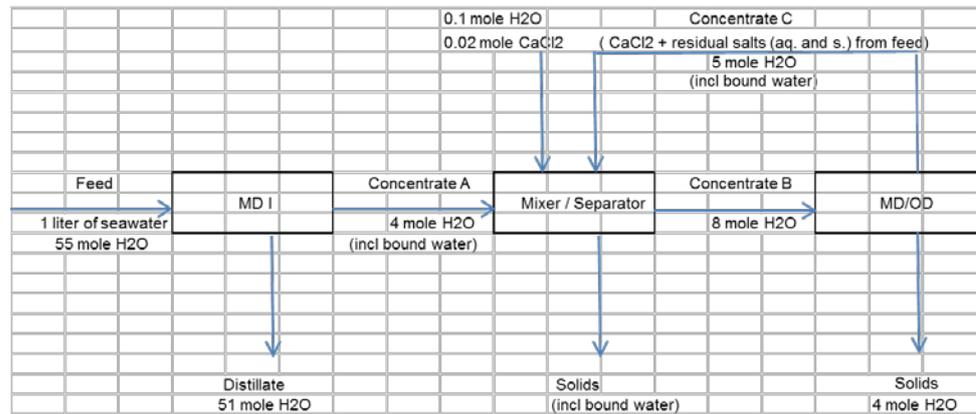


Figure 22: Principle of antisolvent crystallization applied on seawater in combination with MD and OD.

In Figure 22 seawater is concentrated with MD1 to near saturation of NaCl. A CaCl_2 solution is added and as a consequence salts are crystallized (mainly NaCl). The mother liquor is fed to an OD unit where additional salts precipitate and water is removed. The concentrated CaCl_2 solution with other salts from seawater is recycled to the mixer/separator unit. The loss in Calcium in the process is compensated by adding extra Calcium.

The antisolvent experiments have been carried out with CaCl_2 or MgCl_2 . By adding the antisolvent a large part of the NaCl is removed. As a result, the mother liquor contains less NaCl, but is still saturated. The assumption was, that due to the lower NaCl content MD or OD operation could run better.

4.2.2.1 Antisolvent experiments with seawater, CaCl_2 and OD

To obtain a solution with a lower NaCl content a 4 times concentrated seawater solution (1.8 kg) is added to a 40 wt% CaCl_2 solution (3 kg) at room temperature. As a result a large part of the NaCl precipitates. After separating the precipitate the remaining solution is added to the feed vessel. A 4 times concentrated seawater solution is continuously added to the feed vessel in a same amount as distillate produced (see Figure 19). The flux is monitored during the addition of seawater. A typical result is shown in Figure 23.

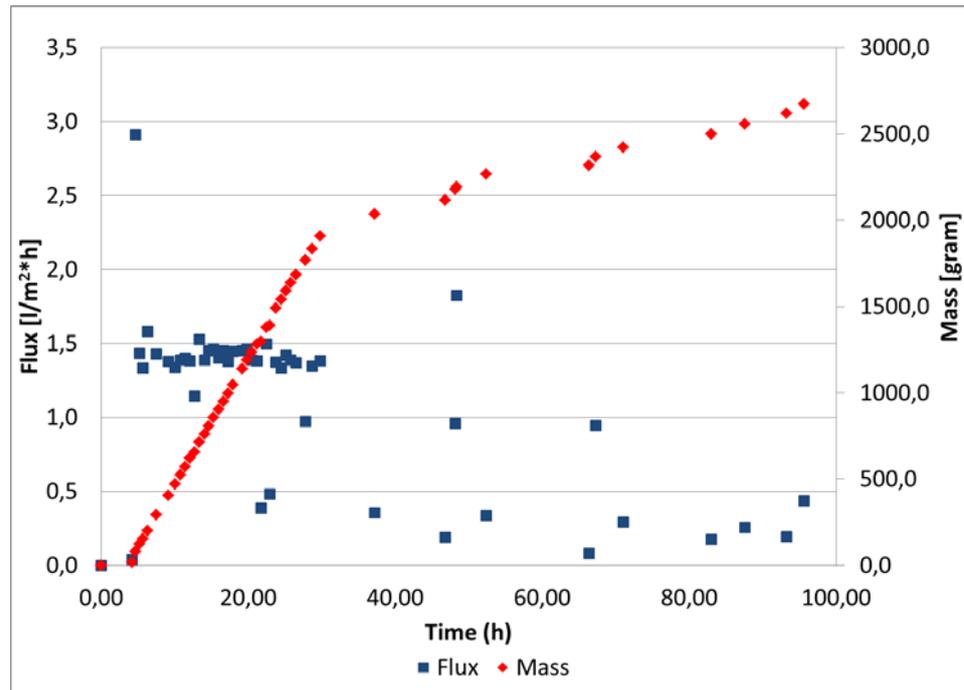


Figure 23: Flux as a function of time and mass of distillate produced. Feed is 4 times concentrated seawater after NaCl removal in a pretreatment which is added to a feed vessel containing a solution which is treated with a CaCl₂ solution to precipitate NaCl out of the seawater. $T_{\text{feed}} = 60\text{ }^{\circ}\text{C}$, $T_{\text{distillate}} = 70\text{ }^{\circ}\text{C}$. Draw liquid at distillate side is a 35-40 wt% CaCl₂ solution

From Figure 23 it follows that the flux remains on a constant level during the production of about 1700 grams of distillate. It should be noted that during this, considerable amounts of NaCl already precipitated. After that point the flux suddenly drops to a low level, but remains on that low level during further production of distillate. During the addition of seawater in the OD experiment the added NaCl continuously precipitated due to the presence of the high CaCl₂ concentration (about 40 wt%) in the solution. This is shown in Figure 24.

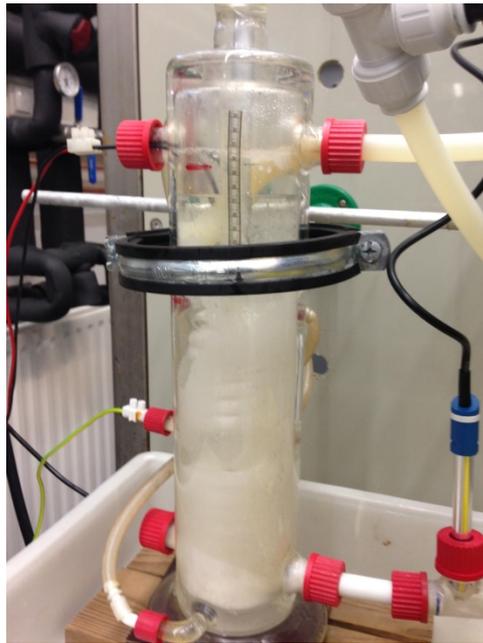


Figure 24: Precipitation of NaCl during addition of seawater to a saturated NaCl solution containing CaCl_2

In the Figure 25 until Figure 30 the concentration of several elements during the concentration experiment described above is shown.

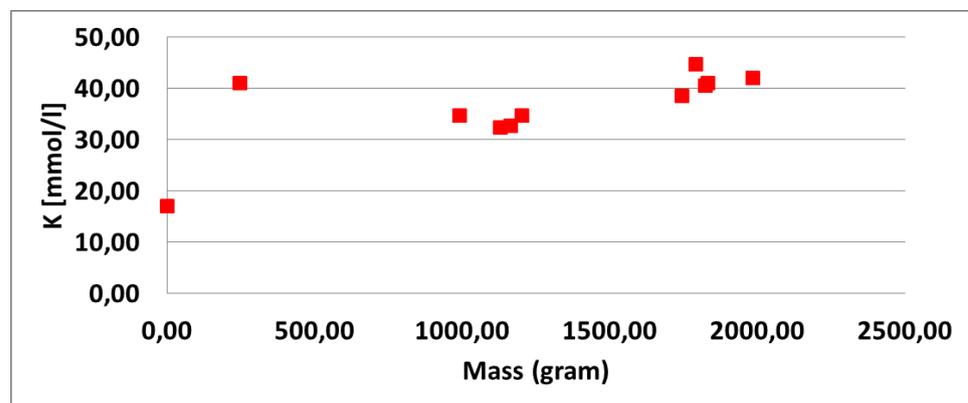


Figure 25: Potassium concentration as a function of produced distillate.

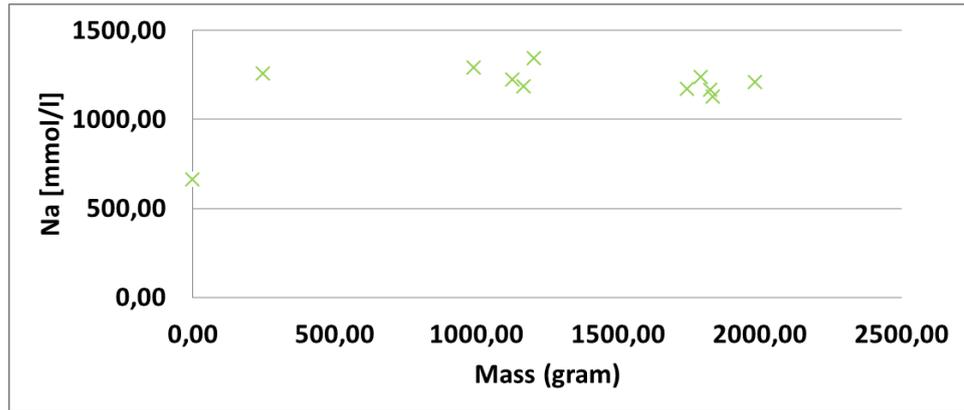


Figure 26: Sodium concentration as a function of produced distillate.

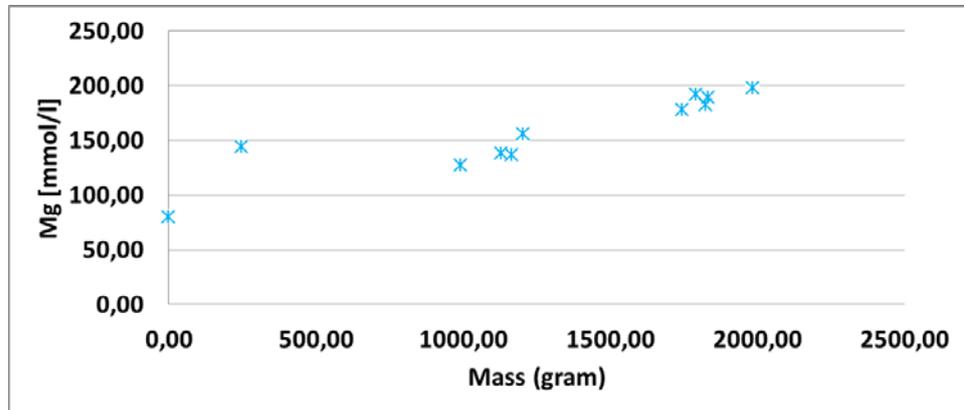


Figure 27: Magnesium concentration as a function of produced distillate.

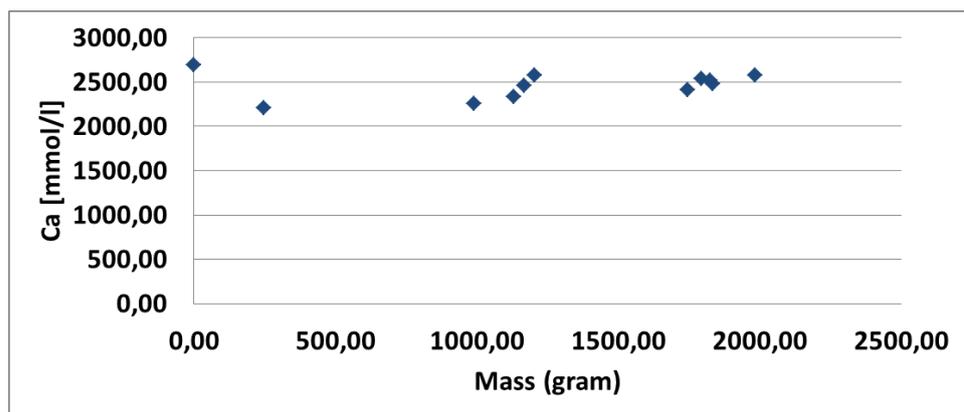


Figure 28: Calcium concentration as a function of produced distillate.

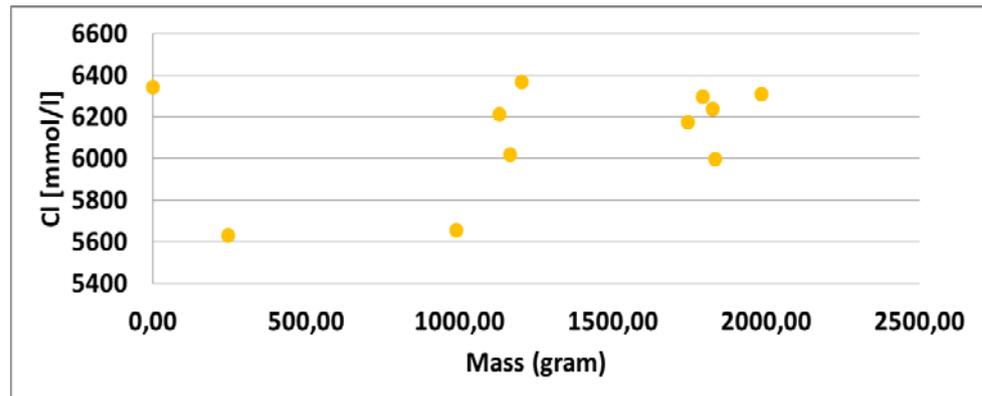


Figure 29: Chloride concentration as a function of produced distillate.

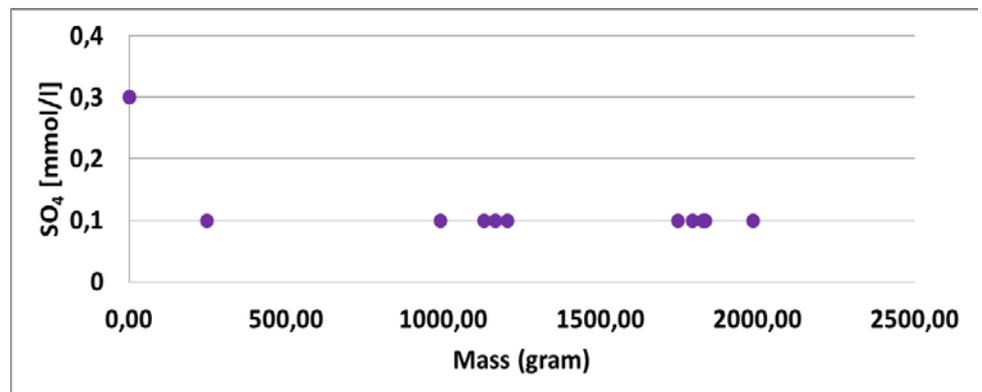


Figure 30: Sulphate concentration as a function of produced distillate.

Potassium: the concentration increases due to supply of fresh Potassium in the concentrated seawater.

Sodium: the concentration increases. This is not expected because the Sodium is already on saturation level at the start of the supply of concentrated seawater. Precipitation of Sodium salts could be expected and as a consequence no increase in Sodium concentration.

Magnesium: the concentration increases due to supply of fresh Magnesium in the concentrated seawater.

Calcium: the concentration is more or less constant. This is expected because the amount of Calcium added by the concentrated seawater supply is negligible compared to the amount present in the starting solution.

Chloride: the concentration increases due to the supply of Chloride in the concentrated seawater. Precipitation of Sodium Chloride should be expected because of an already saturated Sodium chloride solution at the start of the supply of seawater and as a consequence no increase in Chloride concentration. However, also an increase in Sodium concentration is observed what is not expected.

Sulphate: the start concentration is very low and even decreases due to the supply of Calcium in the concentrated seawater, resulting in CaSO₄ precipitate.

This experiment is repeated with different starting fluxes.

The starting flux can be controlled by controlling the driving force by adjusting the CaCl_2 concentration in the drawing liquid at the distillate side. The idea behind the variation in starting flux is the assumption that another size of crystals might be formed depending on the flux. Results of these experiments are shown in Appendix A.

The results in Figure 23, but also the results in Appendix A show that the flux suddenly drops after the production of 1500-2000 mg of distillate. A visual observation is that at the point of the drop in flux the solution becomes clear. Apparently the size of crystals changes during the supply of concentrated seawater and becomes so small that the solution becomes visibly clear. The very small crystals present may block the membrane. It is not clear why the crystals become that small.

It is studied if the concentration of seawater has an effect of the flux behaviour. To obtain the low NaCl content a 9 times concentrated seawater solution (1.8 kg) is added to a 40 wt% CaCl_2 solution (3 kg). As a result a large part of the NaCl precipitates. After separating the precipitate, the remaining solution is continuously added to the feed vessel in a same amount as distillate produced (see Figure 19). The flux is monitored during the addition of seawater. Figure 31 shows the results of this experiment.

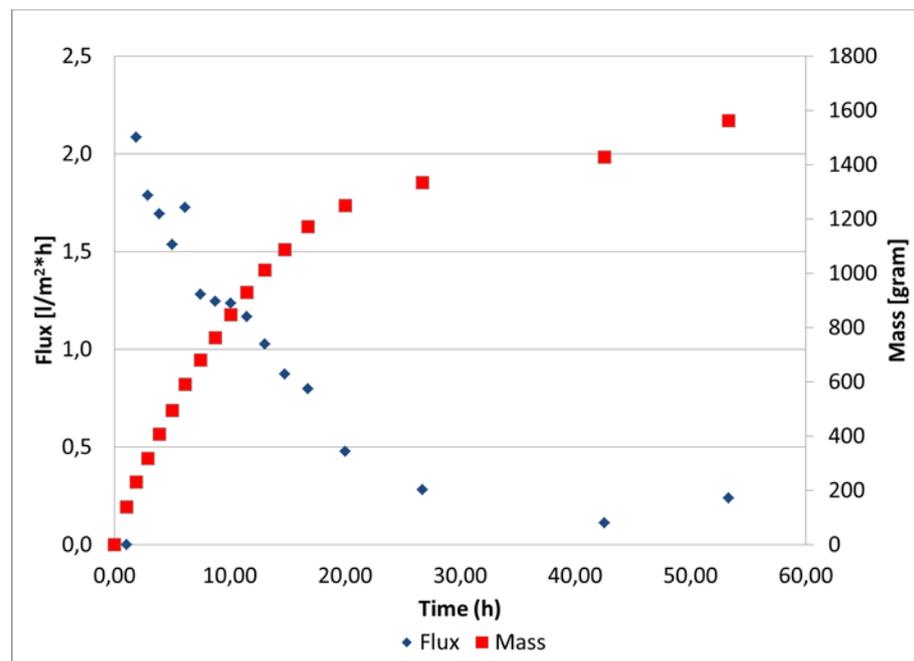


Figure 31: Flux and mass of distillate produced as a function of time. Feed is 9 times concentrated seawater which is added to a feed vessel containing a solution which is treated with a CaCl_2 solution to precipitate NaCl out of the seawater. $T_{\text{feed}} = 60\text{ }^\circ\text{C}$, $T_{\text{distillate}} = 70\text{ }^\circ\text{C}$. Draw liquid at distillate side is a 35-40 wt% CaCl_2 solution.

Figure 31 shows that the flux declines very fast. Even faster than in the previous experiment with less concentrated seawater. Apparently the amount of salt added plays a role in the point of flux decline. More salt added in time leads to a faster flux decline.

4.2.2.2 Antisolvent experiments with NaCl solution, CaCl₂ and OD

In order to determine the effect of the seawater matrix on the crystallization and the flux decline in the previous experiments, similar experiments have been executed using a pure NaCl solution (120 g/L) with a similar concentration as the NaCl concentration in the 4 times concentrated seawater. Flux results are shown in Figure 32.

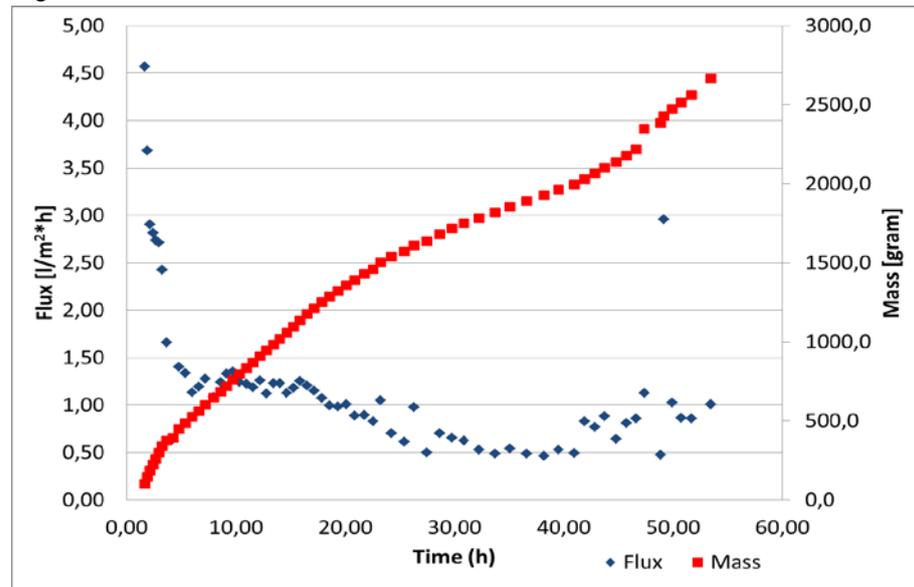


Figure 32: Flux as a function of time and mass of distillate produced. Feed is a concentrated NaCl solution (similar to the concentration of NaCl in 4 times concentrated seawater) which is added to a feed vessel containing a solution which is treated with a CaCl₂ solution to precipitate NaCl out of the seawater. $T_{\text{feed}} = 60 \text{ }^{\circ}\text{C}$, $T_{\text{distillate}} = 70 \text{ }^{\circ}\text{C}$. Draw liquid at distillate side is a 35-40 wt% CaCl₂ solution.

Flux decline is even faster than the flux decline with the concentrated seawater. The starting flux is higher than in the experiments with concentrated seawater. However, also at a lower starting flux (see Figure 33) the flux decline is faster with a pure NaCl solution compared to NaCl in seawater.

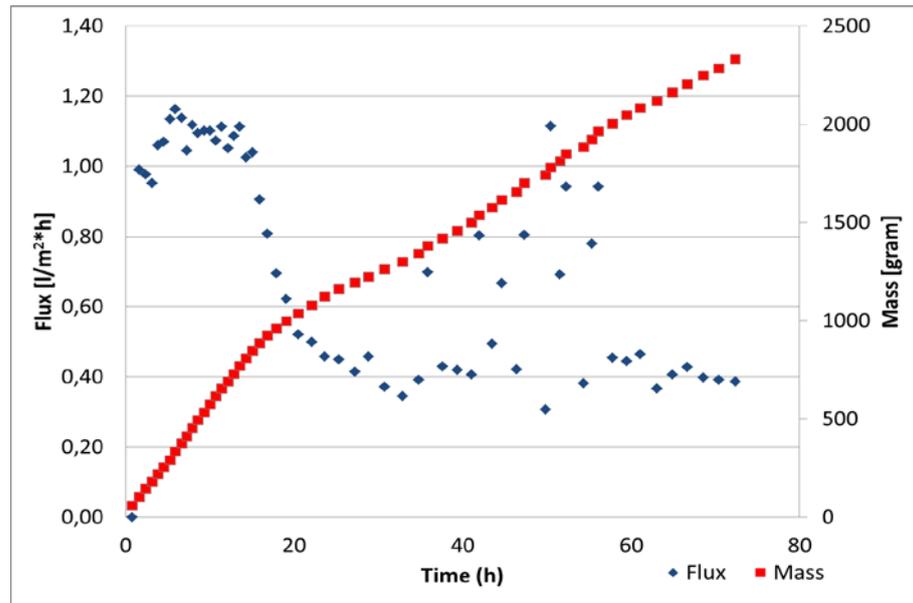


Figure 33: Flux as a function of time and mass of distillate produced. Feed is a concentrated NaCl solution (similar to the concentration of NaCl in 4 times concentrated seawater) which is added to a feed vessel containing a solution which is treated with a CaCl_2 solution to precipitate NaCl out of the seawater. $T_{\text{feed}} = 60\text{ }^\circ\text{C}$, $T_{\text{distillate}} = 70\text{ }^\circ\text{C}$. Draw liquid at distillate side is a 35-40 wt% CaCl_2 solution.

4.2.2.3 Antisolvent experiments with seawater, MgCl_2 and OD

Instead of using CaCl_2 as antisolvent also MgCl_2 can be applied. Advantage of MgCl_2 over CaCl_2 is the fact that there is less loss of Mg compared to Ca. Ca is partly removed by precipitation of CaSO_4 because of the SO_4 content in the supplied concentrated seawater. MgSO_4 however is soluble, so there is no loss of Mg, and less addition of chemicals is required. Another advantage is that the concentrated MgCl_2 solution is produced in the MDC process, after the crystallization of MgSO_4 (Figure 8). Thus, it does not need to be purchased. Disadvantage of a concentrated MgCl_2 solution is the handling because the solubility is more dependent on temperature.

To obtain the low NaCl content a 4 times concentrated seawater solution (1.8 kg) is added to a 40 wt% MgCl_2 solution (3 kg). As a result a large part of the NaCl precipitates. After separating the precipitate the remaining solution is added to the feed vessel. A 4 times concentrated seawater is continuously added to the feed vessel in a same amount as distillate produced (see Figure 19). The flux is monitored during the addition of seawater. Figure 34 shows the results of this experiment.

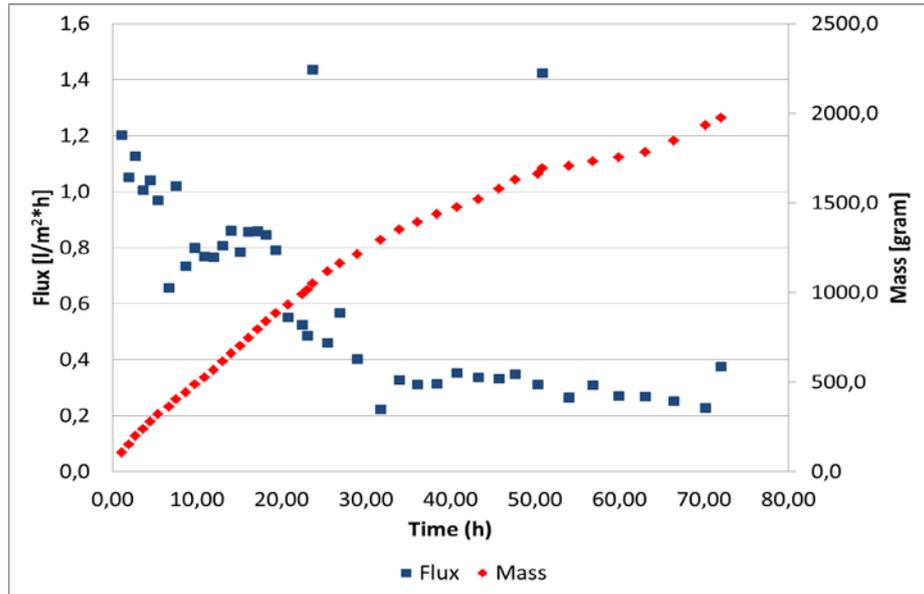


Figure 34: Flux as a function of time and mass of distillate produced in the OD experiment. Feed is 4 times concentrated seawater which is added to a feed vessel containing a solution which is treated with a $MgCl_2$ solution to precipitate $NaCl$ out of the seawater. $T_{feed} = 60\text{ }^\circ C$, $T_{distillate} = 70\text{ }^\circ C$. Draw liquid at distillate side is a 35-40 wt% $CaCl_2$ solution.

Figure 34 shows a flux decline to a constant level at a distillate production of about 1200 grams of distillate. This is faster than the results obtained with $CaCl_2$, but can be considered as a similar flux behaviour. In Figure 35 until Figure 40 the concentration of components in the seawater is monitored during distillate production.

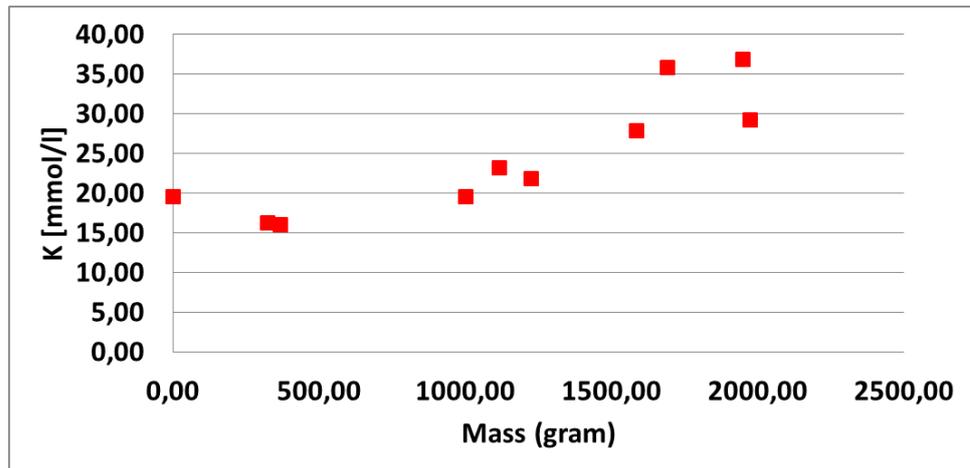


Figure 35: Potassium concentration as a function of produced distillate.

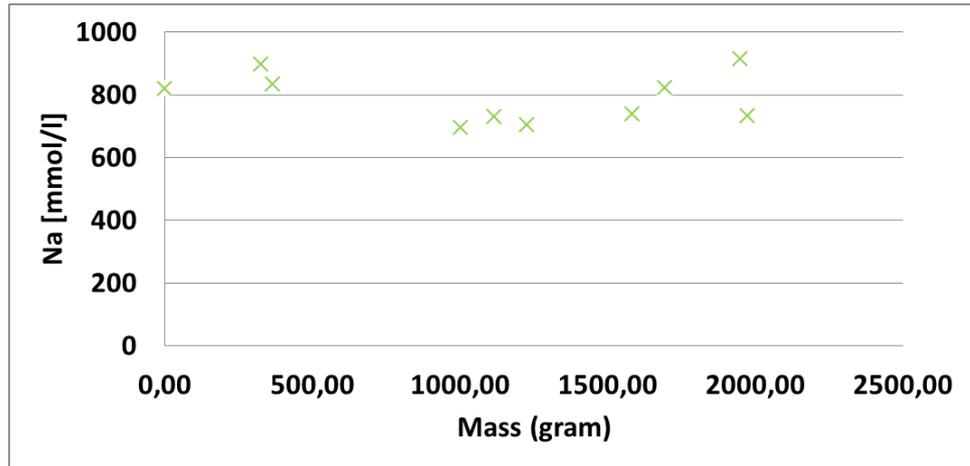


Figure 36: Sodium concentration as a function of produced distillate.

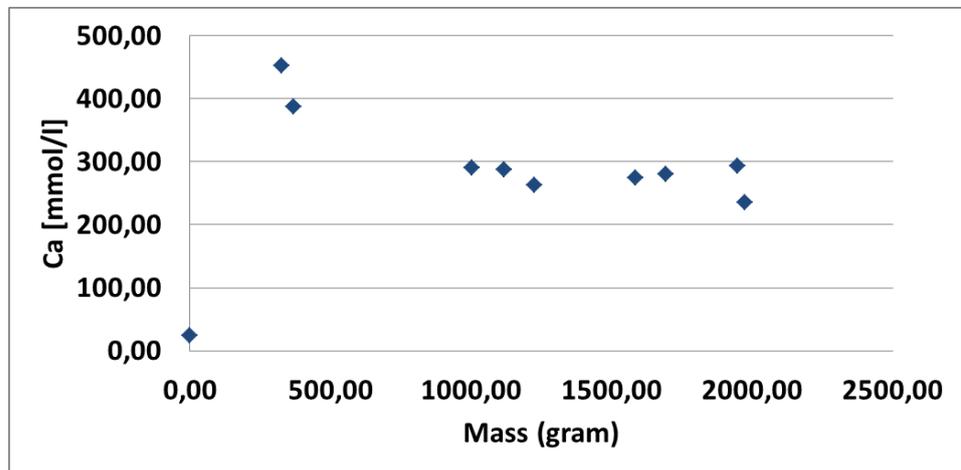


Figure 37: Calcium concentration as a function of produced distillate.

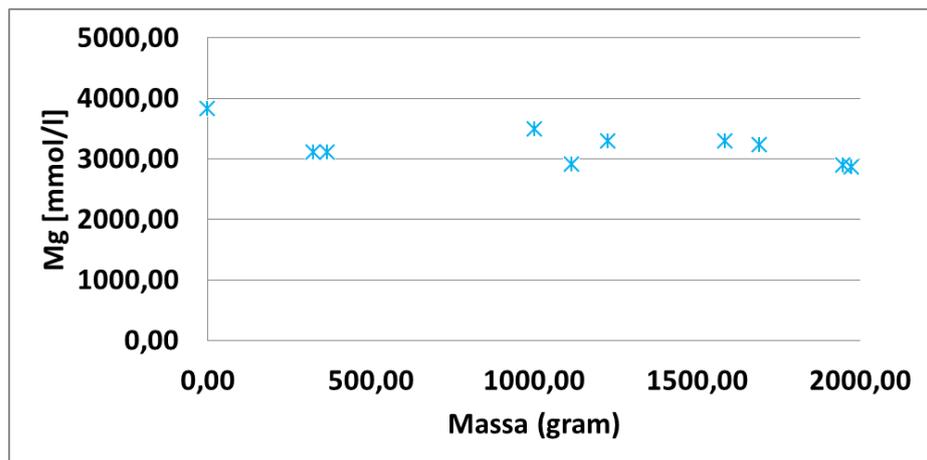


Figure 38: Magnesium concentration as a function of produced distillate.

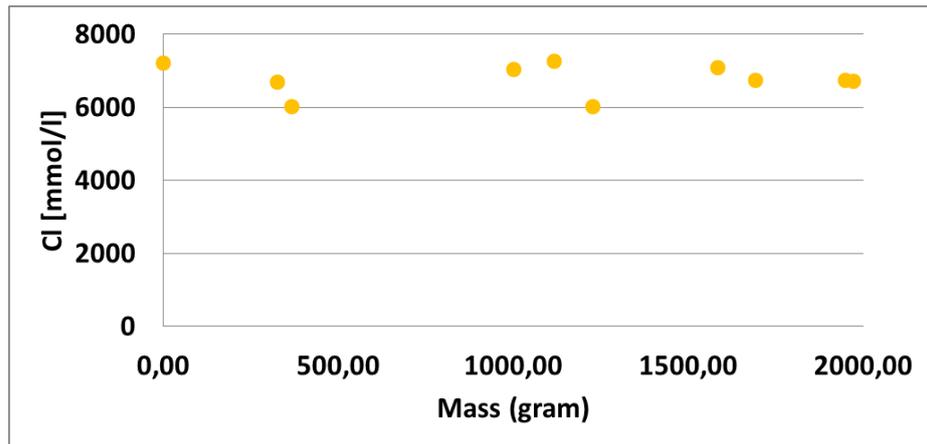


Figure 39: Chloride concentration as a function of produced distillate.

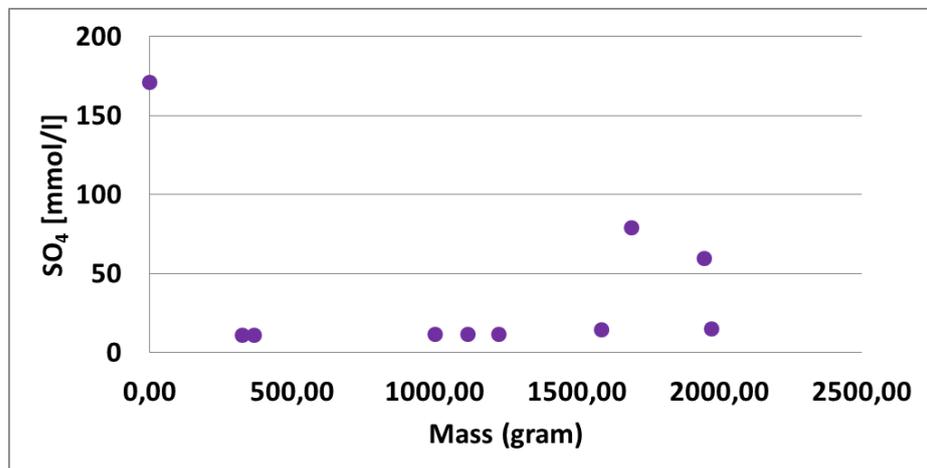


Figure 40: Sulphate concentration as a function of produced distillate.

Potassium concentration: As expected the K concentration increases during the production of distillate because of supply of fresh K in the concentrated seawater.

Sodium concentration: Because of precipitation of NaCl due to the presence of a high MgCl₂ concentration the concentration of Na in solution stays constant during the production of distillate. The sodium concentration is lower than in the similar experiment with CaCl₂ as antisolvent (Figure 26). Apparently the salting out effect of MgCl₂ is better than that of CaCl₂. There is no typical difference in the flux behavior.

Calcium concentration: Ca concentration reduces during distillate production because of precipitation of CaSO₄.

Magnesium concentration: Because of the very high Mg concentration the addition of Mg in the seawater supply has hardly any effect on the total concentration.

Chloride concentration: Because of the very high Cl concentration the addition of Cl in the seawater supply and the precipitation of NaCl have hardly any effect on the total dissolved chloride concentration.

Sulphate concentration: The SO_4 concentration is expected to decrease during distillate production because of the precipitation of CaSO_4 .

An alternative way of executing antisolvent experiments is to start with a concentrated MgCl_2 solution in the feed vessel and add concentrated seawater to the feed vessel. As a consequence a large part of the NaCl in the seawater will precipitate.

The experiment starts with a 36 wt% MgCl_2 solution in the feed vessel. 9 times concentrated seawater is supplied to the feed vessel in a way as shown in Figure 19. OD is executed with a 35-40 wt% CaCl_2 solution at the distillate side.

Flux results as function of time and distillate production as function of time are shown in Figure 41.

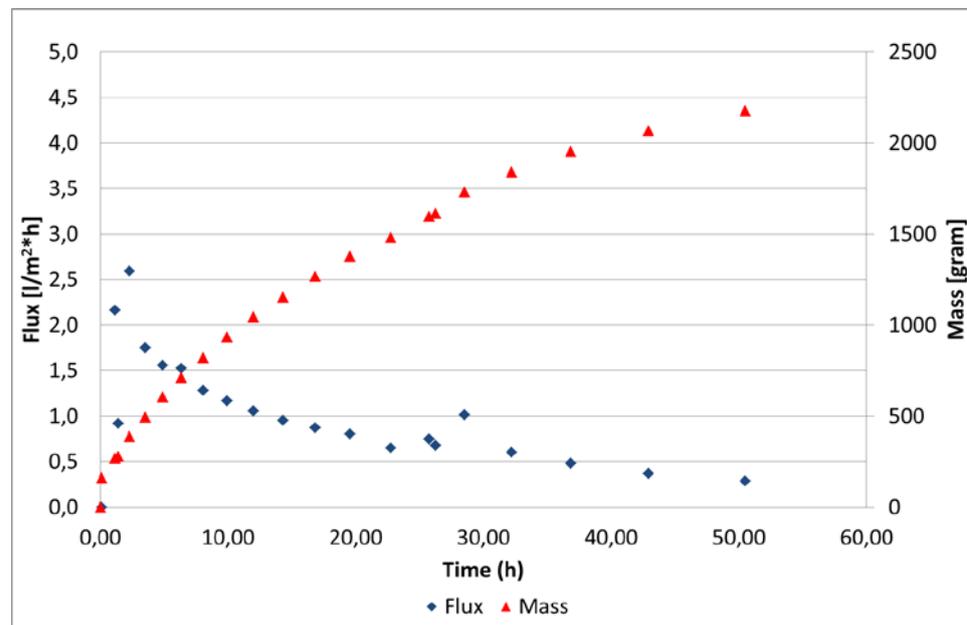


Figure 41: Flux as a function of time and mass of distillate produced. Feed is 9 times concentrated seawater which is added to a feed vessel containing a 36 wt% MgCl_2 solution to precipitate NaCl out of the seawater. $T_{\text{feed}} = 60\text{ }^\circ\text{C}$, $T_{\text{distillate}} = 70\text{ }^\circ\text{C}$. Draw liquid at distillate side is a 35-40 wt% CaCl_2 solution.

Figure 41 shows that there is still a flux decline, but the flux decline is slower compared to e.g. the situation in Figure 34. The increase in flux after about 30 hours is caused by the addition of CaCl_2 to the drawing liquid resulting in an increase in driving force and an increase in flux.

Figure 42 until Figure 47 show the concentration of the components in the feed vessel during the production of distillate.

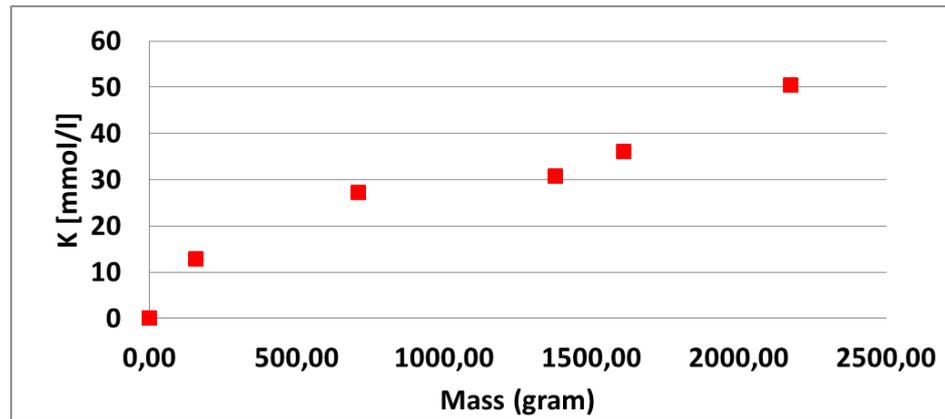


Figure 42: Potassium concentration as a function of produced distillate.

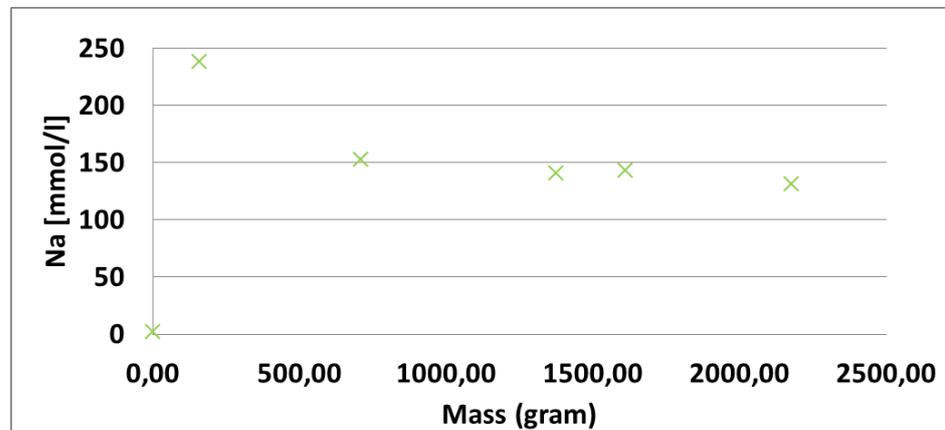


Figure 43: Sodium concentration as a function of produced distillate.

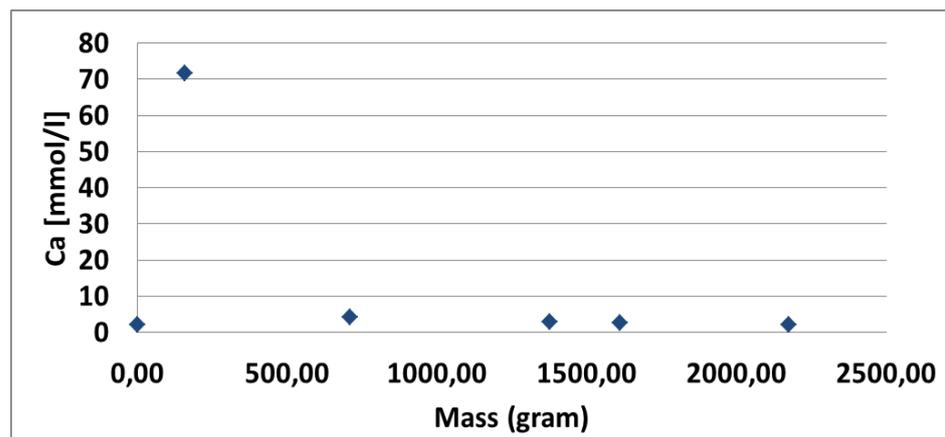


Figure 44: Calcium concentration as a function of produced distillate.

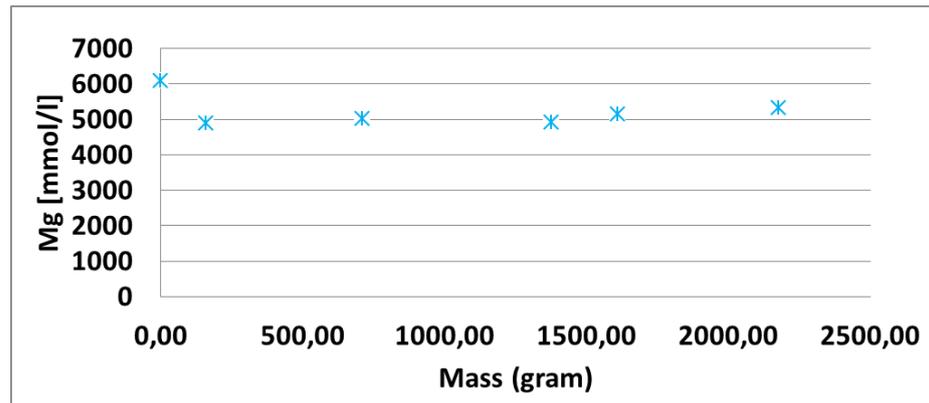


Figure 45: Magnesium concentration as a function of produced distillate.

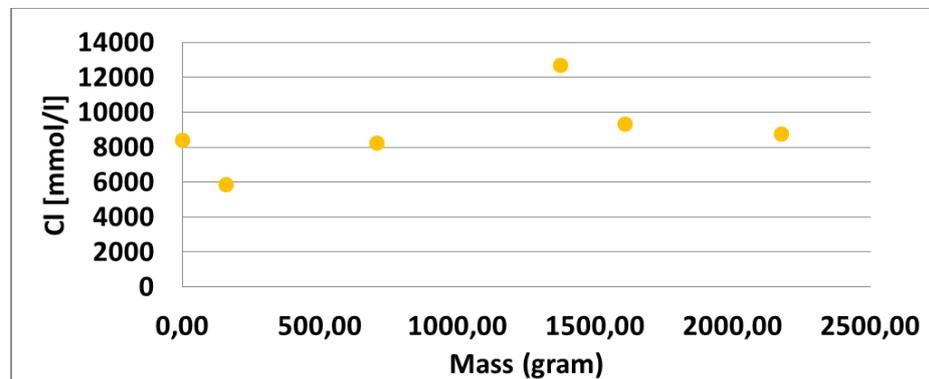


Figure 46: Chloride concentration as a function of produced distillate.

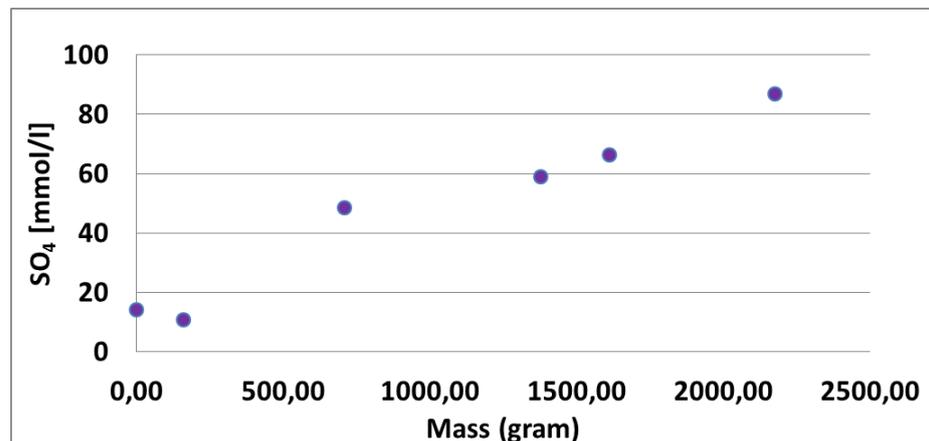


Figure 47: Sulphate concentration as a function of produced distillate.

The concentration profile as a function of produced distillate for most of the components is as expected. Remarkable is the increase in sulphate concentration during concentration. This is different from the previous experiments, but expected considering the concentration level of Calcium. In the 9 times concentrated seawater solution the Calcium concentration is low, so only a limited part of the sulphate present will precipitate as CaSO_4 .

5 Process for the recovery of salts from seawater

5.1 Mass balance of salts precipitating from sea water

During removal of water from sea water (composition in Table 6) at temperatures around 60 °C (MD temperature) the following steps take place (see Figure 8):

1. Until a cf (concentration factor) = 1.8 , (meaning 45% water removal) no super saturation of salts occurs.
2. Starting from cf = 1.8 CaCO₃ crystallizes (total: ca. 2.3 mMol/l).
3. Starting from cf = 3.8 (74% water removal) also CaSO₄ crystallizes (total ca. 7.7 mMol/l), together with the remaining CaCO₃.
4. At cf = 10.6 (90.6% water removal!) super saturation of NaCl takes place (total 457 mMol/l sea water). It may be expected that most of the calcium salts of step 2. and 3. have been separated at this point.
5. Not earlier than at cf = 70 (after 98.6% water removal) the MgSO₄-salts reach saturation. Probably the heptahydrate (epsomite) is crystallized first; however also mono- and hexahydrates can be formed, especially at higher cf and T. In total ca. 19.8 mMol/l MgSO₄-salts will precipitate (until the sulphate ions are depleted).
6. Starting from cf = ca. 100 (99% water removal) sylvite (KCl) is formed: total ca. 9.7 mMol/l sea water.
7. Besides NaCl also MgCl₂ is a major solute in sea water: it is formed at a cf = ca. 200-500 (99.5 – 99.8% water removal), in total ca. 35.4 mMol/l (depletion of both Mg⁺ and Cl⁻ ions).
8. What remains is a small amount of bittern, composed of saturated MgCl₂, remaining NaCl, and the very soluble salt MgBr₂.

The produced amounts are summarized in Table 4, for the treatment of 1m³/s of sea water. For the desalination of the seawater a process with multiple MD en OD steps is proposed.

Table 4: Mass balance and heat consumption for MDC of 3600 m³/h (1 m³/s) sea water. MD = membrane distillation; OD = osmotic distillation; PR = performance ratio (evaporation enthalpy of produced water / heat input).

Salt type	Concentr. factor (end)	Salt production (ton/h)	Water production (ton/h)	Heat input (GJ/h)	Heat input (MW)	Process step and performance ratio (PR)
none	1.8	-	1585	285	81	MD1 13
CaCO ₃	3.8	1.0	1040	410	114	MD2.1 6
CaSO ₄	10.6	4.0	600	470	130	MD2.2 3
NaCl	70	96.5	290	680 ¹⁾	194 ¹⁾	OD1 1
MgSO ₄ (excl H ₂ O)	90	8.6	10	25 ¹⁾	7 ¹⁾	OD2 1
KCl	100	2.6	5	10 ¹⁾	3 ¹⁾	OD3 1
MgCl ₂	500	12.0	30	70 ¹⁾	20 ¹⁾	OD4 1
MgBr ₂	> 1000	0.3	5	-	-	Bittern -
TOTAL		125	3565	1165 ¹⁾	325 ¹⁾	

¹⁾ Based upon PR = 1; The OD heat is recycled to MD process steps, see Figure 2

5.2 Heat balance for treatment of sea water

Table 4 and Figure 48 show the thermal energy inputs per process step. Here, the heat required for MD (MD1, MD2.1 and MD2.2) are based upon lab measurements. For all subsequent OD steps a performance ratio of 1 is assumed, meaning a one-step regeneration of draw liquid without heat recovery. This is a logical route, because all this heat can be re-used as input in the MD-steps, as is depicted in Figure 48. The operation of the OD steps in practice is not successful yet (no successful experiments up to now), which means that the heat analysis is a theoretical analysis.

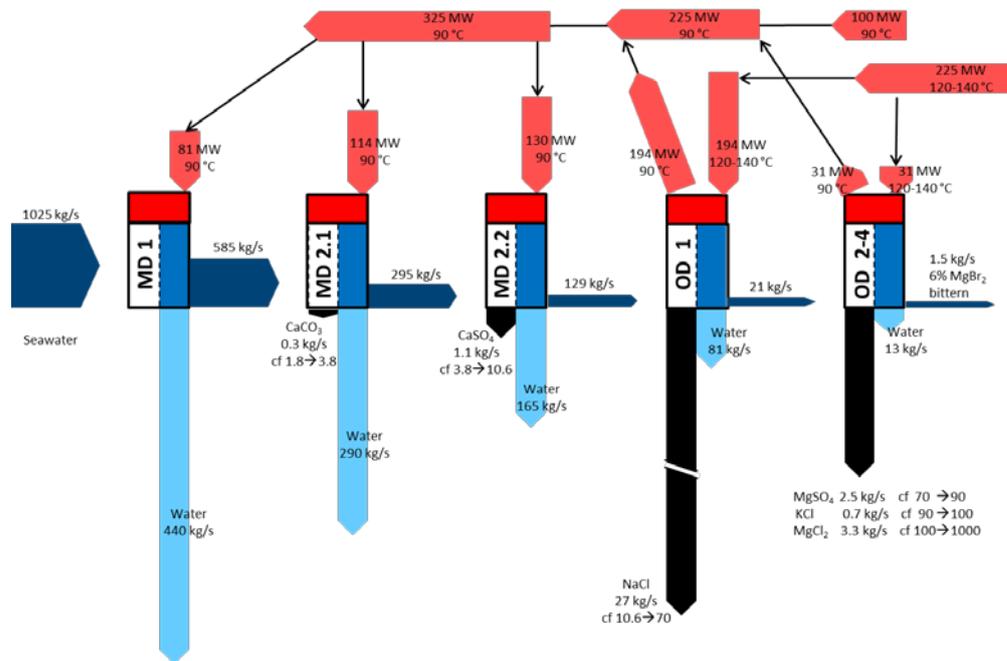


Figure 48: Mass and thermal heat balance for ZLD (Zero Liquid Discharge) treatment of 1 m³/s of seawater by a combined MD/OD process

5.3 Economic considerations for the combined MD/OD process

A preliminary cost estimation has been made for the treatment of seawater (1 m³/s) with a combined MD/OD process. The figures and assumptions are shown in Table 5. The operation of the OD steps in practice is not successful yet, which means that the cost estimation is based on the theoretical assumption that OD will be successful in the future.

Table 5: Preliminary cost estimation for the treatment of seawater with a combined MD/OD process (cost estimation for smaller capacity and less operating hours in Appendix C).

<i>Process step</i>	<i>Water production (ton/h)</i>	<i>Membrane surface (. 1000 m²)</i>	<i>Investment Modules (M€)</i>	<i>Investment Hardware (M€)</i>	<i>Capex (€/m³ sea water)</i>	<i>Heat costs (€/m³ sea water)</i>	<i>Capex + heat + electricity (€/m³ sea water)</i>
MD1	1585	396	13.9	21.2	0.461	0.026	0.73
MD2	1640	273	9.6	14.6	0.318	0.080	0.40
OD	340	68	2.4	3.7	0.080	0.327	0.40
TOTAL	3565	737	25.8	39.5	0.859	0.43	1.53
TARGET						1.50	4.00
<p><i>Criteria:</i></p> <ul style="list-style-type: none"> - 8000 production hours / year (treatment of 28.8 Mm³/year sea water) - Module price: € 100 /m² (estimation for 2015); replacement in 4 years - Additional hardware: estimated at € 500,- per m³/day of sea water (3 x the Memstill estimation for sea water desalination, to account for the extra components for crystallization, solids handling, draw liquid regeneration etc.). - Interest /depreciation auxiliary hardware: Annuity = 16%. - Electricity: total 3 kWh per m³ sea water (4 x Memstill), ad € 0,08 = € 0,24 / m³ sea water. - Waste heat costs: € 1.00 per GJ (363 K) resp. € 1,50 per GJ (393 K) steam. - Maintenance, labor: 5% of Hardware investment (not included in table 5). 							

In the Figure 49, Figure 50 and Figure 51, the effect of the MD flux, OD flux and the heat price on the total costs are shown. The calculations are based on the laboratory results and a module price of € 35 /m² (price on longer term).

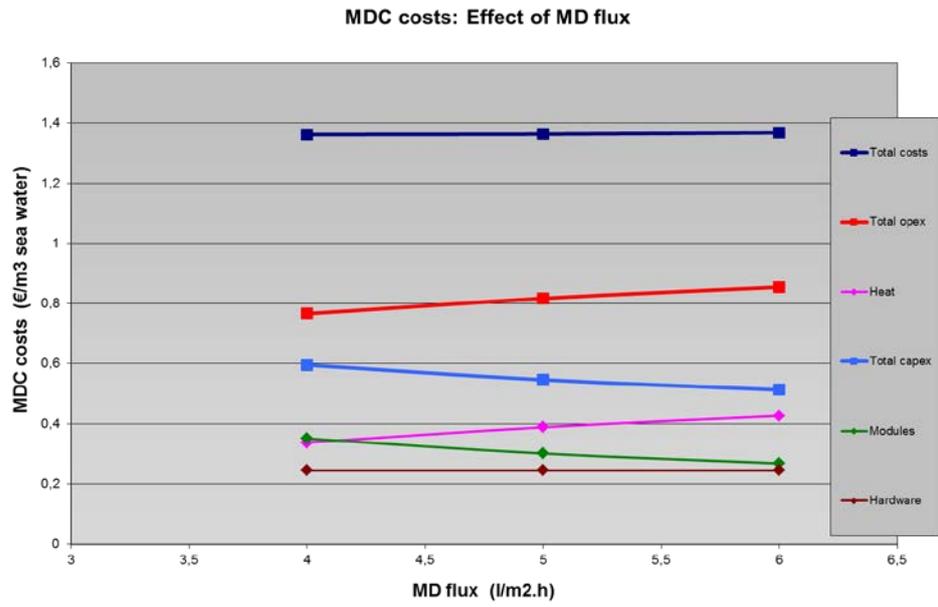


Figure 49: The effect of the MD flux on the MDC costs.

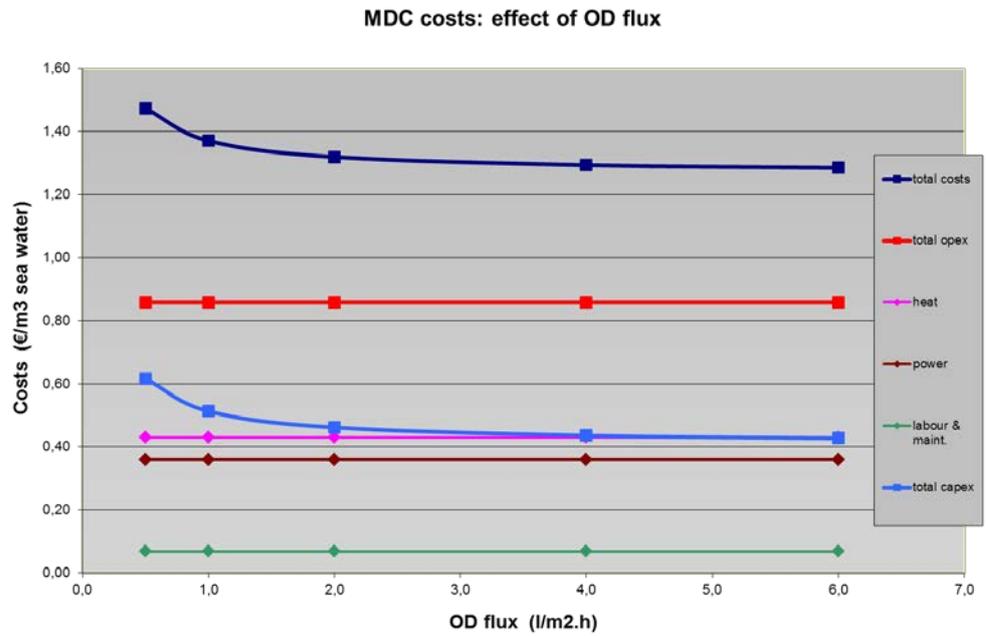


Figure 50: The effect of the OD flux on the MDC costs.

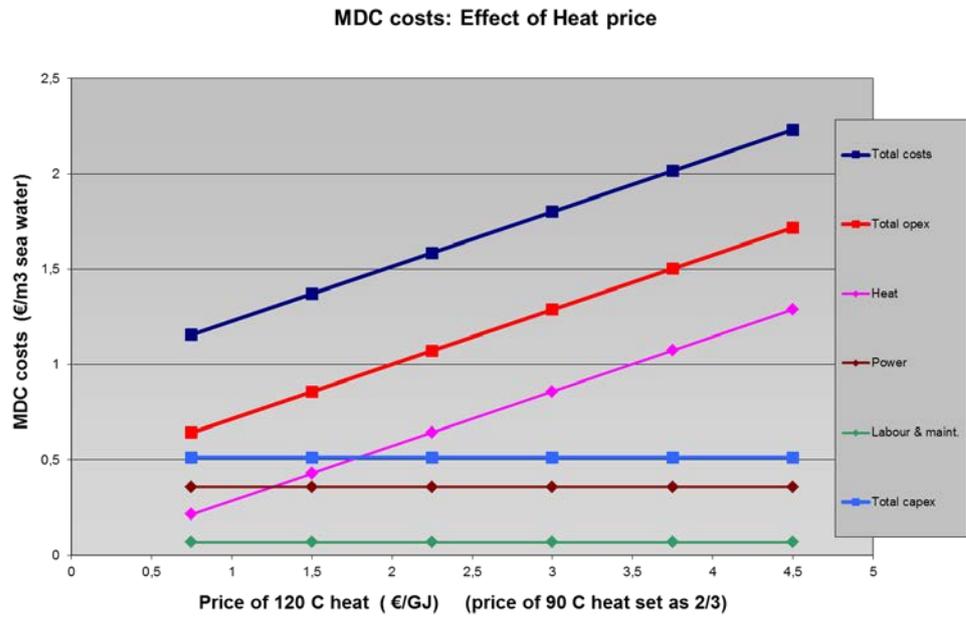


Figure 51: The effect of the heat price on the MDC costs.

It is obvious that the heat price largely affects the MDC costs as can be expected. Because only 10% of the seawater is treated by OD, the effect of the OD flux on the MDC costs is limited (costs are based on the originally amount of water to be treated).

In Appendix C cost tables, similar to Table 5, are given for smaller capacity and less production hours/year.

6 Pilot plant experiments

6.1 Introduction

Pilot plant experiments have been executed with seawater in 2 different pilot plants with 2 different types of modules. Aim of the pilot plant experiments is to concentrate the seawater to a maximum concentration level of NaCl before crystallization of NaCl. Flux behaviour during concentration is an indication of scaling of Ca-salts on the membrane. Although scaling prevention of Ca-salts was not completely successful on laboratory scale, these experiments have been carried out to determine the scaling behaviour of Ca-salts on a more practical scale, where heat transfer and flow profiles will be different from those in the laboratory experiments.

6.2 Pilot plant 1

6.2.1 Principle

Pilot plant 1 is based on the Memstill concept (see Figure 52).

Principle of Memstill-process

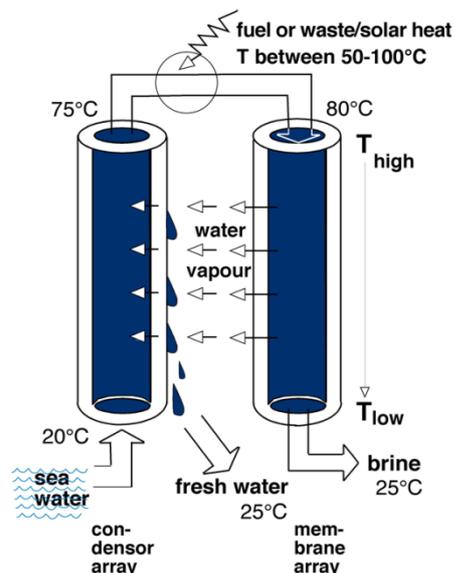


Figure 52: Principle Memstill process.

A Memstill module consists out of a membrane part and a condenser part. In Figure 52 the principle is depicted based on a hollow fibre membrane and condenser, but a flat membrane and flat condenser is also an option. Seawater enters the condenser at a low temperature. It flows counter currently with the seawater which is externally heated after passing the condenser and which is flowing through the membrane.

Because of applying a hydrophobic membrane water vapour passes through the membrane and condenses on the condenser. Driving force is the water vapour pressure difference due to the temperature difference. Memstill is a liquid gap membrane distillation process.

In the pilot plant 1 a flat membrane Memstill module is applied (construction see Figure 53).

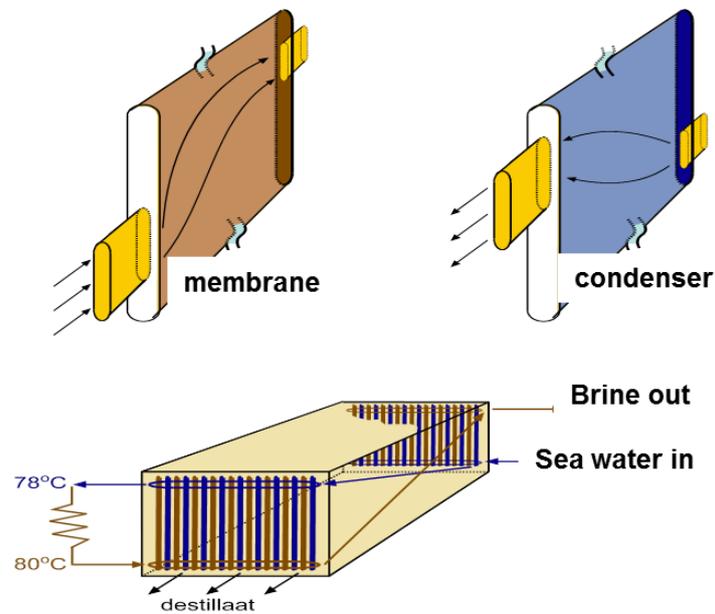


Figure 53: Construction of a flat plate Memstill module.

The pilot plant is shown in Figure 54.



Figure 54: Memstill module in a small scale pilot plant.

The pilot contains 2 modules with a membrane surface area of 18 m² each.
Membrane: Surface modified PES (M-06).

6.2.2 Experiments and results

Experiments have been executed with seawater from the coastal North Sea area near the Netherlands (composition: see Appendix D). Calflo seeds (Calcium silicate) are added to prevent scaling of ca-salts (as CaCO₃) on the membranes. Due to the design of the equipment it was not possible to keep the seeds suspended in the equipment (seeds settled in the membrane module). Flux results are shown in Figure 55 and Figure 56. In Figure 55 the flux is shown during concentration, while in Figure 56 the flux is shown as a function of time at a constant concentration factor (based on conductivity and related to the conductivity of the start solution).

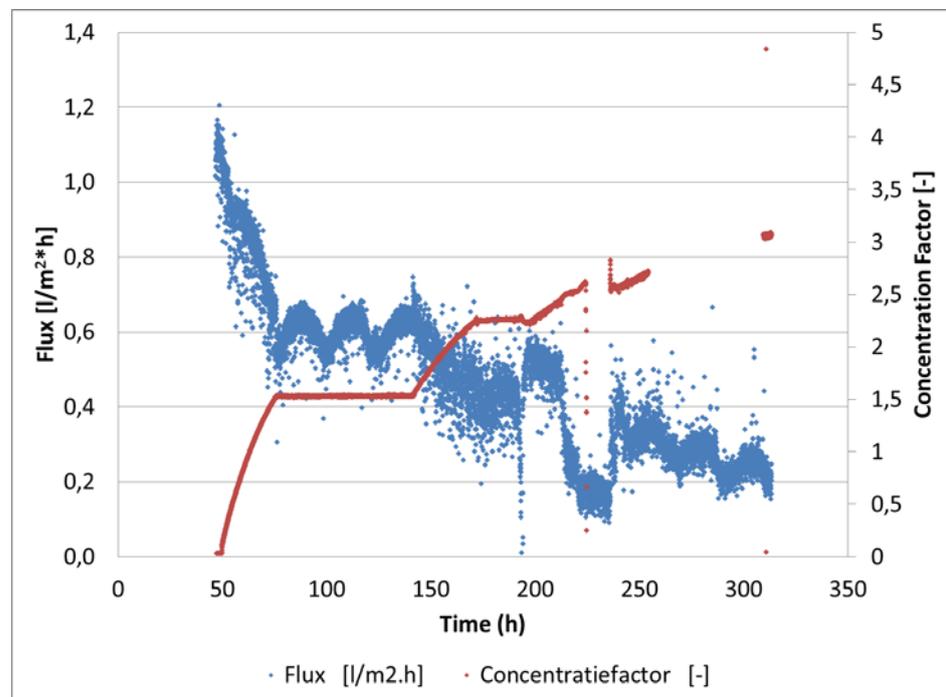


Figure 55: Flux (blue dots, l.m⁻².h⁻¹, left y-axis) during time while concentrating the seawater in pilot plant 1. Concentration factor (red line) on right y-axis. Feed temperature is about 74 °C. Distillate temperature is about 57 °C.

The concentration factor starts below 1, because the installation is filled with demineralized water at the start. After the start the contents will be replaced by seawater (coastal water).

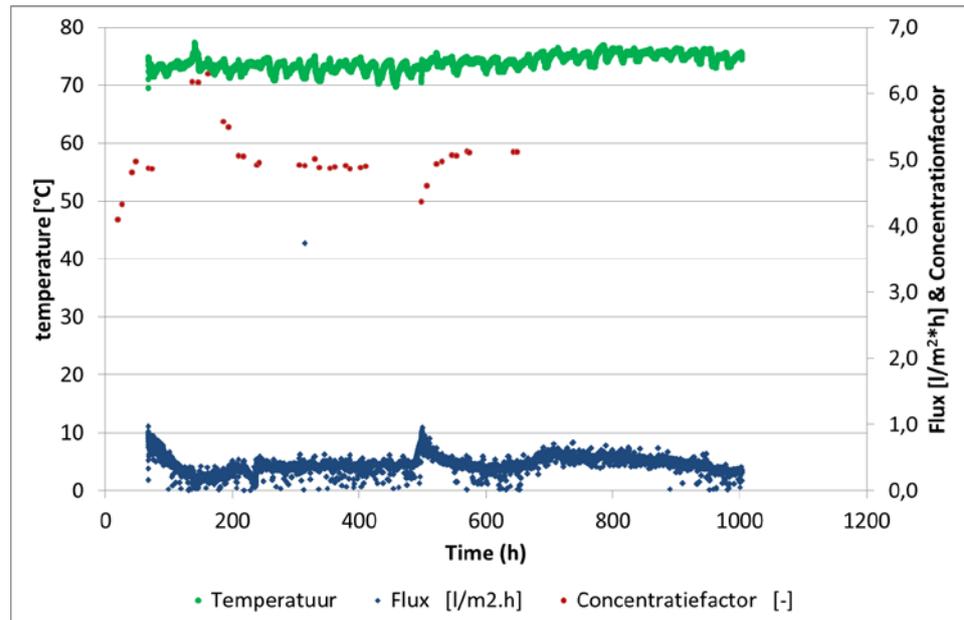


Figure 56: Flux (blue dots, $\text{l}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, right y-axis) during time at a constant concentration factor (red dots, right y-axis). Feed temperature is about 74 °C. Distillate temperature is about 57 °C.

During concentration the flux decreases, but stabilizes at a constant concentration factor of about 5. The decrease in flux is partly due to the increasing concentration and a result of the decreasing driving force across the membrane. Scaling on the membrane seems not to be an issue given the rather constant flux in Figure 56. Ca-salts precipitated during concentration, but apparently not on the membrane. This is shown in Figure 57, where the concentration factor of the elements is shown related to an average composition of seawater. This composition is different from the initial composition of the coastal water used. The average composition of seawater is given in Table 6.

Table 6: Average composition of seawater.

Element	Concentration (mg/l)	Element	Concentration (mg/l)
Oxygen	$8.57 \cdot 10^5$	Molybdenum	0.01
Hydrogen	$1.08 \cdot 10^5$	Zinc	0.01
Chlorine	19000	Nickel	0.0054
Sodium	10500	Arsenic	0.003
Magnesium	1350	Copper	0.003
Sulphur	885	Tin	0.003
Calcium	400	Uranium	0.003
Potassium	380	Chromium	0.0003
Bromine	65	Krypton	0.0025
Carbon	28	Manganese	0.002
Strontium	8.1	Vanadium	0.001
Boron	4.6	Titanium	0.001
Silicon	3	Cesium	0.0005
Fluoride	1.3	Cerium	0.0004
Argon	0.6	Antimony	0.00033
Nitrogen	0.5	Silver	0.0003
Lithium	0.18	Yttrium	0.0003
Rubidium	0.12	Cobalt	0.00027
Phosphorus	0.07	Neon	0.00014
Iodine	0.06	Tungsten	0.0001
Barium	0.03	Lead	0.00005
Aluminium	0.01	Mercury	0.00004
Iron	0.01	Cadmium	0.00011
Indium	< 0.02	Selenium	0.0000

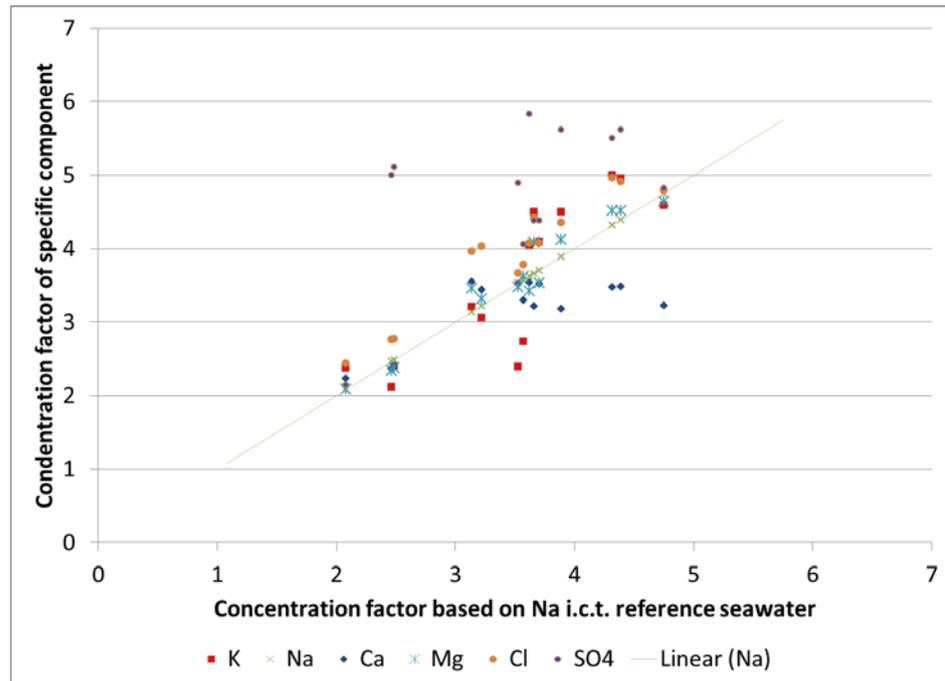


Figure 57: Concentration factor (related to seawater) of the elements in the coastal water during concentration.

From Figure 57 it follows that concentration level of Ca does not increase anymore after a concentration factor of about 3.5. This is expected because of the expected precipitation of CaCO_3 at that point. So, precipitation of Ca-salts occur, but this does not seem to affect the flux.

The composition of the coastal water used is given in Figure 58.

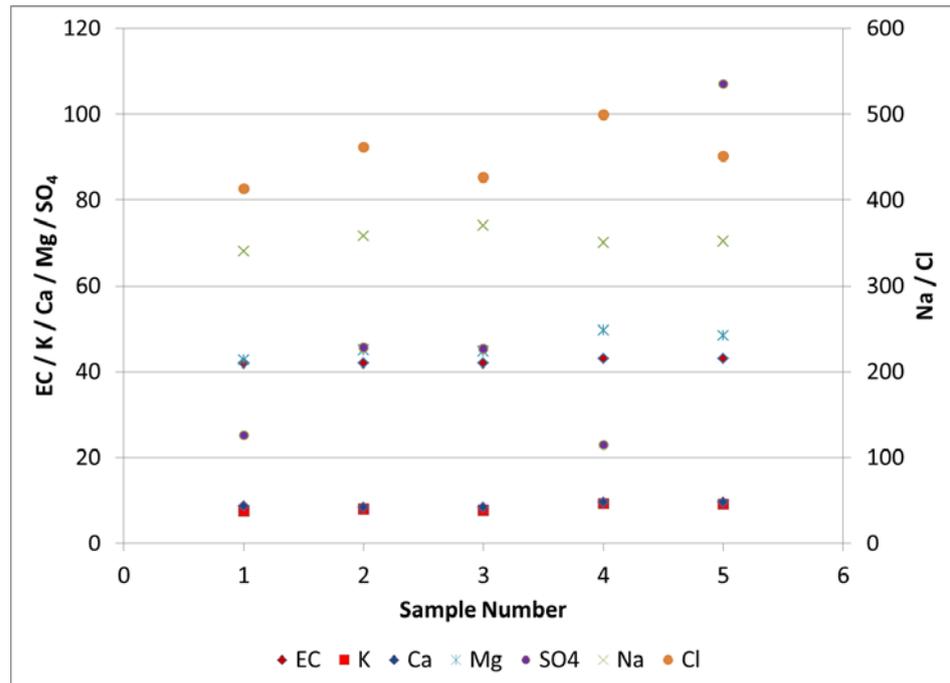


Figure 58: Composition of 5 samples of coastal water. EC in mS/cm, K, Ca, Mg, SO₄, Na, Cl in mmol/l.

The concentration of elements in the coastal water is about 90% of the average concentration of those elements in seawater.

The experiments with the Memstill pilot look promising. However, it was not possible with this installation to obtain a higher concentration factor than 6. For that reason additional experiments have been carried out with a direct contact membrane system from Aquastill.

6.3 Pilot plant 2

6.3.1 Principle

Pilot plant 2 is based on the principle of direct contact membrane distillation (DCMD). The principle is shown in Figure 6 and the flow scheme of the pilot is shown in Figure 2.

A picture of the pilot plant is shown in Figure 59.

One membrane module with a membrane surface area of 10.8 m² is installed.



Figure 59: DCMD pilot plant from Aquastill.

6.3.2 *Experiments and results*

Experiments have been executed with coastal (sea)water (Table 4.1, Appendix D). The water is concentrated without the addition of seeds.

In Figure 60 the concentration factor of components in the coastal water are related to the sodium concentration in seawater (Table 6).

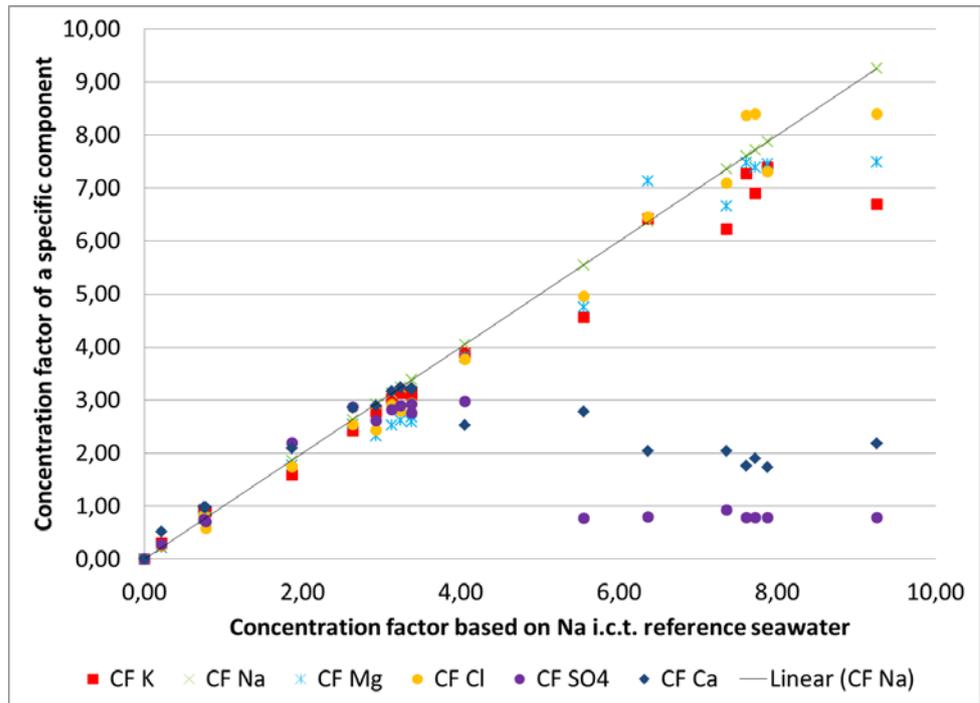


Figure 60: Concentration factor of components in the coastal water are related to the sodium concentration in seawater.

The corresponding (specific) flux during concentration is shown in Figure 61.

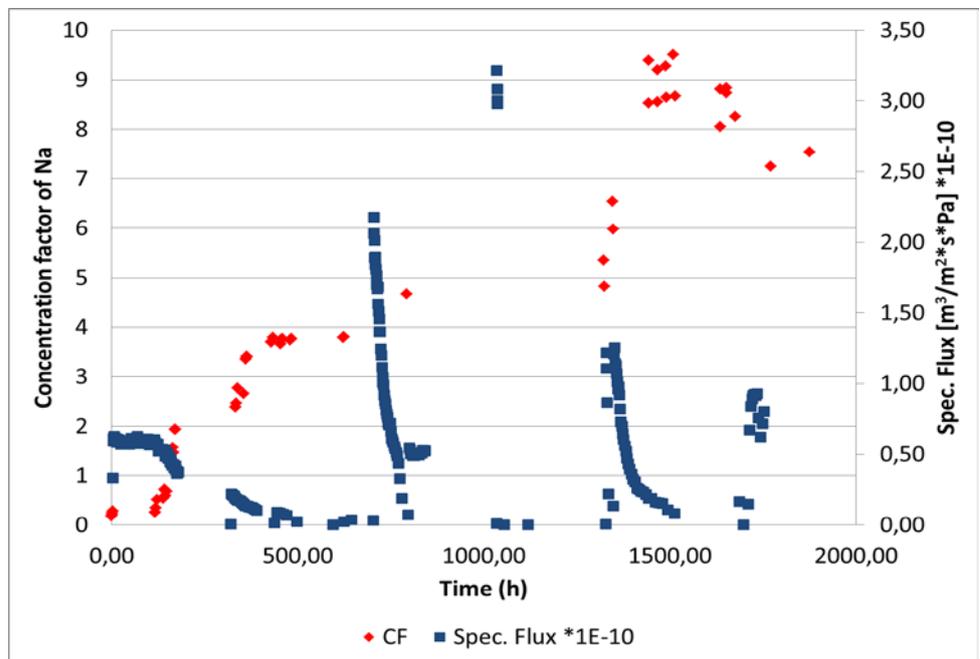


Figure 61: Specific flux during concentration in Aquastill MD pilot. The specific flux is defined as the flux per unit driving force (vapour pressure difference) across the membrane.

During concentration the pressure drop in the pilot increases. This is mainly due to the increase in pressure drop in the heat exchanger. As a result the installation is shut down if the pressure in the installation exceeds 0.5 bar. This explains why the flux totally drops several times during the concentration process. In Figure 62 the pressure at the inlet of the heat exchanger is illustrated.

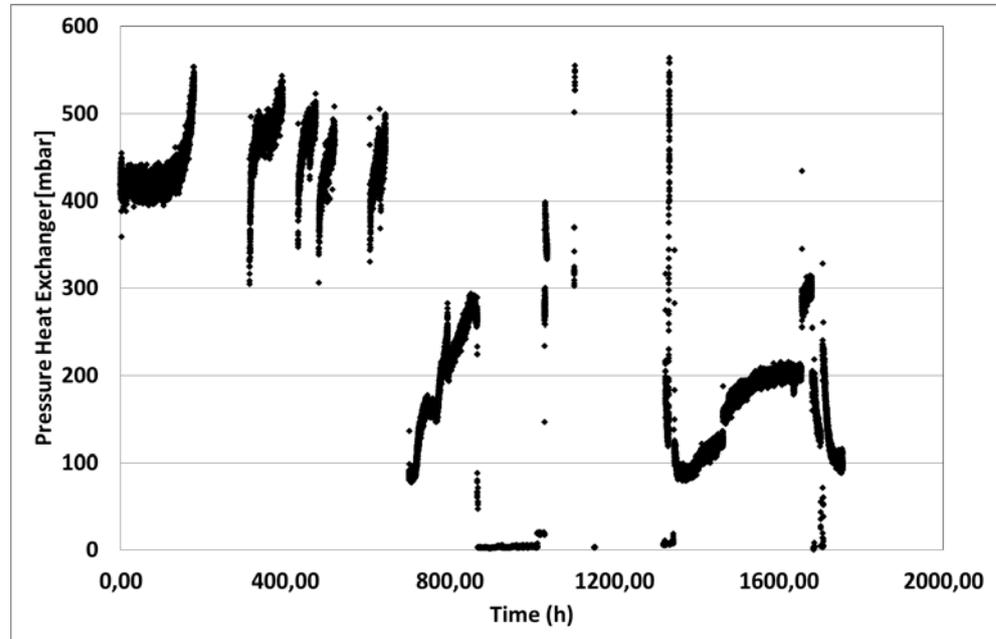


Figure 62: Pressure at inlet of heat exchanger during concentration in Aquastill pilot plant.

The pressure at the entrance of the heat exchanger is at a constant pressure (flow: 500 l/h) in the first 100 to 150 hours of the experiment. After the 150 hours, the pressure suddenly increases above 0.5 bar. As a result the installation is automatically shut down. The installation is restarted after 300 hours.

The pressure increases above 0.5 bar several times between an operation time of 300 and 600 hours. The flow is decreased after every restart. The flow is decreased from 500 l/h to 300 l/h.

The installation is cleaned after 600 hours with hydrochloric acid (pH 4) for several hours and then started (700 h) again with a flow of 400 l/h. The installation operated again from 700 to 850 without shutdown, but with pressure increase. After 850 operating hours, there were crystals (fouling) visible between the heat exchanger plates and a liquid leakage of the heat exchanger. The installation was shut down completely, till the heat exchangers were replaced (950 -1200 h).

After 1300 hours, the installation is started again with a new membrane module and new heat exchanger. The flow is set at 500 l/h. It is noticed that the flux decreases as a result of the pressure increase (Figure 61). The results (Figure 60) show, that it is possible to concentrate a seawater solution up to starvation of NaCl, but measures have to be taken to control the precipitation of Ca-salts.

After 1300 hours, the installation is started again with a new membrane module and new heat exchanger.

7 Conclusions

In the introduction of this report several questions have been formulated to be answered. To which degree is there an answer to these questions?

1. How does the way of operation of membrane distillation effect the crystallization of salts onto the membrane surface?

In the experiments is observed that both in MD and OD it was not possible to control the crystallization of NaCl in the membrane system. By applying OD it seems possible to delay the flux decline in the system during crystallization compared to MD, but it was not possible to obtain a stable operation (flux) during crystallization of NaCl. Control of precipitation of CaCO₃ by adding seeds looks promising (stable flux), but this is less obvious for controlling CaSO₄ precipitation.

2. How does the way of operation of membrane distillation effect the energy consumption?

In the project is shown that the concentration of the target solution can be executed by a combination of a MD and an OD process, although especially the OD process is not yet stable and frequent cleaning (rinsing) is required. Assuming a stable operation, the MD process is energy efficient (about 360 MJ/m³ produced water), especially at rather low concentrations (up to about 2 times seawater concentration the energy consumption for MD is about 180 MJ/m³). Assuming a stable operation, the OD process is less energy efficient. However in the case of the concentration of seawater, 90% can be concentrated by MD, while the remaining 10% can be concentrated by OD or a conventional evaporation-crystallization step. Although the energy consumption of OD or conventional evaporation is high, the relative contribution is limited, because only 10% of the water has to be treated in this way.

3. Is it possible to control the crystallization process during membrane distillation-crystallization by addition of seeds?

Many different types of seeds have been tested to determine the effect on the crystallization of NaCl. Based on the flux behaviour during such a crystallization experiment, it seems not possible to affect the crystallization of NaCl with the added seeds. However, also based on the flux behaviour, it seems possible to affect the crystallization of Ca-salts in the form of CaCO₃ with the addition of seeds. On pilot scale experiments have been executed with (Memstill configuration) and without seeds (direct contact membrane distillation configuration). The results of the experiments by adding seeds in the pilot plant are not reliable, because it was not possible to keep the seeds suspended in the installation (seeds settled in the installation). Problems of blocking by Ca salts occurred in the heat exchanger, but not in the membrane module.

4. Is it possible to fractionate the salts during membrane distillation-crystallization out of a mixed salt solution?

Theoretically, it is possible to fractionate the salts during crystallization. This has not been proven experimentally, because the laboratory set-up and the pilot-set-up were not well equipped to separate the crystals. This was planned, but due to extra effort in the prevention of crystallization on the membrane, this item is not studied within the project.

5. What are the economic forecasts for the process?

With respect to costs it can be concluded that the MD/OD process can be very attractive compared to the costs of conventional brine treatments. On a very large scale costs are estimated to be about €1-1,50/m³ (assuming a stable operation of the process), which is much lower than the target of max €5/m³ estimated for the concentration of seawater. At this moment especially the OD part is running insufficiently, which means that additional costs have to be made for cleaning (rinsing) of the membranes. These additional costs are not quantified yet.

Summarizing, it can be concluded that concentration up to saturation of salts like NaCl (salts that become more soluble with increasing temperature) can be scaled up in an MD installation to be applied at full scale level, while the precipitation of Ca salts can be controlled by the addition of seeds or by a system in which the scaling on the heat exchanger is continuously removed (e.g. scraped heat exchanger). The way of crystallization of salts like NaCl is less obvious. The application of antisolvent crystallization in combination with OD performs better than only application of MD. But the flux decrease during crystallization is still too much. Additional laboratory scale research is required here.

8 Recommendations

- Continuation of the research on MD with pilot scale experiments up to saturation of NaCl (or similar salts) with special attention to the prevention/control of scaling in the heat exchanger. Handling of seeds or application of scraped heat exchanger are possible options.
- Continuation of the research on crystallization of NaCl on laboratory scale. More attention has to be given to controlling the crystallization layer on the membrane instead of preventing the crystallization layer on the membrane.

9 Literature

- [1] E. Drioli, G. Di Profio, E. Curcio, Progress in membrane crystallization, *Curr. Opin. Chem. Eng.* 1 (2012) 178–182.
- [2] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of reverse osmosis desalination, *Desalination* 216 (2007) 1–76.
- [3] M. Ahmed, A. Arakel, D. Hoey, M.R. Thumarukudy, M.F.A. Goosen, M. Al-Haddabi, A. Al-Belushi, Feasibility of salt production from inland RO desalination plant reject brine: a case study, *Desalination* 158 (2003) 109–117.
- [4] X. Ji, E. Curcio, S. Al Obaidani, G. Di Profio, E. Fontananova, E. Drioli, Membrane distillation–crystallization of seawater reverse osmosis brines, *Sep. Purif. Technol.* 71 (2010) 76–82.
- [5] M. Schorr, B. Valdez, J. Ocampo, A. Eliezer, Corrosion control in the desalination industry, in: Michael Schorr (Ed.), *Desalination, Trends and Technologies*, InTech, Rijeka, Croatia, 2011.
- [6] C.M. Tun, A.G. Fane, J.T. Matheickal, R. Sheikholeslami, Membrane distillation crystallization of concentrated salt — flux and crystal formation, *J. Membr. Sci.* 257 (2005) 144–155.
- [7] E. Drioli, E. Curcio, A. Criscuoli, G. Di Profio, Integrated system for recovery of CaCO₃, NaCl and MgSO₄·7H₂O from nanofiltration retentate, *J. Membr. Sci.* 239 (2004) 27–38.
- [8] E. Curcio, A. Criscuoli, E. Drioli, Membrane crystallizers, *Ind. Eng. Chem. Res.* 40 (2001) 2679–2684.
- [9] M. Gryta, Concentration of NaCl solution by membrane distillation integrated with crystallization, *Sep. Sci. Technol.* 37 (2002) 3535–3558.
- [10] M. Khayet, T. Matsuura, *Membrane Distillation Principles and Applications*, Elsevier, Amsterdam, 2011.
- [11] K.W. Lawson, D.R. Lloyd, Review: membrane distillation, *J. Membr. Sci.* 124 (1997) 1–25.
- [12] R.W. Schofield, A.G. Fane, C.J.D. Fell, R. Macoun, Factors affecting in membrane distillation, *Desalination* 77 (1990) 279–294.
- [13] Y. Wu, E. Drioli, The behaviour of membrane distillation of concentrated aqueous solution, *Water Treat.* 4 (1989) 399–415.

10 Authentication

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Names and establishments to which part of the research was put out to contract:

Date upon which, or period in which the research took place:

December 2010 – December 2013

Name and signature reviewer:

Robin van Leerdam



Signature:



Raymond Creusen
Project Leader

Release:



Monique Oldenburg
Research Manager

Experiments with CaCl_2 as antisolvent in combination with OD (with different started fluxes)

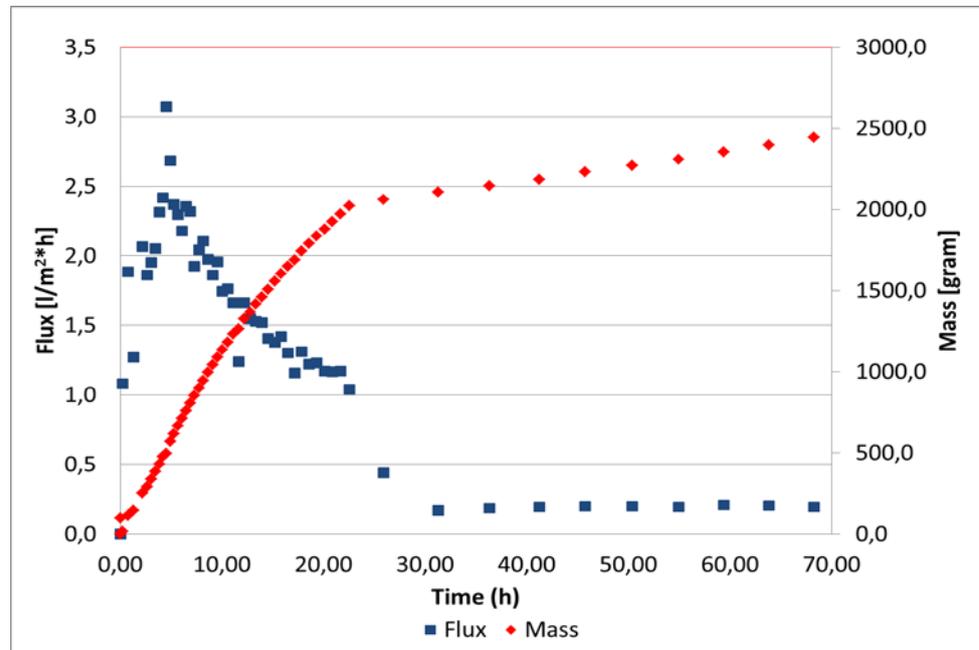


Figure 1.1. Flux as a function of time and mass of distillate produced. Feed is 4 times concentrated seawater which is added to a feed vessel containing a solution which is treated with a CaCl_2 solution to precipitate NaCl out of the seawater. $T_{\text{feed}} = 60\text{ }^\circ\text{C}$, $T_{\text{distillate}} = 70\text{ }^\circ\text{C}$. Draw liquid at distillate side is a 35-40 wt% CaCl_2 solution.

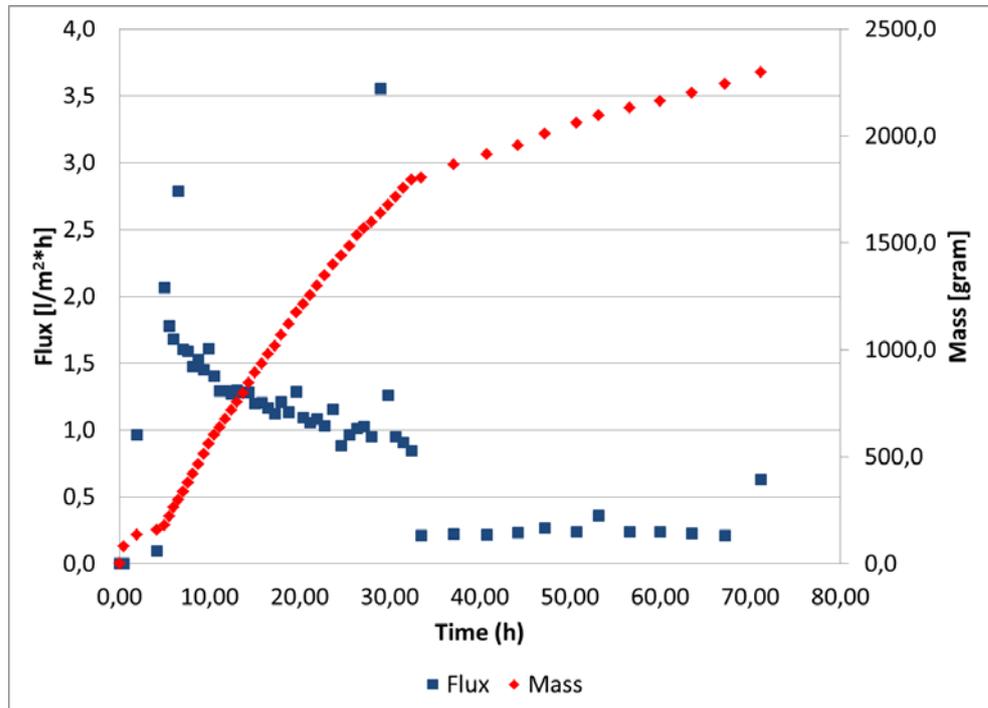


Figure 1.2. Flux as a function of time and mass of distillate produced. Feed is 4 times concentrated seawater which is added to a feed vessel containing a solution which is treated with a CaCl₂ solution to precipitate NaCl out of the seawater. T_{feed} = 60 °C, T_{distillate} = 70 °C. Draw liquid at distillate side is a 35-40 wt% CaCl₂ solution.

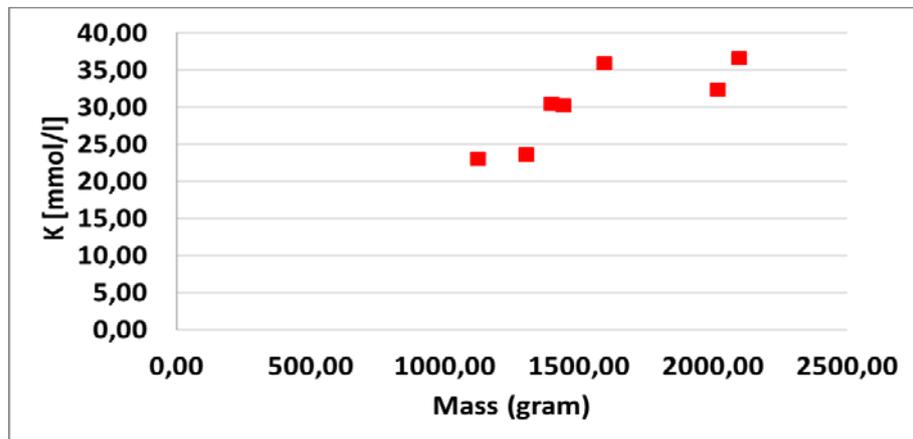


Figure 1.3. Potassium concentration as a function of produced distillate

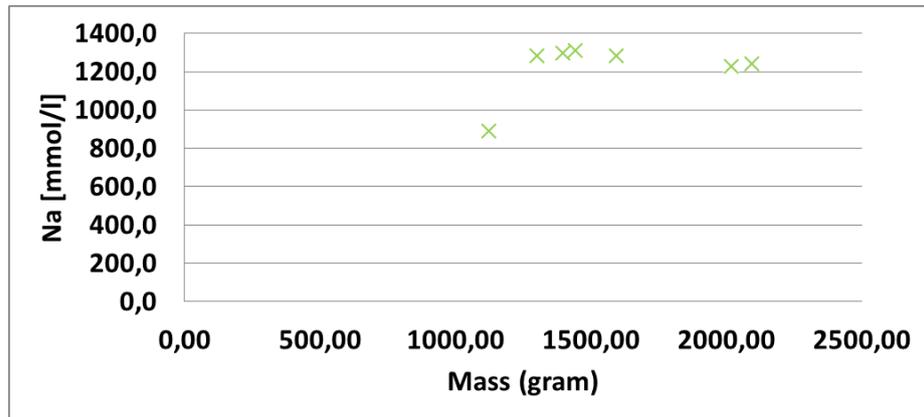


Figure 1.4. Sodium concentration as a function of produced distillate

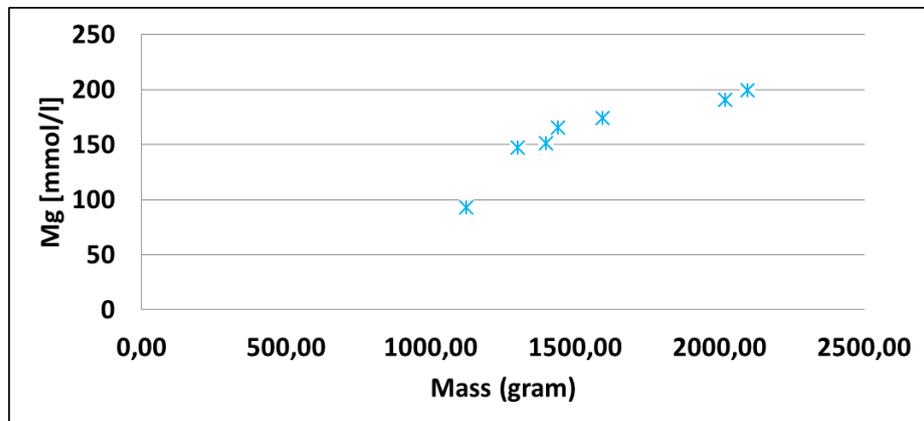


Figure 1.5. Magnesium concentration as a function of produced distillate

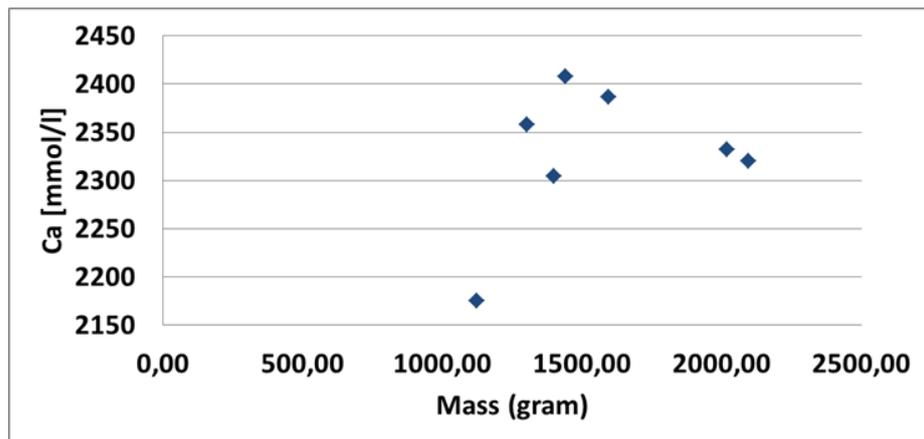


Figure 1.6. Calcium concentration as a function of produced distillate

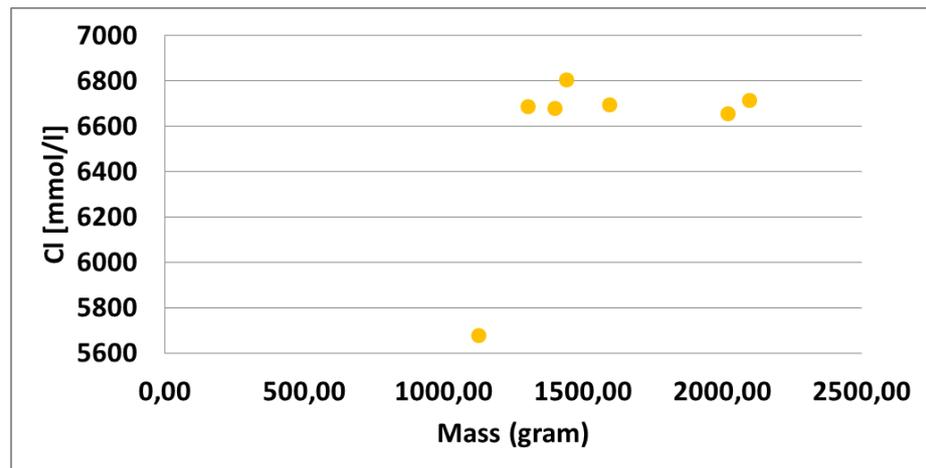


Figure 1.7. Chloride concentration as a function of produced distillate

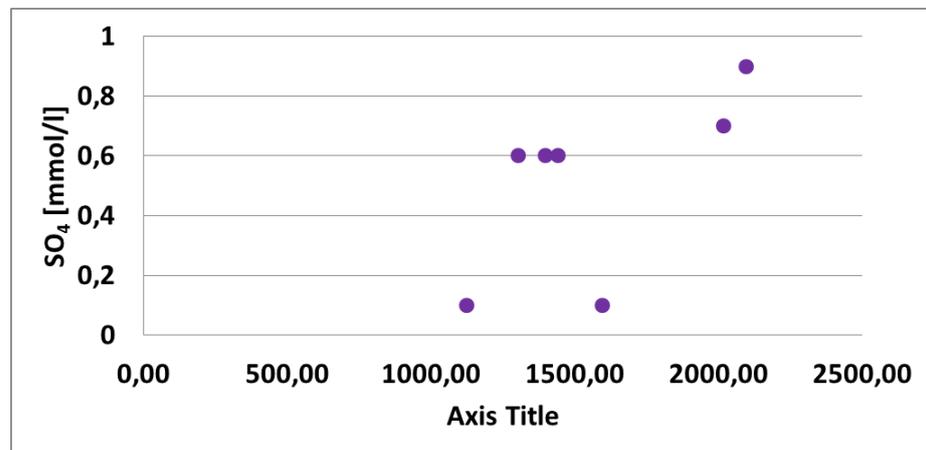


Figure 1.8. Sulphate concentration as a function of produced distillate

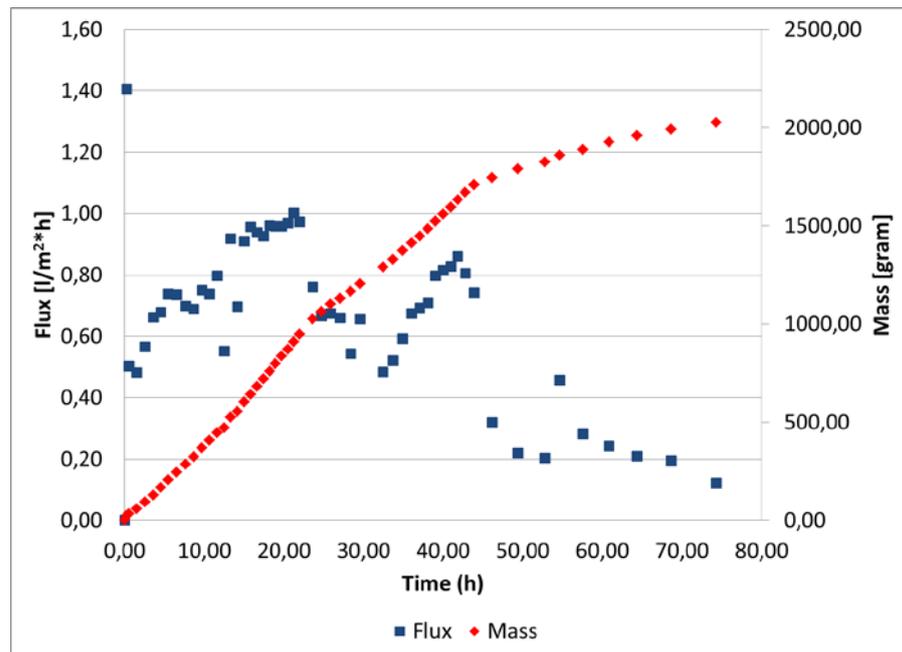


Figure 1.9. Flux as a function of time and mass of distillate produced. Feed is 4 times concentrated seawater which is added to a feed vessel containing a solution which is treated with a CaCl_2 solution to precipitate NaCl out of the seawater. $T_{\text{feed}} = 60\text{ }^\circ\text{C}$, $T_{\text{distillate}} = 70\text{ }^\circ\text{C}$. Draw liquid at distillate side is a 35-40 wt% CaCl_2 solution

Simulation with OLI of precipitation behaviour of several feed water compositions during water removal

OLI's basic electrolyte thermodynamic model - the AQ model - is based on a true speciation model, a predictive equation of state (Helgeson EOS), an activity coefficient model, and convergence heuristics. Combined with 43 years of R & D and a full-time staff of six thermophysical modelers, the OLI AQ model covers 80+ elements of the periodic table. The model is based upon published experimental data. The model uses data regression wherever possible and estimation and extrapolation where required. This model provides general simulation capability giving accurate prediction for almost any water chemistry mixture over the range (source: OLI Systems).

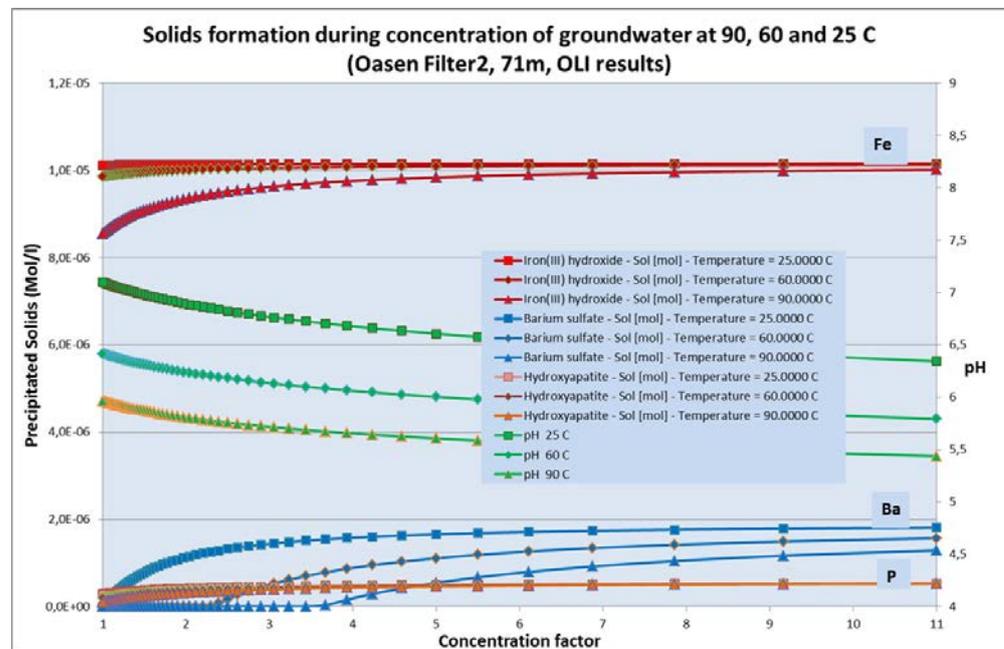


Figure 2.1. OLI simulation results with concentration of Oasen ground water

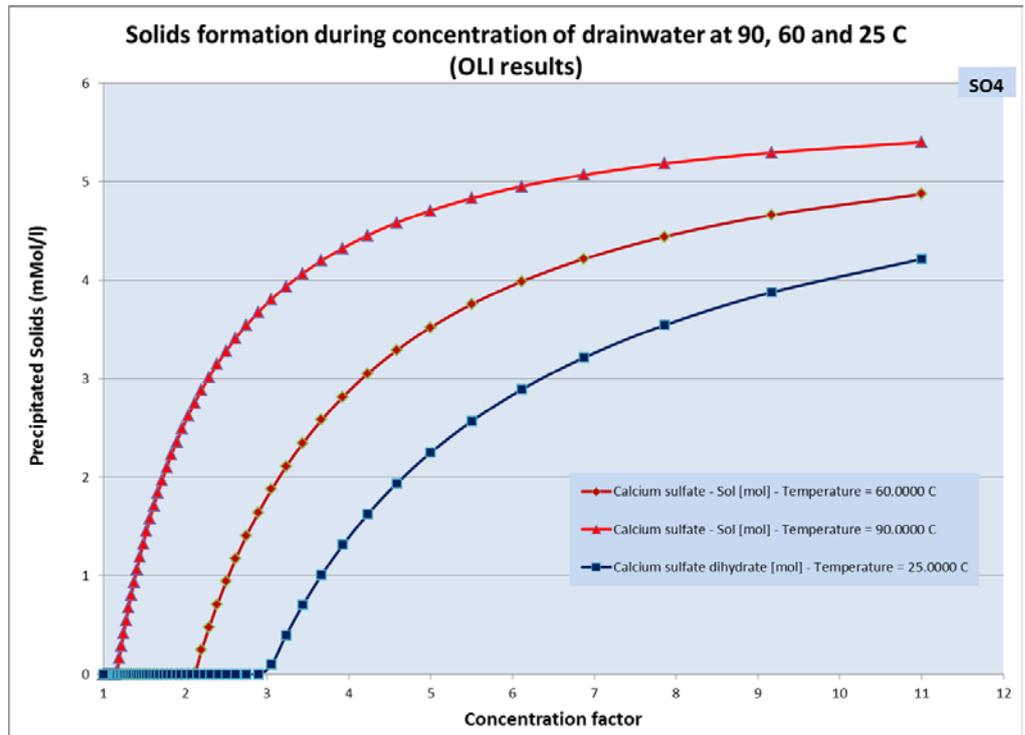


Figure 2.2. OLI simulation results with concentration of drain water

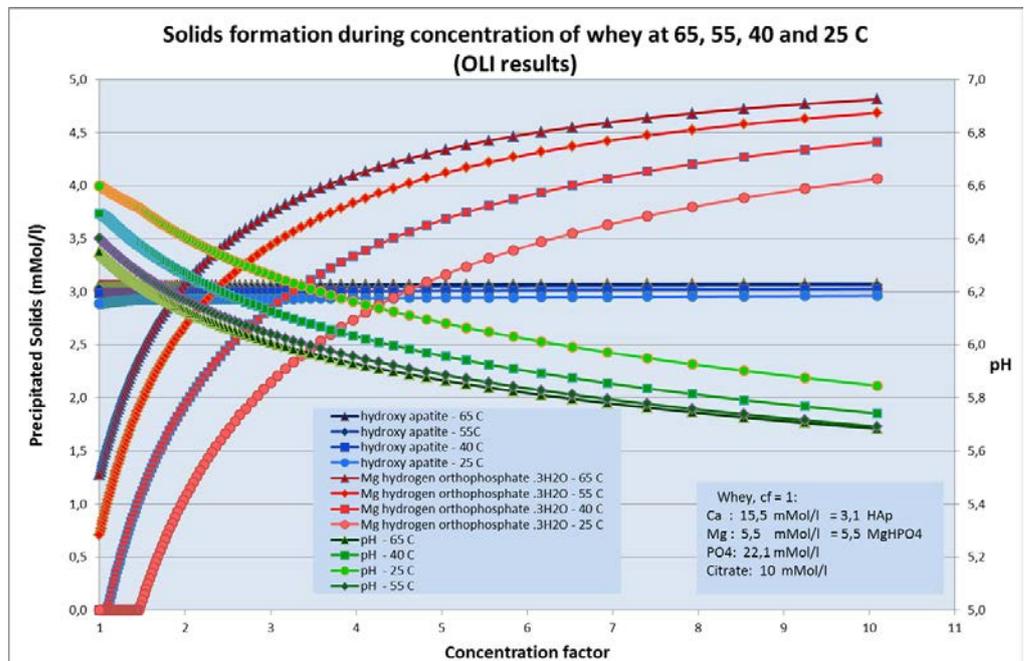


Figure 2.3. OLI simulation results with concentration of whey

Cost tables for small operation capacity and less operating hours/years

<i>Process step</i>	<i>Water production (ton/h)</i>	<i>Membrane surface (. 1000 m²)</i>	<i>Investment Modules (k€)</i>	<i>Investment Hardware (k€)</i>	<i>Capex (€/m³ sea water)</i>	<i>Heat costs (€/m³ sea water)</i>	<i>Capex + heat + electricity (€/m³ sea water)</i>
MD1	7.9	2.0	200	1400	1.90	0.026	
MD2	8.2	1.4	140	970	1.32	0.080	
OD	1.7	0.3	30	250	0.33	0.327	
TOTAL	1	3.7	370	2620	3.55	0.43	4.22
TARGET						1.50	4.00
<p><i>Criteria:</i></p> <ul style="list-style-type: none"> - 8000 production hours / year (treatment of 144000 m³/year sea water) - Module price: € 100 /m² (estimation for 2015); replacement in 4 years - Auxiliary hardware: based on scale factor : 15 times less than based on production of 3600 m³/h. - Interest /depreciation auxiliary hardware: Annuity = 16%. - Electricity: total 3 kWh per m³ sea water (4 x Memstill), ad € 0,08 = € 0,24 / m³ sea water. - Waste heat costs: € 1.00 per GJ (363 K) resp. € 1,50 per GJ (393 K) steam. - Maintenance, labor: 5% of Hardware investment (not included in this table). 							

Table 3.1. Cost estimation for the MDC process with a feed capacity of 18 m³/h in 8000 hr/y operating time.

Table 1 shows that the hardware costs are determining the final costs to a large extend. He hardware costs are estimated just on downscaling rules based on the large plant (costs are 15 times less, while capacity is 200 times less).

<i>Process step</i>	<i>Water production (ton/h)</i>	<i>Membrane surface (. 1000 m²)</i>	<i>Investment Modules (k€)</i>	<i>Investment Hardware (k€)</i>	<i>Capex (€/m³ sea water)</i>	<i>Heat costs (€/m³ sea water)</i>	<i>Capex + heat + electricity (€/m³ sea water)</i>
MD1	7.9	2.0	200	1400	3.80	0.026	
MD2	8.2	1.4	140	970	2.64	0.080	
OD	1.7	0.3	30	250	0.66	0.327	
TOTAL	1	3.7	370	2620	7.10	0.43	7.77
TARGET						1.50	4.00
<p><i>Criteria:</i></p> <ul style="list-style-type: none"> - 4000 production hours / year (treatment of 144000 m³/year sea water) - Module price: € 100 /m² (estimation for 2015); replacement in 4 years - Auxiliary hardware: based on scale factor : 15 times less than based on production of 3600 m³/h. - Interest /depreciation auxiliary hardware: Annuity = 16%. - Electricity: total 3 kWh per m³ sea water (4 x Memstill), ad € 0,08 = € 0,24 / m³ sea water. - Waste heat costs: € 1.00 per GJ (363 K) resp. € 1,50 per GJ (393 K) steam. - Maintenance, labor: 5% of Hardware investment (not included in this table). 							

Table 3.2. Cost estimation for the MDC process with a feed capacity of 18 m³/h in 4000 hr/year operating time.

Table 3.2. shows that a shorter operation time with a same capacity has a large effect on the depreciation costs and as a results a large effect on the operation costs/year. Similar to Table 3.2 the hardware costs are estimated based on general downscale rules, related to the large scale operation (3600 m³/h).

Composition of Dutch coastal water

Composition Dutch coastal water		
EC	[mS/cm]	51,70
NH ₄	[mmol/l]	< 0,1
K	[mmol/l]	11,20
Na	[mmol/l]	445,00
Ca	[mmol/l]	9,50
Mg	[mmol/l]	55,20
Si	[mmol/l]	< 0,1
NO ₃	[mmol/l]	0,10
Cl	[mmol/l]	580,00
SO ₄	[mmol/l]	13,00
HCO ₃	[mmol/l]	13,00
P	[mmol/l]	< 0,4
Fe	[μmol/l]	< 0,1
Mn	[μmol/l]	0,10
Zn	[μmol/l]	578,00
B	[μmol/l]	0,10
Cu	[μmol/l]	0,10

Table 4.1. Composition of Dutch coastal water