Investigation of the regeneration process of the softeners at DWP-Botlek

Determination if other sources can be used as a regenerant

U.P.Ouwerkerk

20-06-2013

Delft University of Technology

evides industriewater

Challenge the future

Investigation of the regeneration process of the softeners at DWP-Botlek

Determination if other sources can be used as a regenerant.

Udo Pascal Ouwerkerk

Section Sanitary Engineering
Department of Water Management
Faculty of Civil Engineering and Geosciences
Delft University of Technology

for the degree of:
Master of Science in Civil Engineering

Date of defence: 20-06-2013

Committee:

prof.dr.ir. L.C. Rietveld	Delft University of Technology Sanitary Engineering Section
prof.dr.ir. A.R.D. Verliefde	Delft University of Technology Sanitary Engineering Section
dr.ir. S.G.J. Heijman	Delft University of Technology Sanitary Engineering Section
dr.ir. H.J.M. Kramer	Delft University of Technology Process and Energy
ir. M.A. Pot	Evides Industriewater

Printed by SiecaRepro, The Netherlands
Cover design: U.P.Ouwerkerk BSc.

Pictures on the cover:
- Top picture: DWP Botlek in construction (Logisticon)
- Bottom left: IEX Softener (Evides Industriewater)
- Bottom right: Experimental setup in the laboratory

Abstract

Evides Industriewater owns a plant called DWP Botlek at the site of Huntsman. DWP Botlek produces demi water of water from the Brielse Meer. The production process is divided into three main steps namely: pre-treatment, softening and desalination. Pre-treatment consists of flocculation, flotation and filtration. Softening is done with strong acid cation ion exchangers. The last step, the desalination consists of reverse osmosis membrane filtration followed by mixed bed ion exchangers as a polishing step.

The focus of the presented research is on the ion exchange softeners. In practice at DWPB, each softener is loaded with 9000 mol hardness and then regenerated. For that regeneration, an excess of NaCl as regenerant is dosed. The total amount of resources needed per softener for the injection of the regenerant is 1735 kg NaCl and 18 m^3 of softened water. For the regeneration of one softener, 93 m^3 of softened water is needed as flush water. The used regenerant and flush water are discharged into the Brittannië harbour. For each regeneration new regenerant needs to be produced. Salt is bought and transported to the location as a consequence of this process. Salt is not expensive, but in the current culture of sustainability it is not desirable that more resources are used than necessary and that raw materials that still can be used or reused are discarded.

With a literature survey, different solutions were found to reduce the amount of regenerant. After comparison of the solutions, only two are selected for the investigation namely: water from the Brittannië harbour and concentrate from the RO as regenerant.

During the experiments, focus was on the effect of the selected regenerants on the resin. Parameters of interest are the operating capacity of the resin, amount of bed volumes of regenerant, precipitation in the bed and applicability into the process of DWP Botlek.
With these experiments is proven that it is not possible to use water from the Brittannië harbour as a regenerant. From the obtained data, it is possible to lower the salt concentration. During regeneration with 3.45% NaCl as a regenerant the resin is fully regenerated, only more bed volumes and also more time is needed. The water from Brittannië harbour contains a high magnesium concentration (30 mmol/l). Because of the high magnesium concentration only a fraction of the hardness is removed during regeneration. Also exchange of magnesium and calcium was noticed during regeneration, so water from the Brittannië harbour is not suitable as regenerant.
Different variants were tested with the use of RO concentrate. Variations were made in sodium concentration, addition of $CaCO_3$, pH, flow velocity and amount of regenerant. According to the experiments can be concluded that concentrate with 1% NaCl or $CaCO_3$ as a regenerant is not possible. RO concentrate with 10% NaCl is based on the experimental research a suitable alternative for the current regenerant. The concentrate contains 0.25% NaCl, which gives a small reduction on the amount of salt that normally is used. A larger effect is created with concentrate as a source for the regenerant and flush water. Then the total amount of softened water (111 m^3/regeneration) is not needed anymore. The consequence is that the production of softened water can be reduced, which results in a longer runtime of the softeners. Therefore, fewer regenerations have to be performed, and 16.7% (3,500 kg) less salt is needed. The amount of water that is discharged to the harbour is also reduced with 16.7% (222 m^3).
With concentrate as a regenerant not all of the concentrate is used, a part is discharged into the harbour. A design is made to reduce that amount, a part of the concentrate is still used as flush water, and the remaining part is transported to another RO unit. According to the simulation with ROSA it is possible with the use of RO membranes to reduce the amount of water that is discharged on the harbour. A part of the remaining concentrate can be used for the production of the regenerant. This results in 85.7% less water (7,200 m^3/day) discharged into the harbour, and less softened water need to be produced compared to the current situation. In total 63.4% (37,500 kg/day) is saved on the amount of salt. Another benefit is that 12% (220 m^3/h) more demi water is produced with the proposed design, resulting in more marketable demi water.

Preface

This thesis is the final product of my study at the Faculty of Civil Engineering and Geosciences of the Delft University of Technology. The title of the thesis is: Investigation of the regeneration process of the softeners at DWP-Botlek. For my master thesis, I wanted to do a subject which was related to practice. After consulting Jasper Verberk contact was made with Evides. They had a topic available that was related to their demi water plant in the Botlek. During the tour at the plant, it was clear for me that DWP-Botlek could be an impressive subject. After the meeting with Marin Pot, it was decided that the scope of research would be the softeners of the DWP-Botlek. DWP-Botlek is a demi water plant from Evides Industriewater. Although the investigation is done to a part of the plant, the experimental research is conducted at Delft University of Technology, laboratory of Sanitary Engineering. The research is focused on the process of the plant itself, and if other regenerants and / or techniques could be used for the regeneration of the softeners. A selection of these solutions is investigated in the laboratory.

I would like to acknowledge Martin Pot from Evides Industriewater for the information, materials and time. Also, Vincent Toussaint from Evides Industriewater I would like to acknowledge for his effort and also the concentrate from DWP-Botlek. Without the support of both the research would not have been possible. Furthermore, I would like to acknowledge all people from the laboratory of Sanitary Engineering for their support when needed. Also, I would like to thank Samuele Oliviero for assistance with the IC.

Also, there is my committee to acknowledge for their efforts in guiding me through the process. My professor Luuk Rietveld needs to be thanked for his expertise and critical notes on the research. Also, I would like to acknowledge Arne Verliefde and David Moed for their support and knowledge, Bas Heijman for the supervision during the graduation process and also for all the useful consultancies and discussions.

I would like to acknowledge my family and friends for their support and advice, especially Marc Ottelé. Finally, I would like to thank my parents for their endless support during my study. Without their support, it would not have been possible to come so far.

Udo Ouwerkerk

June 2013

Table of Content

List of illustrations

List of tables

List of abbreviations

Abbreviation	Description
AVR	Afvalverwerking Rijnmond, waste treatment Rijnmond
BV	Bed volume
CapD-I	Capacitive Deionization
DAFF	Dissolved Air Filtration Flotation
DWP	Demi Water Plant
DWPB	DWP-Botlek
ED	Electro Dialysis
EDI	Electro Deionization
EFC	Eutectic freeze crystallization
FTC	Flow through capacitor
IC	Ion chromatography
MB	Mixed Bed
PV	Pressure vessel
PWP	Process Water Plant
RO	Reverse Osmosis
SAC	Strong-acid cation
SBA	Strong-base anion
SI	Saturation Index
TDS	Total dissolved solids
TH	Total hardness
WAC	Weak-acid cation
WBA	Weak-base anion
WWTP	Waste Water Treatment Plant

List of symbols

Symbol	Quantity	Unity
A_{bed}	Surface of the bed	m^2
b_e	Langmuir adsorption constant of the total hardness	l/eq
BV_R	Bed volumes of regenerant	m^3
BV_{total}	Volume of the resin bed	m^3
C_e	Equilibrium concentration of the hardness in the solution	mmol/l
c_R	Concentration of the regenerant	kg/l
EC	Electro conductivity	mS/cm
h_{bed}	Height of the bed	m
h_{column}	Height of the column	m
$h_{expanded\ bed}$	Height of the expanded bed	m
K_e	Freundlich adsorption capacity parameter	$eq \cdot l^{1/n}/mmol^{1/n} \cdot l$
n	Freundlich adsorption intensity parameter	-
pH	Degree of acidity	-
ρ_R	Density of the regenerant	kg/m^3
q_e	Equilibrium exchange capacity of the resin	eq/l
Q_m	Maximum concentration of hardness on the resin	eq/l
R_1	Regenerant 1 (10% NaCl)	-
R_2	Regenerant 2 (3.45% NaCl)	-
R_3	Regenerant 3 (Artificial seawater)	-
R_4	Regenerant 4 (water from the Brittanniё harbour)	-
R_5	Regenerant 5 (RO concentrate)	-
R_{5-1}	Regenerant 5-1 (RO concentrate with 1% NaCl)	-
R_{5-2}	Regenerant 5-2 (RO concentrate with $CaCO_3$)	-
R_{5-3}	Regenerant 5-3 (RO concentrate with 1% NaCl and increased pH)	-
R_{5-4}	Regenerant 5-4 (RO concentrate with $CaCO_3$ and increased pH)	-
R_{5-5}	Regenerant 5-5 (RO concentrate with 10% NaCl)	-
R_{5-6}	Regenerant 5-6 (RO concentrate with 1% NaCl and gradient increased pH)	-
SLR	Salt loading rate	kg/m^3
T	Temperature	°C
TH_{BMW}	Total hardness of water from Brielse Meer	mmol/l
TH_{loaded}	Total amount of hardness loaded on the resin	mmol
$TH_{removed}$	Total amount of hardness removed from the resin	mmol
V_{system}	Dead volume of the experimental setup	ml

1 Introduction

1.1 DWP-Botlek

Evides has already for many years a distribution net for distilled water (deminet) in operation to distribute distilled water to about sixteen companies. This so called destiwater was a residual product that was produced as residual water of condensation of a WWTP on the basis of vacuum evaporation. For the process of vacuum evaporation, residual heat of the AVR-centrale was used. In 2007, it became clear that this way of production of destiwater would be stopped in 2010. Evides decided to build a multi-client demi water plant, DWP-Botlek, and in January 2010 DWP-Botlek became operational. The plant supplies to 15 chemical companies and to 3 refineries in the Botlek-Europoort. DWP-Botlek is built on the site of Huntsman (see Figure 1) and is connected to deminet to deliver water to several clients. The production capacity of DWP-Botlek is 1.400 m^3 per hour or 12 million m^3 per year.

Figure 1: DWP-Botlek on the site of Huntsman adjacent to the Brittannië harbour (Google Maps).

Operational safety is of immense importance for DWP-Botlek and is connected to two sources namely:

- water from Brielse Meer (surface water)
- drinking water (tap water)

The plant is designed for collection and treatment of surface water from Brielse Meer and drinking water from production location Berenplaat. With the design of the process of DWPB effects of accidental salinization of water from Brielse Meer by climate change, as well as possible structural salinization as a result of government measures (Kierbesluit Haringvliet 2011) were taken into account. DWPB consists of a combination of ion exchange technology and membrane technology, an elaboration of these processes will be given in chapter 2. The focus within the presented research is on the part of the process where the water is softened. The water is softened with ion exchange resin in an ion exchanger. After loading the resin is regenerated. For the regeneration of the resin chemicals are needed, in case of DWP-Botlek sodium chloride (NaCl). To create the regenerant sodium chloride is dissolved in softened water that is produced on site. Sodium chloride needs to be purchased and transported to the location. Also with regeneration flush water and spent regenerant is discharged into the Brittannië harbour. Evides Industriewater is allowed to do the discharge according to the license given by the government. Regulations are becoming stricter towards the amount of constituents that are allowed to be discharged. That is also dependent on the location where the discharge is located. DWP Botlek is located near a harbour with brackish water. According to the regulations it is not a problem to discharge water containing sodium chloride because the receiving water body also contains sodium chloride. When the plant would be near fresh water, the government would only allow to discharge of the spent regenerant after treatment. Nowadays also the awareness increases that one must use the available resources more economically.

1.2 Problem definition

For the regeneration of the softeners at DWP-Botlek, a solution of sodium chloride is used. To ensure that the regeneration functions as planned more sodium chloride is added than actual needed. Used regenerant is discharged into the Brittannië harbour. For each regeneration, a new amount of regenerant is produced. As a consequence of this, salt needs to be bought and transported to the location. Salt is not expensive, but in the current culture of sustainability it is not desirable that more resources are used than necessary. So it is not desirable that raw materials that still can be used or reused are discarded.

1.3 Research objective

The main objective of this research is to investigate possibilities of lowering usage of resources needed for regeneration of the ion exchange softeners.
To reach the main purpose of the research, suitable solutions need to be found and tested on a laboratory scale. Therefore, some sub objectives are investigated as well, namely:

1. Study the current process used at DWP-Botlek in order to have a reference.
2. Search for solutions to lower the usage of salt and / or water.
3. Experimental research of the suitable solutions.

1.4 Research questions

The main research questions are:

- What are suitable solutions to lower the use of resources?
- Can other sources be used to regenerate the resin?
- Is it possible to reduce the amount of resources needed for regeneration of the softeners?
- What are the essential parameters for the process?
- Is it possible to apply the other regenerant at DWPB?

In order to be able to answer the last question some sub research questions were formulated:

- Is water from the Brittannië harbour suitable as a regenerant?
- Is RO concentrate suitable as a regenerant?
- What is the influence of use of another regenerant on the resin?
- Is the amount of bed volumes of regenerant reduced with use of another regenerant?
- Is the amount of salt reduced with use of another regenerant?

1.5 Preconditions

On the site of the plant, there are limitations to the available area and height of buildings / factories that can be constructed.

Available area	: 15.6 m^2 (2.5 x 6 m)
Maximum allowable height of buildings	: 13.0 m

No significant changes are allowed to the current process of DWP Botlek.

1.6 Thesis methodology and chapter setup

The report consists out of seven chapters. The chapters can be divided into three basic sections: a literature overview, experimental research and conclusions.

The literature overview comprises chapter 2, 3 and 4. In chapter 2, an analysis of the process of DWP Botlek is given and also detailed information of the softeners. Chapter 3 gives a description of the technique of ion exchange in order to identify parameters that are relevant to the process. In chapter 4, an overview is given of solutions which can be applied in or to the process to lower the usage of regenerants. Also a consideration is given which solution(s) is or are investigated in the experimental research.

Chapter 5 and 6 are reserved for the experimental research carried out in the laboratory. In chapter 5, the experimental research and used methods are discussed. Results of the experiments of the selected solutions are presented and discussed in chapter 6.

In chapter 7, a design is presented for the use of another regenerant at DWP Botlek.

The last chapter of the thesis is chapter 8, which contains conclusions and recommendations for further research and practical implementation.

Visualization of the research approach and methodology with relevant research questions is shown in Figure 2.

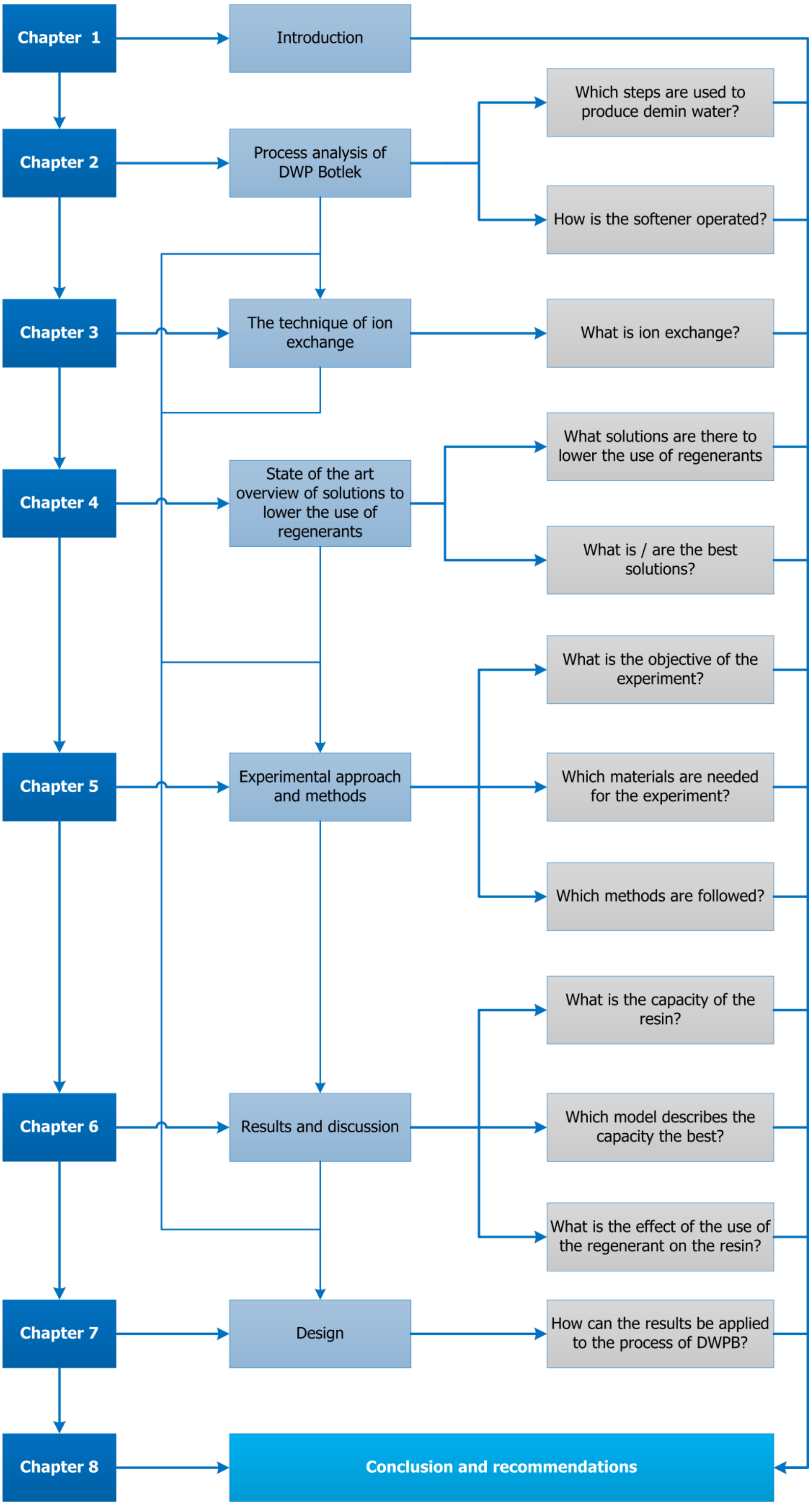


Figure 2: Visualization of the thesis.

2 Description of the production process at DWP-Botlek

In this chapter, a description will be given of the process at BWP-Botlek. As mentioned already before, the plant is designed for collection and treatment of surface water from Brielse Meer and drinking water from the production location Berenplaat. DWPB has multiple clients and Evides Industriewater has to ensure a high reliability of supply:

1. The DWPB has two independent water sources, in sufficient quantity available. This means that the supply of water to the DWPB is always ensured.
2. The design of the installation is based on redundant processing. This redundancy and knowledge of Evides Industriewater with the applied technologies results in an operation that guarantees continuity.
3. The plant has spare capacity in both tanks and pump power. This buffering capacity ensures that fluctuations in the demand can be handled. The capacity of the buffer is 10 hours of maximum production.

The distribution pipe from DWPB into the direction of the customers is entirely duplicated. This allows Evides to ensure the supply of demineralised water during maintenance and emergencies. When it is not possible to deliver demineralised water to the clients; mobile RO units can be placed at the clients' location to ensure the delivery of demineralised water.

2.1 General overview of the production process

An overview of the complete production process is given in Figure 3. From each step a short description will be given.

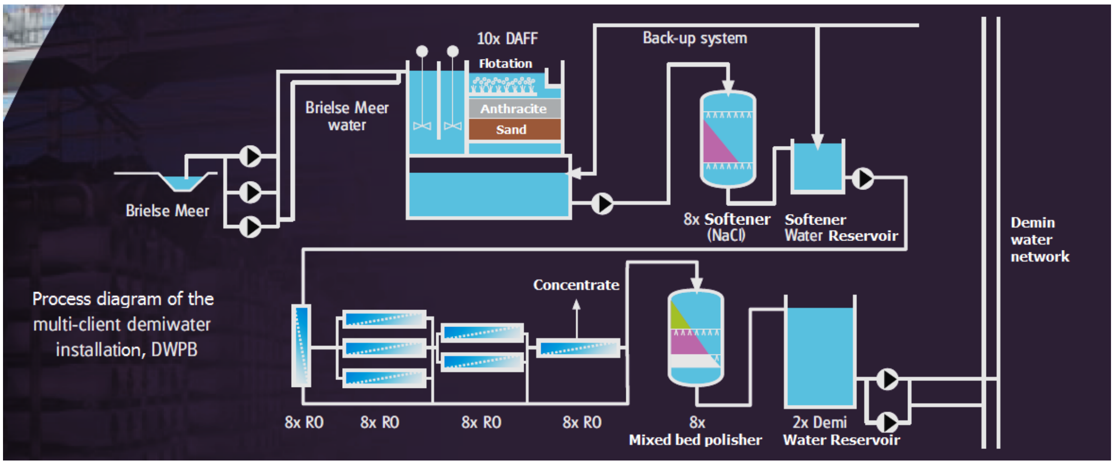


Figure 3: Schematic drawing of the process at DWP-Botlek (Evides Industriewater).

The production process can be divided into three main steps:

1. Pre-treatment (flocculation, flotation and filtration)
2. Softening (strong acid cation ion exchangers)
3. Desalination (RO membrane filtration followed by mixed bed ion exchangers)

2.1.1 Pre-treatment with DAFF technology

Water from Brielse Meer is transported from the lake to the plant by pumping stations Geervliet or Brielse Maasdam. When water arrives at DWPB pre-treatment with DAFF technology will take place. Dissolved Air Filtration Flotation (DAFF) is a water treatment process used as an alternative to sedimentation. For the pre-treatment 10 DAFF units are available. The pre-treatment consists of coagulation and flotation to remove algae and a dual layer sand filtration to remove all suspended solids. Flock formation is reached with the dosing of iron chloride ($FeCl_3$).
From the pre-treatment the water is transported to the softeners.

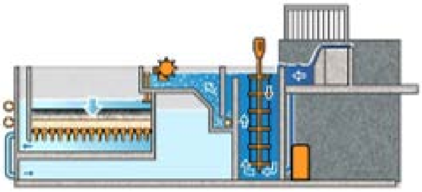


Figure 4: Pre-treatment (Evides Industriewater).

2.1.2 Softeners

With the use of a cation ion exchanger as softener, calcium (Ca_2^+) and magnesium (Mg_2^+) are removed from the water. If present in the water strontium (Sr_2^+) and barium (Ba_2^+) are also removed. This minimizes the treatment needed in the membrane phase because no precautions have to be taken to prevent scaling on the membranes. When the ion exchanger is saturated, it is regenerated with an excess of sodium chloride (NaCl). The excess of the dosed sodium chloride is 65%. The contaminated brine is drained to the surface water of the Brittannië harbour, which is in connection with the North Sea (See Appendix A: Map of the harbour). For each cubic meter that is discharged € 0.0075 is paid to Rijkswaterstaat. A more detailed description of the softeners is given in paragraph 2.2. The produced water is stored in a softened water reservoir.

Figure 5: Cation ion exchange softener (Evides Industriewater).

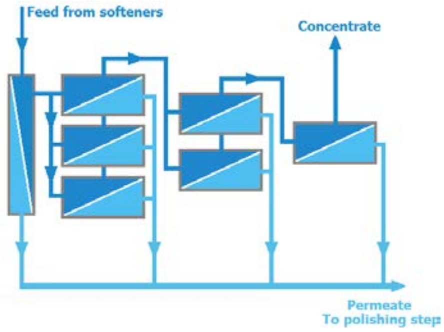


Figure 6: RO treatment (Evides Industriewater).

2.1.3 Desalination

The water is transported from the softened water reservoir to the RO treatment. Before desalination the pH of the softened water is increased by dosage of caustic soda (NaOH). With the conduct of the process is chosen to dose a concentration of 8 to 16 mg/l NaOH and not to perform the dosage on the value of the pH. The goal of the increase in pH is to slow down the biological growth on the membranes and the candle filters. The increase of the pH can also have an effect on the carbon dioxide concentration in the water. When the pH is increased above a value of 8.9 the carbon dioxide (CO_2) that is present in the water is than converted to bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). Bicarbonate and carbonate will not pass the membrane instead of carbon dioxide that will pass the membrane. Evides expect that the increase in pH has an effect on the fouling, but this is still under investigation.
Before the desalination the water is treated with candle filters to remove particles. Desalination takes place with the use of reverse osmosis (RO) membranes. In the installation, both vertical and horizontal membranes are placed. The used membranes are the Filmtec Le440i from DOW. Research has shown that most of the bio fouling will occur in the first

modules of the RO installation. By placing these modules in a vertical position the fouling of the membrane is more manageable. Because of the vertical position it is also possible to clean these membranes by injection of air, so the use of cleaning chemicals can be reduced. The overall recovery of the RO treatment is 85% and the flux is 25 LMH (L/m^2/h). In total there are 8 streets, each street consists of 252 membrane modules and is capable of a production of 200 m^3 per hour. A drawing of the process of the desalination is given in Figure 6. The permeate is transported to the polisher.

2.1.4 Polishing

The demineralized water gets a high quality by using a downstream polishing step existing of a mixed bed ion exchanger. The bed of the mixed bed ion exchanger consists of a cation and an anion resin. The cation resin is the Lewatit S100 and is regenerated with HCl. The anion resin is the Lewatit M800 and is regenerated with NaOH. In total, there are 8 MB (= Mixed Bed) ion exchangers at the plant available. From this point the demineralized water flows to the storage tanks (2 tanks of each 7,000 m^3) and is then pumped into the demineralized water system.

2.1.5 Reservoirs

Two softened water reservoirs (each 800 m^3) are present at the site. Also there are two rinse water tanks with a volume of 600 m^3.

2.1.6 Back-up system

At DWPB drinking water is available as backup in case that the pre-treatment is down. In that case drinking water from the production location Berenplaat is fed to the process after the pre-treatment. When the softeners are down, two types of backup can be used. The water from the pre-treatment can directly be fed to the RO membranes. Because in that case water is used that is not softened, the dosing of antiscalants is necessary to prevent scaling on the membranes. When both the pre-treatment and the softeners are down, drinking water can be used as a feed for the RO membranes. In that case also precautions haven to be taken to prevent scaling on the membranes. The worst case scenario is that whole plant is down and that no demineralized water can be produced. Then the water from the storage tanks can be used as a buffer until the mobile RO units are placed at the customers.

2.1.7 Water quality

Parameters relating to the quality of the demineralised water at the customer are shown in the table below.

Table 1: Quality of the demiwater at the customer (Evides Industriewater).

Parameter		Maximum value	Unit
pH		9.0	-
Iron	Fe	0.05	mg/l
Cupper	Cu	0.05	mg/l
Hardness	TH	0.04	mmol/l
Conductivity (at 25°C)	EC	4	μS/cm
Silica	SiO_2	0.03	mg/l Si

2.2 Softeners

In this paragraph more information is given on the process of the softeners. Hardness of water from the pre-treatment is equal to hardness of the water from the Brielse Meer. The total hardness varies between 2.0 and 2.5 mmol/l and is removed from the water by the use of ion exchange treatment. In paragraph 2.2.1 information is given about loading of the resin. When resin is loaded it has to be regenerated with a regenerant. After regeneration the resin can be loaded again. The regeneration process is described in paragraph 2.2.2. In the last paragraph is described how the used regenerant is produced and what is needed for the production.

2.2.1 Loading of the resin

Figure 7: Softener at DWPB (Evides Industriewater).

The water that comes from the pre-treatment is fed to the softener (see Figure 7 for an example of a softener at DWPB). At the plant a total of 8 softeners are present. Not every softener is used because when the redundancy of n-1 is taken into account only 7 softeners are operational. The flow to each softener varies between 150 and 360 m^3/h, and the nominal production is 300 m^3/h. As mentioned earlier before the hardness of the feed water varies between 2.0 and 2.5 mmol/l. The loading of the resin is with a downward flow, co-current. The water enters the vessel from the top and flows downward through the resin which is divided into two beds in different compartments of the vessel. The upmost bed functions as a filter. The mesh size of the filter is the same because the filter consists of the same resin as the lower bed. The filter can remove suspended solids and is not effective anymore as a softener. Softening of the water takes place in the lower bed.

To ensure an equal distribution of the flow, the water enters the compartments through nozzles. In the bed exchange of calcium and magnesium for sodium ions takes place. More information on the process of ion exchange can be found in chapter 3.

In the vessel is a strongly acidic, gel-type cation resin of the company Lanxess called Lewatit S100 heterodisperse (alternative name: S1428). According to the analysis certificate the maximum capacity of the resin is 2.1 eq/l resin.

With the loading of the resin at DWPB is chosen to do an incomplete loading. The resin of one softener is loaded to a level of 9000 mol (= 18,000 eq) total hardness. At the feed side of the vessel is measured and counted how much hardness is loaded. When the total amount of hardness is reached, or a breakthrough of the bed is measured, the column is regenerated. One softener contains 21,900 litre of resin. So the maximum loading of one softener in practice is 0.82 eq/l resin. The water quality and the stability of the process benefit from the incomplete utilization of the available capacity.

The softened water that is produced is stored in softened water reservoirs. Different processes use this softened water. The largest part is lead to the RO membranes for desalination. The other processes which the softened water is used for are:

- Regeneration.
- Process water plant (PWP).

The process water plant is another installation of Evides Industriewater at the location of Huntsman and is no part of DWPB.

In Table 2 a summary is given of the mentioned parameters of the softeners.

Table 2: Parameters of one softener at DWPB.

Parameter	Description	Minimum value	Maximum value	Unit
Q	Flow	150	360	m^3/h
TH_{BMW}	Total hardness water Brielse Meer	2.0	2.5	mmol/l
TH_{loaded}	Total hardness loaded on resin	-	9000	mol

With these parameters a graph (Figure 8) can be constructed in which can be seen what the run time of one softeners is with a certain flow and hardness of the feed.

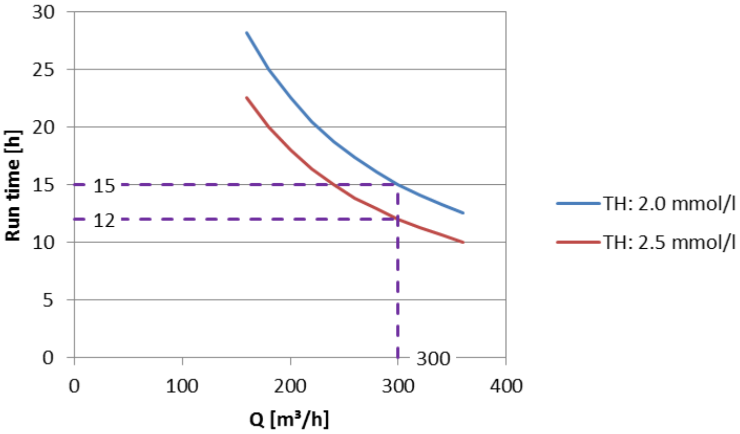


Figure 8: Run time of one softener of DWPB loaded with water from Brielse Meer.

In the graph the runtime is given for the nominal production as an example. The runtime of a softener varies between 12 and 15 hours dependent on the hardness of the feed water. A technical drawing of a softener with dimensions is given in Figure 9.

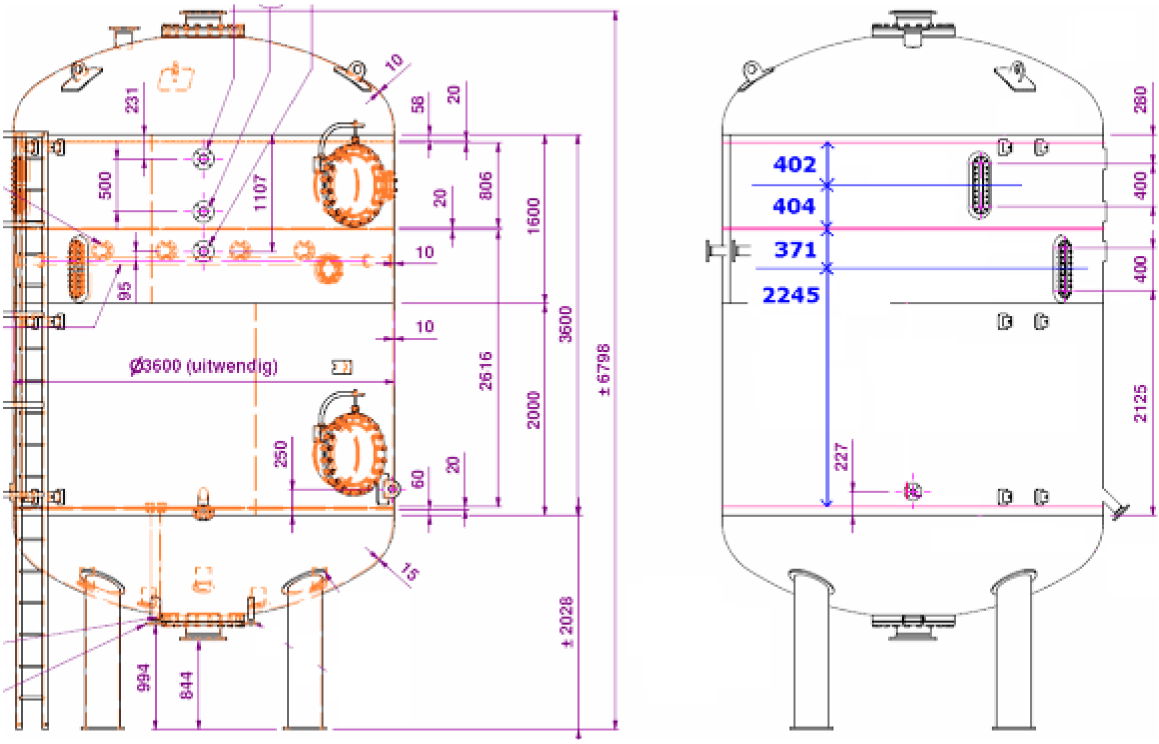


Figure 9: Technical drawing of a softener at DWPB with dimensions [mm] (Evides Industriewater).

A softener has an internal diameter of 3580 mm and an area of 10.1 m^2. The volume of the bed (BV) occupied by the resin in the column is 21.9 m^3.

2.2.2 Regeneration

After the resin is loaded with the desired amount of hardness, it is regenerated. The regeneration can be divided into the following sub processes:

1) Backwash with softened water, 5 minutes at 38 m^3/h.
2) Injection of regenerant (9% NaCl) at 38 m^3/h, until more or less 1735 kg of sodium chloride is dosed.
3) Displacement with softened water at 38 m^3/h; 2.3 BV of softened water.
4) Downward rinse with 260 m^3/h; 1.8 BV of softened water.

The total time that is needed to regenerate a softener is approximately 2 hours (Table 3). The injection of regenerant is done with an excess of 65% to ensure that the driving force during the regeneration is enough to remove the hardness of the resin.

With the design of the vessel the expansion of the bed during regeneration is taken into account. The expansion of the bed is 4% per m/h.

$$\left.\begin{array}{l} U = \frac{Q}{A_{bed}} = \frac{38}{10.07} = 3.78\ {}^{m}\!/\!_{h} \\ h_{bed} = \frac{BV}{A_{bed}} = \frac{21.9}{10.07} = 2.17\ m \end{array}\right\} \Rightarrow h_{expanded\ bed} = \left(1 + \frac{4 \cdot 3.78}{100}\right) \cdot 2.17 \approx 2.50\ m \tag{1}$$

The height of the expanded bed is indeed lower than the available height (see Figure 9).

All the water and regenerate that is used during the regeneration is discharged on the Brittannië harbour. Evides Industriewater has a permit for the discharge. In Table 2 an overview of the amount of water that is used is given. Also is given what has to be paid to discharge the water on the harbour.

Table 3: Amount of water used for regeneration of one softener at DWPB.

Sub process	**Description**	**Amount of softened water** [BV]	[m^3]	**Time** [min]	**Costs for the discharge** [€]
1	Pre injection	0.15	3.2	5	0.02
2	Injection of regenerant	0.82	18.0	28.5	0.14
3	Repression	2.30	50.4	79.5	0.38
4	Downward rinse	1.80	39.4	9	0.30
Total		**5.07**	**111.0**	**122**	**0.83**

At BWPB a regeneration level of 79 g NaCl / litre resin is used. In the softener a total amount of 21,900 l resin is present. Therefore with regeneration of a softener a total of 1735 kg (=29,658 mol) NaCl is used. Stoichiometric a total of 18,000 mol NaCl is needed to remove the loaded hardness from the resin. After the regeneration an operational capacity of 0.95 eq / litre resin is expected [7].

Table 4: Parameters for regeneration of one softener at DWPB.

	Unit	**Value**
Regeneration level	g NaCl / l resin	79
Operational capacity	eq / l resin	0.95
Amount of resin	l	21,900
Amount of salt	kg	1735

An example of the regeneration of a softener is given in Figure 10. In the figure can be seen that after a flush with softened water regenerant is injected during 28.5 minutes. After the injection starts it takes some time before the regenerant reaches the softener. The delay in the increase of the conductivity at the top indicates that it takes time for the regenerant to pass the bed. In the bed sodium is exchanged for calcium and magnesium. That can be noticed with the increase of the total hardness at the same time that the conductivity at the top increases. After the injection of regenerant is stopped the conductivity decreases slower than it increased with the start of the injection. That can be explained by the fact that when the injection is stopped still mixing occurs, and no plug flow is present. So due to the mixing the concentration decreases slower and therefore the conductivity shows a slower decrease.

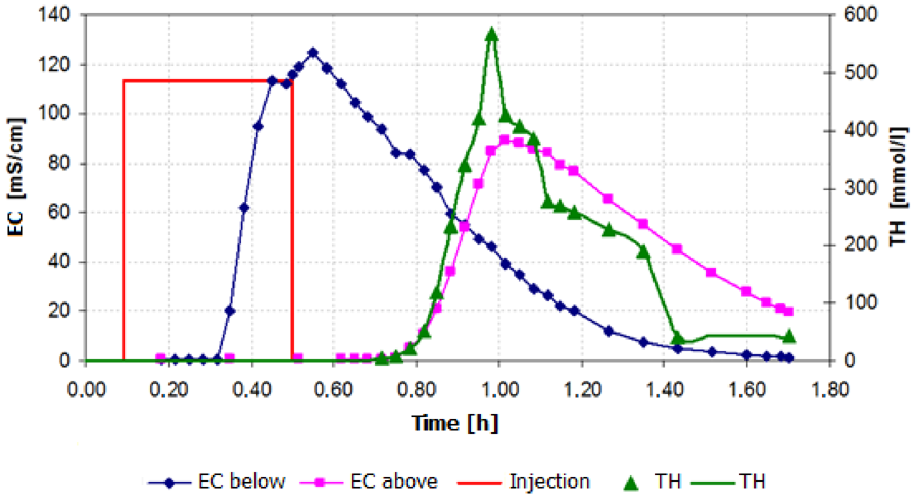


Figure 10: Softener 2 of DWPB (10-03-2010) (Evides Industriewater).

2.2.3 Production of the regenerant

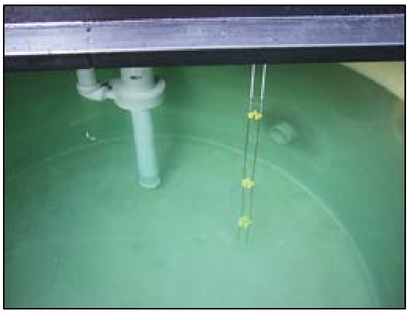


Figure 11: Brine reservoir with level measurement (Evides Industriewater).

To regenerate the resin a solution of salt is needed. Salt water is made by dissolving salt in water to create brine. The brine is produced in the so called salt tower. In this tower dry salt is dumped on a layer of water. A natural brine solution of 26 % NaCl is created, due to contact between salt and water at the bottom of the tower. In the vicinity of the tower a reservoir is present in which the brine solution is stored. The reservoir is automatically filled again when the level of brine is too low. In Figure 11 the inside of a brine reservoir with the level measurement is presented. Brine is diluted with softened water (brine injection) in the pipe with a static mixer to create a solution with 9% NaCl. A schematic drawing of this process is given in Figure 12. In total there are three salt towers present on the plant, from which 1 is a reserve.

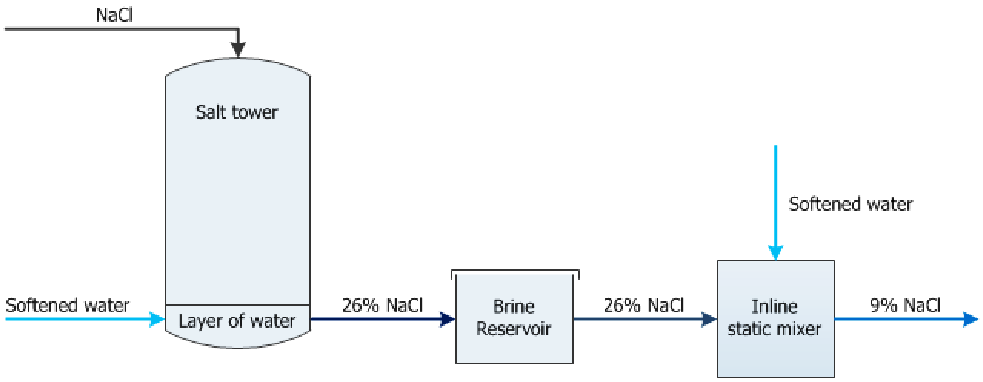


Figure 12: Process scheme of the regenerant production.

The total amount of salt that is used in a year is 7,599,300 kg. This number is based on maximum production of DWPB with 12 regenerations per day.

3 Technology of ion exchange [2][3][4]

In this chapter a short overview is given about what ion exchange is and which types there are. After that the type of resin used at DWPB is dealt with. Then definitions and formulas are given related to ion exchange. Finally, some guidelines are given for performing small scale experiments and the consequences on the results.

3.1 Ion exchange

The technique of ion exchange is the exchange of one ion by another. The exchanged ion is originally a part of an insoluble material (the resin), and the displacing ion is originally in solution. At the completion of the process, the two ions are in reversed places: the displaced ion moves into solution and the displacing ion becomes a part of the insoluble material. For the ion exchange two different types of ion exchange materials are used. That material is dependent on the ions that need to be removed from the solution. If cations need to be exchanged, a cation exchange material is needed. For the removal of anions from a solution anion exchange material is used. With the exchange of ions the affinity is a fundamental aspect. The affinity of the resin for an ion that needs to be removed needs to be greater than the affinity for the ion that is on the resin. In the past natural and synthetic alumina silicates called zeolites were used as exchange materials. Nowadays also synthetic resins are available. Synthetic resins are insoluble polymers to which acidic or basic groups are added. These so called functional groups are capable of performing reversible exchange reactions with ions in a solution. The total number of these groups determines the exchange capacity of the resin. The ion selectivity is determined by the type of functional group that is present on the polymer. When the exchange capacity of the resin is reached it can be regenerated by reversing the reaction. The exchange is than taking place against the affinity of the resin for that ion, so more ions are needed than necessary.

Within the ion exchange resins mainly four types of resin can be distinguished:

- Strong-acid cation (SAC)
- Weak-acid cation (WAC)
- Strong-base anion (SBA)
- Weak-base anion (WBA)

For ion exchange the following properties are important:

- engineering properties
- physical properties

The engineering properties consist out of the exchange capacity and selectivity of the resin. With specified operating conditions the exchange capacity and selectivity can be used to determine the performance of the resin. The physical properties consist out of particle size, stability, swelling, moisture and density of the resin. For the selection of resin for a specific water treatment the physical properties are important.

The ion exchange process is taking place in a fixed bed of resin while the water is flowing through the bed. The loading of the resin is stopped when a certain treatment objective is reached. If the resin is needed again regeneration of the resin is conducted. When necessary another column is used for the treatment of the water to guarantee a continuous supply.

The regeneration steps of an ion exchange resin are important to the overall efficiency of the process. There are two methods for regenerating an ion exchange resin: co-current and counter-current. In a co-current regeneration the regenerant is passed through the resin in the same flow direction as the loading is done. With a counter-current regeneration the regenerant is passed through the resin in the opposite direction of the loading.

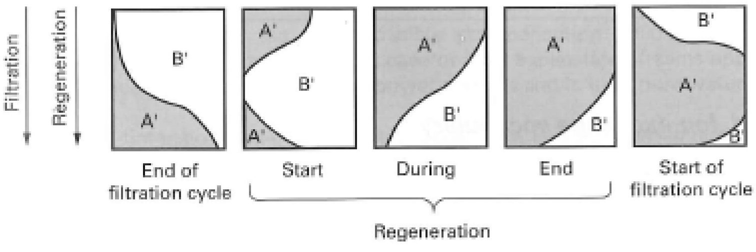


Figure 13: Co-current regeneration (Degremont).

Important engineering considerations in

developing an ion exchange treatment process include preliminary process analysis, bench- and pilot-scale studies, and development of process design criteria.

3.2 SAC resin as a softener

At DWPB a SAC resin is used in the softener to soften the water. A SAC resin can be in two forms, the sodium form and the hydrogen form. The resin used at the plant is in the sodium form. The order of the affinity of that resin is:

$Pb^{2+} > Ca^{2+} > Mg^{2+} > Na^{+} > H^{+}$

So the affinity of the resin for calcium is higher than the affinity for magnesium. And both can easily exchange the sodium on the resin. The following reaction takes place with the loading of the resin with calcium:

$$2\ R - Na^{+} + Ca^{2+} \rightleftarrows 2\ Na^{+} + R - Ca^{2+} \qquad (2)$$

The reaction for the loading of the resin with magnesium is:

$$2\ R - Na^{+} + Mg^{2+} \rightleftarrows 2\ Na^{+} + R - Mg^{2+} \qquad (3)$$

When the resin needs to be regenerated the reaction is driven to the left by increasing the concentration of the sodium ion on the right. The resin is regenerated by using a concentration of NaCl of about 5 to 10%, in case of DWPB 9% NaCl. At the plant the resin is regenerated with a counter-current regeneration. The counter-current regeneration will result in a lower leakage level and a higher chemical efficiency than co-current regeneration. The exchange capacity and regeneration requirement can be determined with data from the manufacturer. When that data is not available, an experiment has to be conducted to retrieve the needed data. Important is to realize that the capacity of an ion exchanger in terms of volume of influent treated varies with the nature and concentration of ions in the solution. That is almost equal to the characteristics of activated carbon. The experimental procedures of both are almost the same and therefore the same isotherms can be used for the determination of the capacity of the resin. The used isotherms are the Freundlich and Langmuir isotherm. The Freundlich isotherm is given by:

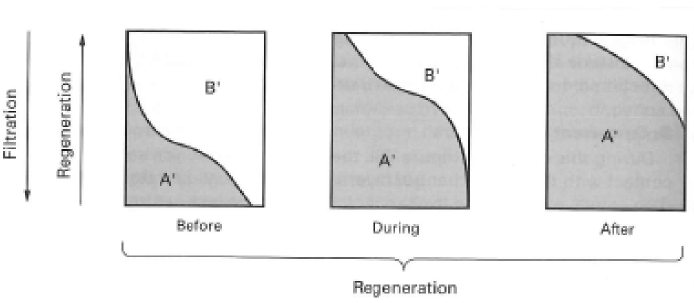


Figure 14: Counter-current regeneration (Degremont).

$$q_e = K_e C_e^{1/n} \qquad (4)$$

C_e = equilibrium concentration of the hardness in the solution [mmol/l]
q_e = solid phase hardness concentration at equilibrium [eq/l]
K_e = Freundlich adsorption capacity parameter [(eq/l) (l/mmol)$^{1/n}$]
$1/n$ = Freundlich adsorption intensity parameter [-]

The equation can also be written in the linear form:

$$\log(q_e) = \log(K_e) + \left(\frac{1}{n}\right)\log(C_e) \qquad (5)$$

The Langmuir isotherm is given by

$$\frac{c_e}{q_e}=\frac{1}{Q_M b_e}+\frac{1}{Q_M}c_e \Rightarrow q_e=\frac{b_e Q_M c_e}{1+c_e b_e} \tag{6}$$

C_e = equilibrium concentration of the hardness in the solution [mg/l]
q_e = solid phase hardness concentration at equilibrium [eq/l]
Q_M = maximum concentration of the hardness on the resin [eq/l]
b_e = Langmuir adsorption constant of the total hardness [l/eq]

The parameters used in both equations can be determined with performing a batch experiment. A batch experiment is performed by putting the same known amount of solution into different containers. To these containers different amounts of resin are added and mixed with the solution. After that the mixture of solution and resin is allowed to come to equilibrium.

In the figure to the left the principle of the determination of the isotherm is given. Before the addition of the resin the concentration in all containers is the same, C_0. Now for example three different amount of resin (V_1, V_2 and V_3) is added to three different containers. When equilibrium is reached the concentration of the liquids in three containers (C_{e1}, C_{e2} and C_{e3}) is determined. Form these concentrations can be determined how much is loaded on the resin (q_{e1}, q_{e2} and q_{e3}). The parameters of the Langmuir isotherm are determined by making a plot of q/C_e versus C_e. To determine the parameters of the Freundlich isotherm the same plot is made only on a logarithmic scale.

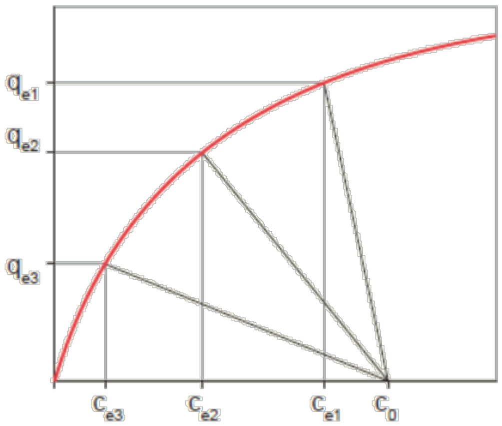


Figure 15: Determination of the isotherm.

To determine the essential parameters for the loading and regeneration of the column small scale column tests are performed. The two main types of data retrieved from small scale column testing are breakthrough curves and elution curves. Data developed from these curves form the basis for the pilot plant studies and the development of full-scale designs.

3.3 Definitions and formulas

In this paragraph some definitions and formulas applicable to ion exchange are explained.

Attrition

The mechanical wear of the ion exchange resin during operation.

Bed load

The bed load is the amount of water that is loaded on a specific amount of resin, a bed volume.

$$\text{Bed load} = \frac{\text{Volume per hour of liquid to be treated}}{\text{Volume of resin}} \left[\frac{V}{V \cdot h}\right] \tag{7}$$

Bed Volume

The amount of resin that is present in one vessel is expressed as a bed volume.

$$BV = A_{bed} \cdot h_{bed} \qquad (8)$$

BV = Bed volume [m^3]
A_{bed} = Surface area of the bed [m^2]
h_{bed} = Height of the bed [m]

Sometimes the bed volume is also given as the volume per hours of liquid to be treated divided by the volume of resin.

Breakthrough point

The breakthrough point is defined as the point where the ions that need to be removed first appear in the column effluent.

Breakthrough curve / saturation loading curve

The saturation loading curve is obtained by passing the process stream or a simulated stream of the same chemical composition through a fully regenerated column of resin. During the runs, samples of the effluent are collected and analysed. That process is continued until the effluent concentration of the contaminant of interest equals the influent concentration. To develop the breakthrough curve the effluent concentration is plotted in terms of percent breakthrough or equivalents per litre versus the number of bed volumes treated.

Co-current regeneration

The regeneration is conducted in the same flow direction as the loading.

Counter-current regeneration

The regeneration is performed in the opposite direction of the loading.

Elution curve

An elution curve is obtained by passing the regenerant through a fully loaded column of resin. During the run samples of the effluent are collected and analysed. With the analysis is determined what the concentrations of the ions of interest are. The bed volumes of regenerant that are used can be converted in terms of a salt loading rate.

$$SLR = \frac{BV_R \cdot c_R \cdot \rho_R}{BV_{total}} \qquad (9)$$

SLR = Salt loading rate [kg/m^3]
BV_R = Bed volumes of regenerant [m^3]
c_R = Concentration regenerant [kg/l]
ρ_R = Density of the regenerant [kg/m^3]
BV_{total} = Volume of the resin bed [m^3]

To develop the elution curve the effluent concentration is plotted versus the number of bed volumes or salt loading rate.

Exchange capacity

The exchange capacity is the quantity of ions that can be exchanged onto the resin. The capacity is expressed as equivalent per unit of weight (eq/g) or volume (eq/l) of resin. A difference is made between the total capacity and the useful capacity. The total capacity is the maximum quantity of exchangeable ions. The useful capacity is the useable fraction of the total capacity and depends on the hydraulic and chemical conditions.

Total capacity

See exchange capacity

Useful capacity

See exchange capacity

Ion flow / flux

$$\text{Ion flow / flux} = \text{Bed Load} \cdot \text{Water salinity} \tag{10}$$

Leakage

Leakage is defined as the appearance of a low concentration of influent ions in the column effluent during the initial part of the loading. Leakage is caused by residual ions in the resin at the bottom of the column due to incomplete regeneration that are displaced by other ionic species coming down the column.

Particle size

Ion exchange resin beads are spherical in shape and are available in particle diameter sizes of 0.04 to 1.0 mm. The particle size has an influence on the rate of ion exchange, it decreases when the particle size increases. Also influenced is the head loss through the bed that increases when the particle size decreases.

Regeneration level

The quantity of regenerant used in the regeneration cycle of an ion exchange system. The regeneration level is expressed in grams per litre of resin.

Selectivity

Ion exchange resins have a certain affinity or preference for ions in a solution. This affinity or preference of a resin is called selectivity. Resin selectivity depends upon the physical and chemical characteristic of the exchanging ion and resins. Chemical properties of the ions that impact selectivity are the magnitude of the valence and the atomic number of the ion. The physical properties of the resins that influence selectivity include pore size distribution and the type of functional groups on the polymer chains.

Swelling, moisture content and density

When resins exchange ions, the volume of the resin beads can change. Swelling of a resin due to exchange of ions can be reversible or irreversible. Reversible swelling is when the resin beads undergo a reversible volume change between one ionic form and another. The internal osmotic pressure of the resin bead increases when the resin swells and decreases when the beads shrink. Over time, the osmotic pressure swings can cause the beads to fracture. Irreversible swelling is observed with acrylic SBA resins were during the first few regeneration cycles the resins can irreversibly swell 7 to 10 percent over and above the reversible volume changes. Because the water content of a resin can vary, the resin densities of different forms of the resin can also vary. The density will depend upon the quantity of water and the ionic form of the resin.

Stability

The stability of an ion exchange resin can be an important process design consideration under certain physical, chemical, and/or radioactive conditions. Chemical reactions between the resin matrix and dissolved constituents in water, physical impairment of resin performance due to fouling by organic and inorganic constituents, and some process operating conditions can significantly affect the resin performance and cost. Consequently, it is important to understand these interactions and take steps in the design stages to identify and prevent conditions that would negatively alter the resin's performance and the possible release of material from the resin to the finished water.

3.4 Development of column design criteria

The results of bench-scale studies or data from the manufacturer of the resin can be used to develop design criteria for the full-scale installation. Important for that development is:

- Scale-up considerations
- Column design details
- Regeneration requirements

3.4.1 Scale-up considerations

Small-diameter columns can be used in experimental research to develop process data. Column studies are used primarily to evaluate and compare resin performance in terms of capacity and ease of regeneration.

Because the main issues of concern are mass transfer and operating exchange capacity, small (1.0 to 5.0 cm inside diameter) columns can be scaled directly to full-scale design if the loading rate and empty-bed contact time are the same. The error due to channelling of water in the column is minimized, because the resin particles are small and the ratio of column diameter to particle diameter is large. The hydraulics of full-scale operation cannot be modelled completely by small-scale columns because deviations in flow patterns can exist and should be evaluated at the pilot scale.

Increasing the height of the bed in a full scale design is possible when the small column experiments were done with a reasonable bed height (0.6 to 1 m). The increase of the height of the bed will not change the shape of the breakthrough curve, it will extend the service time. When the separation factor is greater than 1 for the ion to be removed, the exchange zone will be relatively small with respect to the column height. Increasing the column depth for the same flow rate will not increase the breakthrough capacity with respect to bed volumes.

3.4.2 Column design details

When the volumetric flow rate is kept at the same values as is determined with the small-scale experiments, cycle times and effluent concentration profiles will be similar. If the height of the column is kept constant, than the superficial velocity will also remain equal.

When the column is deepened and the volumetric flow rate is kept the same, the superficial velocity will be increased. That increased flow should not be a problem, unless a critical range of flow velocities is reached. Typical superficial velocities are in the range of 10 to 36 m/h. Excessive velocities will increase the pressure drop through the column and could adversely affect the stability of the resin beads. Once the optimum service flow rate is known, the design details of the full-scale columns, including volume of resin, surface area of columns, number of columns, side wall height, and pressure drop, can be determined.

With the amount of resin needed to treat a given flow of water and the desired depth of the resin, the diameter of a single column can be determined. If the required diameter is larger than 4 m, two or more columns should be used. Typical bed depths used in the industry range from 0.75 to 3 m. The feed must be distributed uniformly over the resin surface and collected uniformly from the bottom of the column to prevent channelling, misdistribution of flow and density currents. Premature breakthrough and excessive leakage can occur when the ion exchange columns are not properly designed.

3.4.3 Regeneration requirements

The three variables of concern during the regeneration are:

- Concentration of the regenerant
- Regenerant flow rate
- Regenerant dosage

Once the parameters have been established, it is necessary to operate the column to an allowable breakthrough point and leakage level for a number of cycles (3 to 5) to stabilize the system. To prevent interruption of the delivery of treated water, two or more columns or a treated water storage reservoir are required. When the loading time is long (16 to 24 h), a reservoir can provide sufficient water during regeneration time, normally 1 to 2 h. For most ion exchange applications, a typical regeneration cycle is as follows:

1. End of service run
2. Backwash
3. Regeneration
4. Slow displacement rinse
5. Fast rinse
6. Stand-by (optional)
7. Beginning of service cycle

Backwashing is typically done to reclassify the resin so that there will be a gradual increase in particle size from top to bottom and to help prevent channelling. Ion exchange media is also a good filter media. So the backwash of the resin will also remove trapped particulate matter from the bed. With the design of the column the expansion of the bed during regeneration should be taken into account.

The leakage is also influenced by backwashing. With a co-current regeneration backwashing after each regeneration is performed to reduce the leakage by mixing the resin. With a counter-current regeneration backwashing is performed before the regeneration to minimize the leakage.

Regenerant consumption per cycle based on design criteria must be determined. The slow rinse for one to two bed volumes at the regeneration flow rate to displace most of the regenerant from the bed and the fast rinse at the rate of service flow rate for 10 to 30 min. The rinse can be monitored using an online conductivity meter at the effluent of the column to determine when the cycle is complete.

The amount of used regenerant and rinse volumes has to be determined to prepare for the disposal. The disposal can be very costly because sometimes extra treatment steps are needed before it can be discharged. So the disposal of may be the critical factor in many potential applications.

4 Solutions to lower the use of regenerant.

In this chapter the possible solutions are given and discussed on which way they can be implemented in the current process. Distinction is made between the solutions in the application to the master process or applied to the regeneration.

The solutions applied to the master process are:

- Capacitive Deionization (CapD-I)
- Limeteq converter
- Electro dialysis (ED)
- Electro deionization (EDI)

The solutions applied to the regeneration are:

- Eutectic Freezing
- Selective Ion Exchange
- RO concentrate as regenerant
- Water from the Brittanniё harbour as a regenerant
- Dosing of sodium carbonate in combination with precipitation

4.1 Solutions for the master process

4.1.1 Capacitive Deionization (CapD-I)

Capacitive Deionization (CapD-I) is an innovative and energy efficient technology to remove salt from brackish water. The water flows through an electric field to attract and remove ions without a significant pressure loss. The technology is compatible with proven technology such as reverse osmosis. The principle of CD uses a so called flow through capacitor system (FTC). A FTC system consists out of two opposite charged electrodes and cation and anion membranes.

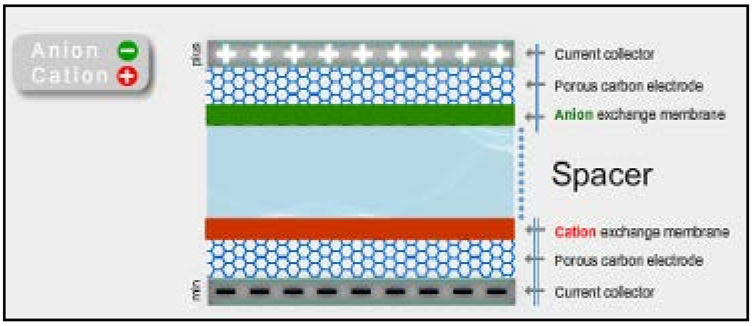


Figure 16: FTC cell (Voltea).

When water containing ions flows through the cell, the electrodes attract the ions and will pass the selective membranes. The difference in voltage between both electrodes is 1.5 volt. The energy that is stored in the electrode during deionization is used again by the system. From the FTC cell flow deionized water.

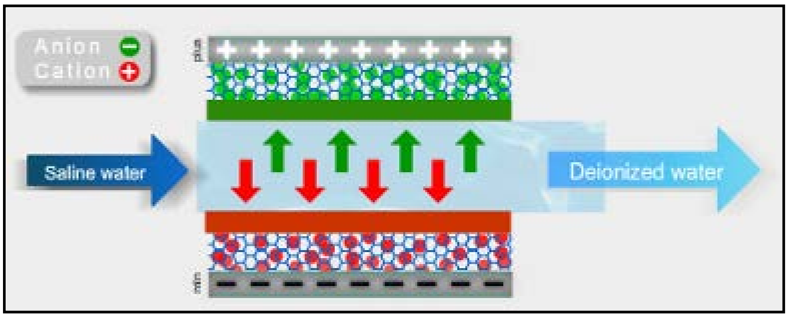


Figure 17: FTC cell in operation (Voltea).

When the surface of both electrodes is completely loaded with ions the system is regenerated. The regeneration is done by switching the polarity which causes that the ions are rejected instead of attracted. Between the two selective membranes a concentrated salt solution is formed, which is discharged.

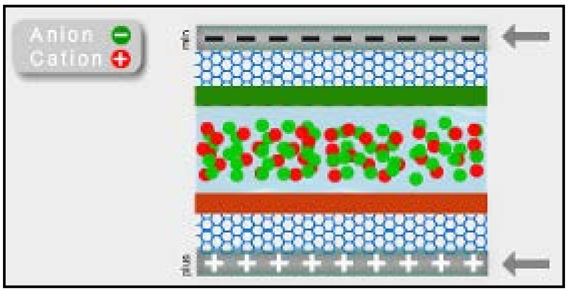


Figure 18: Regeneration of the FTC cell (Voltea).

After the regeneration the polarity of the electrodes is switched again and the system is ready for operating.
CapD-I is insensitive for particles. The system has also no problems with biofouling or scaling. The water flows through the system with a high velocity because of the low resistance and therefore impurities are flushed away. CapD-I needs also less maintenance and down-time. Also a benefit is that it works without chemicals. Applications for the process vary from desalination of groundwater, industrial applications to softening water for domestic machines. The standard industrial system can produce up to 10 m^3 per hour. CapD-I has a recovery of 80% to 90%.

Application to the process

When CapD-I is applied instead of the current softeners not only calcium and magnesium are removed from the water, all ions are removed. In that case RO is not necessary for removal of ions, but still needed for removal of NOM. To procedure the current nominal production (300 m^3/h) with CapD-I, 30 standard industrial systems are needed. To replace the current softeners a total of 240 standard industrial systems are needed. The benefit of CapD-I is that salt is not needed any more as a regenerant. Another benefit is that the production facility of the brine needed for the regenerant is also not needed anymore. The waste water from the regeneration of the FTC cell is of a better quality than that is now discharged with the regeneration of the softeners. The sodium chloride concentration is much lower.
An option could be to use selective membranes through which only bivalent or multivalent ions can pass. In that case calcium, magnesium and other multivalent ions will be collected on the electrodes. The water that is flowing from the cell is softened. With the regeneration of the FTC cell waste water is produced that only contains multivalent ions. So no sodium is present in the waste water, which can have a benefit when the discharge of wastewater containing sodium chloride is not allowed.
According to Seok-Jun Seo, et all the efficiency of CapD-I is for a longer period of production higher for multivalent ions than for monovalent ions. Based on that article the application of a membrane that only let multivalent ions pass through will function better.
Another benefit could be that CapD-I also can be applied as a polisher, but that is not a part of the scope of the research.

4.1.2 Limeteq converter

In a Limeteq converter a strong and stable vortex is created by means of the Vortex process technology. In the middle of the vortex negative pressure is present, which causes that gas is extracted from the water. That process is controlled cavitation. All non-bound gasses such as carbon dioxide are extracted from the water. With the extraction of carbon dioxide calcium carbonate will be formed, the water is softened.

The calcium carbonate that is formed in the vortex crystallises on a different way. The forces of the vortex prevent the crystal to form as calcite, polymorph aragonite is formed instead.
The formed aragonite cultures cause that when more calcium carbonate is formed also more aragonite is created. The major property of aragonite is that it does not attach, so the formed calcium carbonate stays in solution and will not precipitate on heat sources or other surfaces. Another important property is that aragonite is harder than calcite. When aragonite is present in a solution it even can remove (old) calcite deposit.

Figure 19: Limeteq converter (Pathema).

The length of the vortex determines the amount of gas that is extracted from the water. With this process the use of salt is not necessary anymore.

Application to the process

The suggestion is to replace the current softeners by the Limeteq converter. Benefit of that is that the production unit of the regenerant is not needed anymore. Also less softened water is needed so the production can be lowered. Another benefit is that the Limeteq converter is a small scale installation, so less surface is required. Only when a Limeteq converter is used a filter need to be placed after the converter. That is because the formed aragonite can cause damage to the membranes and needs to be removed from the water. In the figure above an example of a Limeteq converter is given.
With the application of this technique the question rises if enough hardness is removed from the water to achieve the required hardness concentration. The technique is limited by the amount of carbon dioxide that can be removed from the water.

4.1.3 Electro dialysis (ED)

Electro Dialysis (ED) is a membrane process in which ions are transported through a semi permeable membrane under the influence of an electrical potential.
The membranes are cation-or anion-selective, which means that either positive ions or negative ions can pass through the membrane. Cation-selective membranes are polyelectrolytes with negatively charged matter, so negative charged ions are repelled and positive charged ions pass through the membrane.
By placing multiple membranes in a row, in which alternately positively or negatively charged ions are able to pass through the membranes, the ions can be removed from the water. In a number of columns ion concentration will take place and in others ions are removed. The concentrated brine stream is circulated until the point is reached that precipitation is possible. When that point is reached the brine stream is discharged.
This technique can be used to remove ions from water. Particles that are not charged cannot be removed from the water with ED.
Cation-selective membranes are composed of sulphonated polystyrene and anion-selective membranes of polystyrene with quaternary ammonia.
Pre-treatment of water may be required before the ED. To prevent clogging suspended particulate matter with a diameter greater than 10 microns should be removed. There are also substances that are able to neutralize the membrane. That are substances such as large organic anions, colloids, iron oxide and manganese oxide. These substances interfere with the selective operation of the membrane. Treatment methods to prevent this are active carbon filtration (for organic matter), flocculation (for colloids) and filtration techniques.

Application in the process

In this solution the suggestion is to use the technique of Electro Dialysis (ED) at the plant instead of the softeners and the RO membranes. ED can remove all of the charged ions form the water. As mentioned before than active carbon filtration is needed before the ED to remove the organic matter from water. Also flocculation is needed, but that is already present at the plant.

The application of ED to the process gives a large impact on the process. The softeners, regenerant production unit and the RO filtration are removed. Instead of those units carbon filtration and ED needs to be build.

Other remarks with the use of ED are what amount of energy is that is needed for the use of this process on a large scale. And also if it is possible to treat a large stream with ED. Another remark is that with the application of active carbon filtration, not all of the NOM is removed from the water. The filter has only a complete removal in the first period with a new bed.

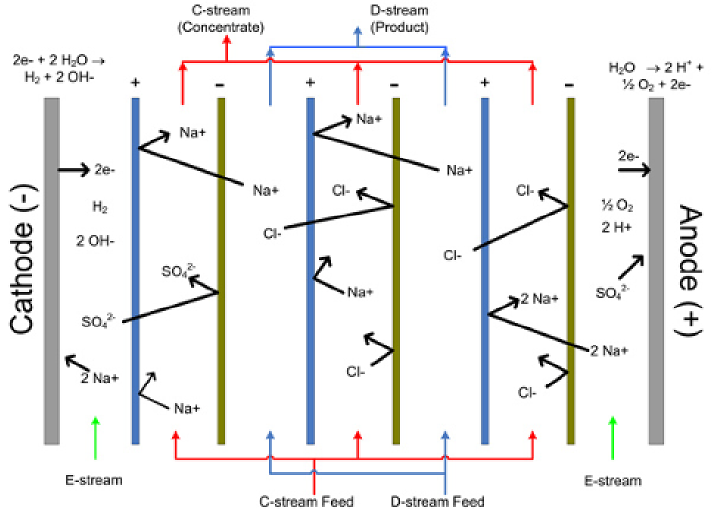


Figure 20: Process of Electro Dialysis (ED).

4.1.4 Electro deionization (EDI)

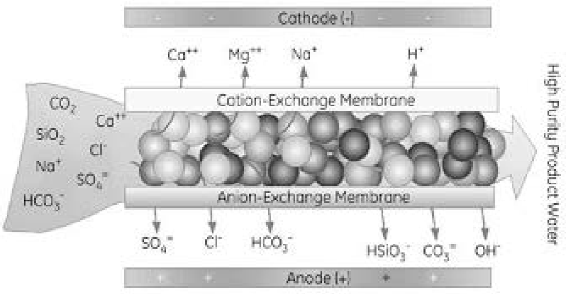


Figure 21: Process of Electro deionization.

EDI is a further refinement of electro dialysis in that it combines the semi-permeable membrane technology with ion-exchange media to provide a high efficiency demineralization process. The fundamental concept is a basic desalting unit being an ED dilute cell filled with mixed-bed ion-exchange resin. Within that resin-filled cell some complex chemical reactions take place. These reactions cause that water with a very high purity can be produced. When flow enters the resin-filled diluting compartment of an EDI stack, several processes are set in motion. Strong ions are exchanged out of the feed stream by the mixed bed resin. Under the influence of the strong DC field charged ions are pulled off the resin and drawn toward an electrode. Dependent on their charge, positive or negative, ions are transported to a cathode or to an anode. As these strongly charged ions, such as sodium and chloride, migrate toward the ion-exchange membrane, they are continuously removed and transferred into the adjacent concentrating compartments (see Figure). As the strong ions are removed from the dilute process stream, the conductivity becomes quite low. This relatively pure water helps to set the stage for further chemical reactions. The electrical potential splits water at the surface of the resin beads producing hydrogen and hydroxyl ions. These ions act as continuous regenerating agents of the ion-exchange resin. These regenerated resins, in turn, act as micro-regions of high or low pH permitting ionization of neutral or weakly ionized aqueous species such as carbon dioxide or silica. Once these species acquire a charge through this ionization process, they become subject to the influence of the strong DC field and are removed from the diluting compartment through the ion exchange membranes (see Figure). The membranes used in EDI stacks are flat sheet, homogeneous, ion exchange membranes which help to provide efficient ion transfer.

Application in the process

Electro deionization is a continuous and chemical-free process of removing ionized and ionizable species from the feed water using DC power. EDI can be used to polish RO permeate and to replace conventional mixed bed ion exchange. In that case it is not needed anymore to store and handle hazardous chemicals used for the regeneration of the resin.
The idea now is that if the technique can be implemented as a polisher, the technique also can be applied as a softener. The question than is if the EDI can handle a stream with a higher amount of species present. And if the technique still gives water with a good quality. The most important ions to remove are calcium and magnesium, but the technique also removes other ions. So when the technique is performing exceptionally well it could be possible that the RO unit is not necessary anymore, but research has to confirm that. For the implementation of EDI it is also important that is determined how much energy is needed for the process and also the number of cells that are needed to treat the desired volume.

4.2 Solutions for the regeneration

In this paragraph the solutions are given which can be applied to the regeneration of the softeners.

4.2.1 Capacitive Deionization (CapD-I)

With this solution CapD-I is used to treat the water that is released during the regeneration. The calcium, magnesium, and sodium are removed from the water. After treatment the water can be used again as softened water, or if the quality is good enough pumped to the demi water storage. Another option is that the spent regenerant is treated in such way that it can be used again. The membrane allows all positive ions to pass, both Na^+ and Ca^{2+}. In order to obtain a true solution, it is necessary that one of them cannot pass through the membrane. It is then necessary to apply a monovalent ion selective membrane so that only the sodium can pass the membrane. A note should be made that the total amount of water that is used in the regeneration still is discharged on the surface water.
The choice can also be made to use membranes that are only selective for bivalent or multivalent ions. Then calcium, magnesium, and other multiple ions are collected on the electrodes. A pure regeneration solution is then created, only with a lower concentration. The latter is dependent on which monovalent ions are present in the solution besides Na^+ and Cl^-.
According to Seok-Jun Seo, et all the efficiency of CapD-I is higher for longer use with multivalent ions than for monovalent ions. Based on this article, therefore, the solution of using a membrane that let multivalent ions pass will function better.
A remark has to be made with this solution that the technique is tested with brackish water. With the treatment of the spent regenerant salt concentrations up to 9% NaCl can be expected. That is much higher than is present in brackish water. So it is expected that the efficiency will be very low or even that the technique will not work.

4.2.2 Eutectic Freezing

Eutectic freeze crystallization (EFC) is an energetically efficient process for the separation of aqueous solutions into pure water and pure solidified solutes. This technique is based on the fact that when aqueous solutions are cooled at or below their eutectic point, ice and solid salt are formed simultaneously as two separable solid phases. These solid phases are then separated utilizing the density difference between the phases. The ice crystals are washed and melted to produce pure water, and the salt crystals are filtered to produce pure crystals.

Application in the process

EFC can be used to treat the spent regenerant and flush water. Than a separation is made into pure water and pure solidified salts. The ice crystals are melted to produce pure water, which can be transported to the polisher if the quality is good enough or even to the demi water storage. Or the water can be transported back to the storage of the softened water. The solidified salts need to be filtered, because magnesium chloride, calcium chloride and sodium chloride are present. In order to reuse the sodium chloride for the production of regenerant it needs to be separated from the other salts. When with the filtration of the salt also the magnesium chloride and sodium chloride can be separated, these salts can be stored and sold if the purity is high enough. The disadvantage of the technique is that it consumes a lot of energy. All the spent regenerant and flush water need to be frozen. That is a total of 111 m^3 of liquid for 1 regeneration.

4.2.3 Selective ion exchange

A chelating resin is exactly the same as a 'normal' type of resin, only the functional group on polymer is now sensitive for a specific ion. In this case calcium and magnesium needs to be removed from the solution. So a resin is used that is selective for those ions. From the spent regenerant and flush water the present calcium and magnesium is removed. The water can then be used again for the regeneration. Only the sodium concentration is lower because some is used for the exchange with hardness and also due to the dilution with flush water. Therefore extra sodium chloride needs to be added.

Application in the process

This technology can be applied by the placing of an extra columns or columns, dependent on the amount of water that needs to be treated and the design of the column. The columns are filled with a chelating resin that is selective for calcium and magnesium, for example TP208 from Lewatit. The regeneration of the resin is conducted with HCl. During the loading of the resin the water is also conditioned with NaOH because of the release of H^+ form the resin. The conditioning has as an advantage that the sodium concentration is increased, so less sodium chloride needs to be added to create new regenerant.

With the application of this technique more chemicals are used and still a waste stream is present, but less than before. For the regeneration of the chelating resin also softened water is needed as flush water, so also waste is created. The water that treated with the chelating resin is much more than is needed for the regeneration, so a part of that has to be discharged. It cannot be used for the flush of the resin because of the fact that it contains sodium chloride. Also two more storage vessels are needed in the process; one for the collection of the flush water / spent regenerant and one for the treated water.

4.2.4 RO concentrate as a regenerant

With this solution the concentrate of the RO unit is used as a regenerant. Therefore a storage vessel needs to be built to collect the concentrate to ensure that always enough is available for the regeneration of a softener. For this solution needs to be determined what the sodium concentration in the concentrate is. The sodium concentration is important for the determination of the regeneration process. If the concentration is lower than 9% NaCl more bed volumes of regenerant are needed. Also more time is needed with the use of more regenerant. When the sodium concentration is very low extra sodium chloride needs to be added. But in that case it might be possible to use the concentrate also as flush water. In the concentrate also bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) are present. Both can react with calcium according to the following reactions:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3(s) + CO_2 + H_2O \tag{11}$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3(s) \tag{12}$$

The same reactions are valid for magnesium. In which proportion the bicarbonate and carbonate are present is depending on the pH of the concentrate. The water that is flowing to the RO unit has a pH of 8.9. In the figure below can be seen that at that value of the pH almost only bicarbonate is present and almost none carbonate. The value of the pH of concentrate is expected to be more or less the same.

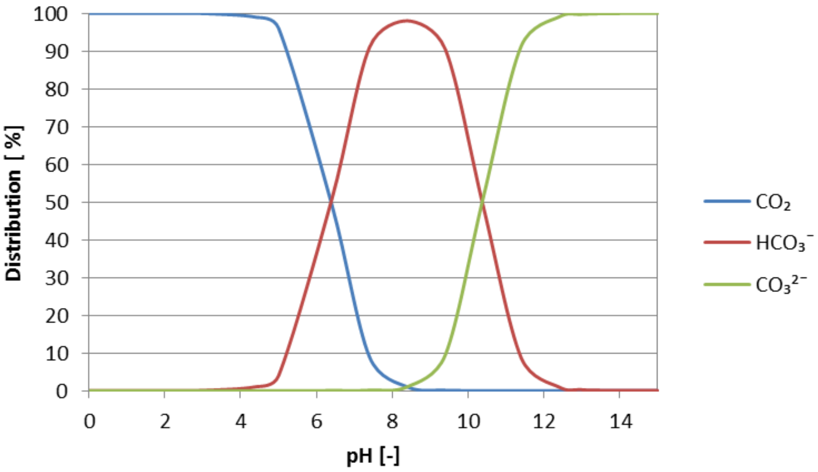


Figure 22: Relation between pH, CO_2, HCO_3^- and CO_3^{2-}.

With carbonate present in the water calcium carbonate is formed during the regeneration of the resin. The formed calcium carbonate can deposit on the resin. This can cause a decrease in the capacity of the resin. That process needs to be carefully monitored.

4.2.5 Water from the Brittannië harbour as a regenerant

The area in which DWP-Botlek is situated is located next to the Brittannië harbour. This port is connected to the North Sea through the Nieuwe Waterweg (Appendix A: Map of the harbour). Therefore is expected that the salinity of the water in the port is between the salinity of fresh water and seawater. The water contains sodium and maybe can be used to regenerate the ion exchangers.

The water from the port cannot be directly used for the regeneration of the ion exchangers. In the water from the harbour also suspended solids will be present which have an adverse effect on the regeneration and the ion exchange resin. In order to be able to use the water as a regenerant extra filtration steps will be needed.

Prior to research of this solution first has to be determined what the salinity of the water in the harbour is and what contaminants are present in the water.

Application to the process

The application of this solution in the current process is dependent on what additional purification steps are needed in order to be able to use the water from the harbour as a regenerant. If no extra filtration steps are required, the water can be pumped from the harbour when an ion exchanger needs to be regenerated. The flush of the resin before and after the dosing of the regeneration still needs to be done with softened water. This water can then be directed back to the beginning of the production process to be treated again and so no flush water is lost.

4.2.6 Dosing of sodium carbonate (Na_2CO_3) in combination with precipitation

In this solution no change is made to the current regeneration process. Only the spent regenerant is treated. The used regenerant is now transported to a vessel. At this vessel sodium carbonate (Na_2CO_3) is dosed and mixed. The liquid is then transported to another vessel, a so-called precipitation tank. In this tank the formed calcium carbonate will precipitate on the bottom and also some formation of calcium carbonate will take place. A portion of the precipitated $CaCO_3$ is recycled back towards the vessel were the Na_2CO_3 is dosed. That is done in order to increases the efficiency of the precipitation.

For this solution two tanks need to be built. Also should be determined if the flush water also needs to be treated. With treatment of that water the regeneration liquid is diluted, and dosing of extra salt is necessary. But also should be taken into consideration that when the flush water is treated more regenerant is created than needed. So after the treatment a part of the volume needs to be discharged.

4.3 Comparison of the solutions

One of the demands of Evides is that no significant changes are allowed to the main process. In all of the solutions that are related to the main process the softeners are replaced by another technique. Also in all of the solutions extra filtration steps are added to be able to use the technique. Therefore these solutions are not feasible and not looked at further anymore. The solution that are related to the regeneration of the resin are compared with the current situation on the following aspects:

- Energy
- Use of softened water
- Use of resources
- Cost

For energy is looked at if a solution needs more energy than in the present situation. With the softened water is determined if the used amount will be lower or higher. The resources are a combination of different aspects; the focus is on the use of chemicals is needed. Also is looked at the use of salt, with some solutions it is possible to recover the salt or to save on the use of salt. For the costs is determined if a solution has a positive or negative effect.

The comparison is given in the table below, the following scores are used:

++ = Strong positive effect
\+ = Positive effect
0 = No effect
\- = Negative effect
-- = Strong negative effect

Table 5: Comparison of solutions for the regeneration.

	Energy	Softened water	Resources	Costs
CapD-I	-	+	+	-
Eutectic freezing	--	++	++	--
Chelating resin	-	--	--	-
Concentrate as regenerant	0	++	+	+
Water Brittannië harbour as regenerant	0	+	++	+
Dosing of $NaCO_3$	-	0	-	-

From the table can be concluded that the best solutions are the use of concentrate and water from the Brittannië harbour as a regenerant. Both solutions have no effect on the energy consumption because the process is not changed, only the regenerant. That the concentrate is scoring higher on the softened water is because of the fact that more softened water can be saved when the concentrate can be used as flush water. The water from the harbour is scoring higher on the resources because the salinity of that water is higher than the salinity of the concentrate. And with the concentrate is expected that the addition of extra sodium chloride is necessary.

The chelating resin is scoring very badly, because an extra ion exchanger is used with the use of more softened water and chemicals. Also extra pumps are needed which demands more energy. The dosing of $CaCO_3$ also needs more energy and also more chemicals are used resulting in more costs.

5 Experimental approach and methods

In this chapter is elaborated which materials are used and what procedures are followed while performing the experiments in the laboratory. First the batch experiment is elaborated. After that the regeneration experiment is dealt with.

5.1 Batch Experiment

5.1.1 Objective

The objective of this experiment is to determine the capacity of the ion exchange resin as used at DWPB. To determine the capacity an exchange curve needs to be constructed. Therefor two models are compared, the model according to Freundlich and Langmuir. The maximum capacity of the resin is determined and compared to the value given by the manufacturer of the resin.

5.1.2 Materials

The materials used for this experiment are:

- *Measurement devices*
    - 1 thermometer
    - 1 pH meter
    - Photometer Nova 60-3
    - Pipette for a pipetting volume of 1.0 ml
- *Test kits*
    - Total harness cell test of Merck (1.00961.0001)
- *Chemicals*
    - Calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$) or Calcium chloride anhydrous ($CaCl_2$)
    - Magnesium chloride ($MgCl_2$)
- *Liquids*
    - Demi water
- *Ion exchange*
    - Ion exchange resin Lewatit S100 (S1428)
- *Storage vessels*
    - 6 bottles with a capacity of 2 l
    - 6 small jars

5.1.3 Experimental Setup

Figure 23: Experimental setup of the batch experiment.

To determine the exchange curve 6 jars of equal size are taken and filled with the same amount of the prepared solution (see 5.1.4). In these 6 jars different amount of resin (5, 10, 15, 20, 25 and 30 ml) is added. A stirrer is added to the bottles and put on a stirrer platter. After a period of at least 24 hours a sample is taken from each jar and the total hardness, magnesium and calcium concentration are measured. For this measurement the hardness cell test of Merck is used. Also the temperature and the pH of the samples have to be determined. For the hardness cell test the temperature has to be between 20 and 30 °C and the pH of the sample has to be between 3 and 9. When the hardness level of the samples is above the

measuring range (215 mg/l = 5.38 mmol/l) of the cell test, it needs to be diluted.
After that the results are evaluated and will be decided if the experiment is repeated with different amounts of resin. The experimental setup is given in the Figure 23.
The amount of hardness that can be loaded on the resins depends on the hardness concentration, the characteristics of the resin, the temperature and pH of the water. There is a relation between the amount of adsorbed hardness per litre of resin and the equilibrium concentration in the water, under the conditions that temperature and pH are held constant. This relation is called an isotherm and can be described with the Langmuir or / and Freundlich isotherm equation. The Langmuir isotherm is given by equation (6) in chapter 3. And the Freundlich isotherm can be determined with equation (4) from chapter 3.
The values of K and n can be determined with the measured data of the exchange capacity of the resin at different concentrations of the hardness.

5.1.4 Preparation of the solutions

For each measurement an amount is taken from a so called stock solution. In this way is guaranteed that each solution that is made has the same start concentration, only the dilution is different. For a stock solution a larger amount of calcium and magnesium chloride can be taken, that is easier to weigh.
For the stock solution calcium chloride dehydrate is used. Important to know is that calcium chloride is used in dehumidifiers and attracts water very easy. To be certain that no water is present in the calcium chloride, it is dried in an oven at 104 °C. According to the literature the drying has to be a minimum of 2 hours [Binnemans, 2003]. The chemical equation for drying calcium chloride dehydrate is:

$$\mathrm{CaCl_2 \cdot 2H_2O(s) \rightarrow CaCl_2(s) + 2H_2O(g)} \tag{13}$$

The chemical equation for solving calcium chloride in demi water is:

$$\mathrm{CaCl_2(s) \rightarrow Ca^{2+} + 2Cl^{-}} \tag{14}$$

The chemical equation for solving magnesium chloride in demi water is:

$$\mathrm{MgCl_2(s) \rightarrow Mg^{2+} + 2Cl^{-}} \tag{15}$$

It has to be taken into account that both reactions are exothermic and therefore precautions have to be taken when dissolving these salts.

To create a stock solution the following procedure is followed:

- Calcium chloride dehydrate is weighed (126.88 g)
- The calcium chloride dehydrate is dried in an oven at 104 °C for at least 2 hours
- The dried calcium chloride is weighed (119.32 g) and added to the bottle
- Magnesium chloride is weighed (34.04 g) and added to the bottle
- The bottle is filled up with demi water to a level of 2 litres.

If calcium chloride is available, the step of drying is not necessary anymore and the right amount can be weight directly. The stock solution is stored in a refrigerator, available to use when needed.

To prepare the solutions in the 6 bottles the following steps are taken:

- Add 20 ml of the stock solution
- Add 980 ml of demi water

The hardness of the solution in the bottles is 13.32 mmol/l (Ca^{2+} = 10.6 mmol/l and Mg^{2+} = 2.72).

5.2 Regeneration with different regenerants

5.2.1 Objective

The objective is to determine if it is possible to use other regenerants for the regeneration of the resin. And also to determine what the best configuration is for the regeneration. The following regenerants are used:

- Sodium chloride as used at DWP-B
- Water from the Brittannië harbour
- Concentrate from the RO of DWP-B

Sodium chloride as used at DWPB is researched in order to have a reference, were the other results of the experiments can be compared with. And to evaluate the performance of the experimental setup. Before water from the Brittannië harbour is used as a regenerant first sodium chloride with the same concentration as in seawater and artificial seawater is used. Finally, RO concentrate with some variations is used as a regenerant.

5.2.2 Materials

The materials used for the experiments are:

- *Pump*
    - 1 pump, Watson Marlow 505DU
    - 3 pump heads, Watson Marlow 313
- *Measurement devices*
    - 1 thermometer
    - 1 multi-meter, WTW
    - 1 pH sensor, WTW
    - 1 conductivity sensor, WTW
    - 3 inductive conductivity transmitters, Bürkert 8223
    - Data logger Dataq DI710UHS
    - Measuring PC
    - Photometer Nova 60
    - Pipette for a pipetting volume of 1.0 ml
    - Pipette for a pipetting volume of 5.0 ml
- *Test kits*
    - Total harness cell test of Merck (1.00961.0001)
- *Chemicals*
    - Calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$) or calcium chloride anhydrous ($CaCl_2$)
    - Magnesium chloride ($MgCl_2$)
    - Sodium Chloride ($NaCl$)
    - Hydrochloric acid (HCl)
    - Caustic soda ($NaOH$)
    - Sea salt (Sera marin basic salt)
- *Liquids*
    - Tap water
    - Demi water
- *Ion exchange*
    - Ion exchange resin Lewatit S100 (S1428)
- *Columns*
    - 3 columns with a length of 460 mm and an inner diameter of 36 mm
- *Valves*
    - 6 4-way ball valves, EM-Technik
    - 9 3-way ball valves, EM-Technik
- Tubes
    - 3 tubes for the pump, nr 16 with bore 3.2 mm Watson Marlow
    - 3 tubes for the pump, nr 17 with bore 6.4 mm Watson Marlow
    - Festo 8 mm tube (inside diameter 5.9 mm)

- *Mixers*
    - 1 Magnetic stirrer
    - 1 Gradient mixer
- *Storage vessels*
    - 1 storage vessels of 150 l
    - 4 jerry cans of 10 l each
    - 3 storage vessels of 50 l
- *Transport vessels*
    - 6 jerry cans of 10 l each

5.2.3 Experimental Setup

To determine if it is possible to use other regenerants an experimental setup has to be designed. With the design is taken into account that it is not possible to use loaded resin from DWPB and that the resin is loaded in the laboratory. Also has to be taken into account that the same procedure is followed in the laboratory as is performed at DWPB:

- Loading of the resin
- Regeneration:
    - Flush with demi water
    - Injection of regenerant
    - Displacement with demi water
    - Downward flush with demi water

In the setup a vessel is needed for the storage of water for the loading of the resin. Also a storage vessel is needed for the regenerant and the flush water. With the application of three columns 1 larger vessel for the loading of the resin is enough, because each column is loaded with the same type of water. That is also the case for the flush water. It has to be possible that each column can be regenerated with a different type of regenerant; therefore each column has its own storage vessel. To pump the liquid from the storage vessel a pump is used with three pumpheads, 1 channel for each column. The loading of the resin is performed with a higher velocity than the regeneration and therefore two different tubes are needed. Both tubes are installed in the setup. To switch from loading to regeneration a 3-way valve is used to select the correct tube and the correct tube is placed in the pumphead. In that situation only 1 pump is needed. With another 3-way valve the selection can be made between demi water and the regenerant. The flow can be directed towards the top or the bottom of the column with the use of other 3-way valves. With the use of 4-way valves the flow is redirected in such way that with both downward and upward flow the measurement of the conductivity always is on the effluent of the columns. Before the water is discharged on the sewer it is possible to take samples from the effluent. At the bottom and top of the columns also sample points are created. At these sample points water can be drawn from the system, but it is also possible to inject a liquid or air. In Figure 24 a schematic drawing is given of the experimental setup.

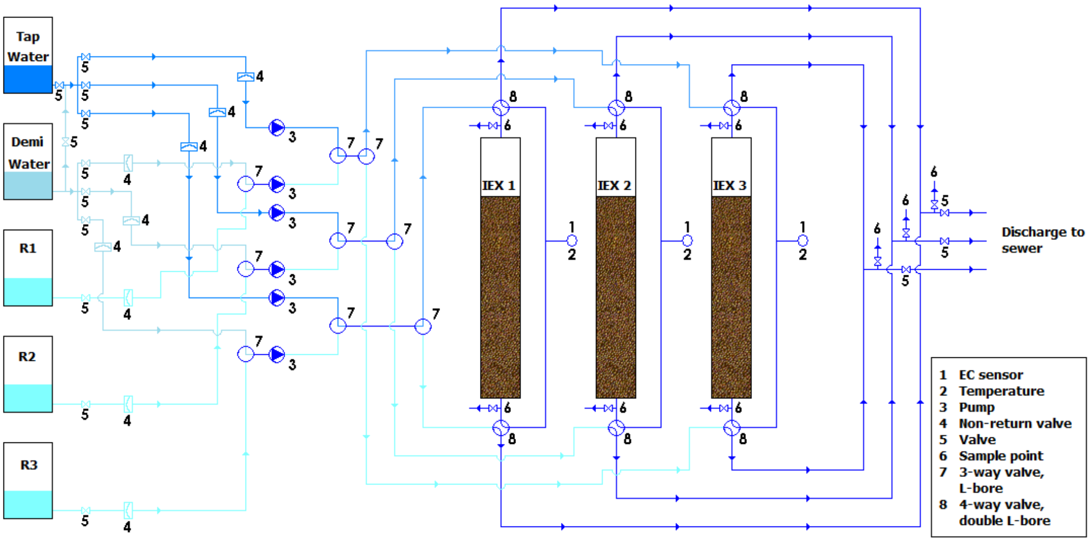


Figure 24: Schematic drawing of the setup.

In the figure below a picture is given of the experimental setup.

Figure 25: Experimental setup with a detailed view of column 1 and the filter present at the top of the column.

The length of the columns used in the experiments is 460 mm and are made from pvc. The internal diameter of the columns is 36 mm. The total volume that is available in the column is 468 ml. A filter plate is used at the bottom of the column to prevent loss of the resin. Also a filter plate is added at the top of the column, which is done to prevent loss of resin during regeneration. The size of the holes in the filter plates need to be smaller than resin. The

Lewatit S100 resin has a bead size of 0.4 to 1.2 mm; therefore the holes in the plates have a diameter of 0.35 mm. Also the column is not completely filled with resin to take into account that the resin expands during regeneration. A drawing of the used columns with the relevant data is given in the figure below. With the dosing of some regenerants was noticed that clogging of the pores of the filter plates occurred. The filter plates at the top of the column were replaced by fine meshed gauze (See Figure 25 right picture).

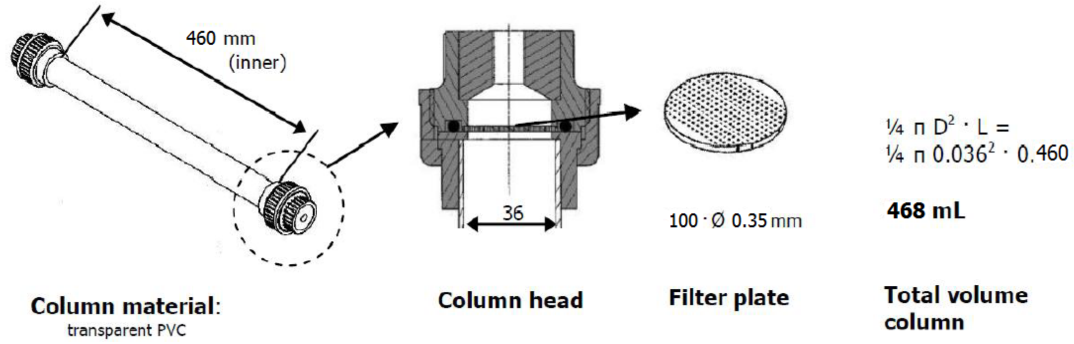


Figure 26: Columns used in the experiment.

The flow velocity in the bed during regeneration is kept at the same value as applied at DWPB, 3.76 m/h (equation (1)). According to the information of the manufacturer of the resin an expansion of the bed of 4% per m/h can be expected. So with the given flow velocity a bed expansion of 15% has to be taken into account.

$$h_{bed;max} = \frac{h_{column}}{\left(1 + \frac{expansion}{100}\right)} = \frac{460}{1.15} = 400 \text{ mm} \tag{16}$$

The maximum height of the bed in the column can be 400 mm. To limit the time needed for the loading of the resin the height of the bed applied in each column is 250 mm. The bed volume is:

$$BV = A \cdot h_{bed} = {}^{1}\!/_{4} \cdot \pi \cdot \left(36 \cdot 10^{-3}\right)^2 \cdot 250 \cdot 10^{-3} = 2.54 \cdot 10^{-4} \text{ m}^3 \tag{17}$$

The three columns are filled with dry resin. The amount of resin in the columns is determined by the weight of the amount of resin that was put in the column. With the density of the resin (860 g/l) given by Lanxess the mass is converted to volume. The values are given in the table below.

Table 6: Amount of resin in the three columns of the experimental setup.

		Column		
		1	**2**	**3**
Start weight of bottle	[g]	704.8	495.4	286.7
End weight of the bottle	[g]	495.4	286.7	77.1
Mass of the resin	[g]	209.4	208.7	209.6
Volume of resin	[ml]	243	243	243

The height of the bed applied in each column is lower than the maximum height, so during regeneration enough space is available for the expansion of the bed. See Figure 25 for a picture of column 1.

At DWPB the softeners are operated to get a good quality of softened water; therefore an incomplete loading of resin is done. The goal of the experimental setup is to research the possibilities of other regenerants. In order to be able to make a good comparison between the results of the different regenerations the resin is completely loaded. In that case can be seen what the effect of the regenerant is on capacity of the resin and what amount of hardness is removed from the bed. Also the control on the process of loading and regeneration is better in that situation. The process in the experiment can be divided into two different situations:

- Loading of the resin
- Regeneration of the resin

For both of the situations a more detailed description of the installation shall be given.

5.2.4 Loading of the resin

Tap water is pumped from a vessel with a total capacity of 150 litres and is divided into 3 streams. For more flexibility it is possible to switch off one or more of these streams with a valve (Figure 27). Before the pump non-return valves are applied, so that no water can be pumped back to the vessel. The pump is equipped with tube 17 to be able to pump a flow of 29.8 m/h. The loading of the columns is performed with a downward flow, so the water is pumped to the top of the columns. After the water is passed through the bed it flows through a conductivity meter. The measurements of the conductivity are logged on a computer with a data logger. Before the water is leaving the setup samples can be taken for the determination of the total hardness, calcium and magnesium concentration. The water leaving the setup can either be discharged on the sewer or collected in a vessel for a mixed sample.

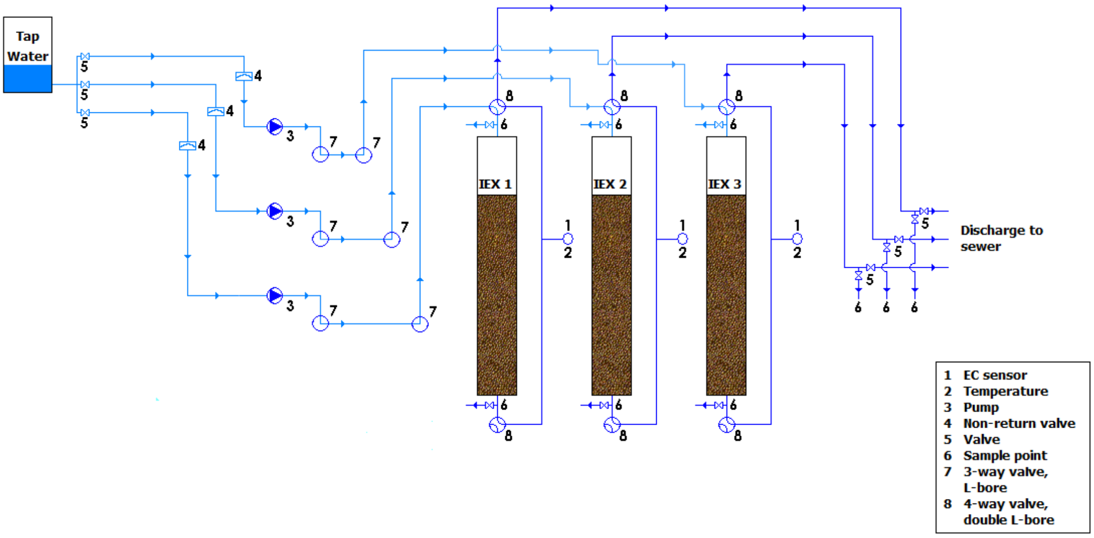


Figure 27: Schematic drawing of the process: the loading of the resin.

The flow in the bed is kept at the same value as in the bed of the softener at DWPB. Dependent on the softened water demand the flow is between 14.9 m/h and 35.7 m/h (based on the values given in Table 2). The nominal production of the softener is 300 m^3/h, which gives a flow of 29.8 m/h. When using tap water a loading time is expected of at least 6 hours, which is inconvenient because also the regeneration has to be performed. To reduce the time needed for loading, the hardness is increased to 6 mmol/l. In that case 44.5 litre of water (with TH = 6 mmol/l) is needed and a loading time of 1:28 h is expected. For this calculation the assumption is done that all of the hardness present in the water is loaded on the resin. In practice this is not true, at a certain moment breakthrough occurs and hardness is passing the bed. While conducting the experiment the fact has to be taken into account that for the complete loading of the bed more time and water is needed. That was indeed noticed during the first experiment (for the results of the experiment see 6.2), the loading time was 2 h and 62.5 litres of water was used. When in that case all of the columns are in operation, a total amount of 187.5 litre of water is needed. The vessel can only contain 150 litre. Therefore is chosen to increase the hardness to 8 mmol/l in order to lower the total amount of water that is needed for the loading of the resin. Now at least 33.3 litre per column of water (with TH = 8 mmol/l) is needed and a loading time of 1:06 h is expected.
The description of the preparation of the tap water with the increased hardness is given in 5.2.6.

For the loading of the resin the following procedure is followed for the column(s) that is / are loaded:

- Fill the vessel with tap water with increased hardness
- Place tube(s) 16 in the pumphead(s)
- Open the valve(s) of the stream(s) from the tap water vessel
- Check/switch all the 3-way valves to the correct position (co-current)
- Check/switch the 4-way valves to the correct position (co-current)
- Start the pump with 29.8 m/h
- Pump is stopped when complete breakthrough is observed
- Close the valve(s) of the stream(s) from the tap water vessel

5.2.5 Regeneration of the resin

The same procedure of the regeneration of the resin is followed as at DWPB:

- Backwash with demi water
- Injection of regenerant
- Displacement with demi water
- Downward rinse with demi water

The only difference is that at DWPB softened water is used and in the laboratory demi water. In the experimental setup the resin is completely loaded. During the process of loading breakthrough occurs and hardness is present in the softened water. For the process it is not desirable that water is used with any hardness, therefore is chosen to use demiwater.
The flow velocity in the bed is kept at the same value as present in the vessel at DWPB, 3.78 m/h. This velocity is used in the backwash, injection and displacement. For the downward rinse a different flow velocity is used, 25.82 m/h. In the table below a summary is given.

Table 7: Parameters of the sub processes of the regeneration.

	Q [m^3/h]	V [m/h]	Tube [-]	Pump rate [rpm]
Backwash with demiwater	38	3.78	16	64.2
Injection of regenerant	38	3.78	16	64.2
Displacement with demiwater	38	3.78	16	64.2
Downward rinse with demiwater	260	25.82	17	128.4

Backwash with demiwater

In the figure below a schematic drawing of the backwash is given.

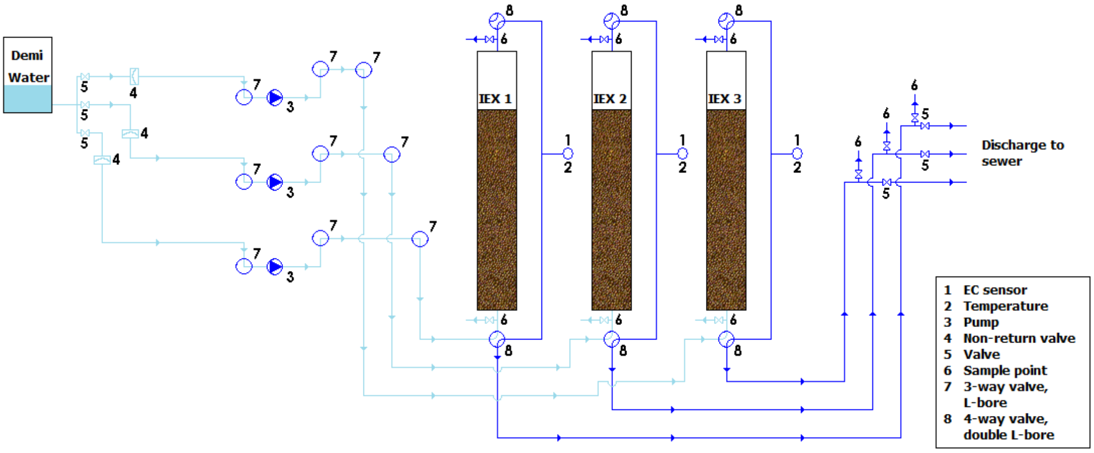


Figure 28: Schematic drawing of regeneration: Backwash / Displacement with demiwater.

Demiwater is used to backwash each column and is stored in one jerry can of 10 l. The water is pumped from the storage vessel to the columns. For flexibility in operation valves are present in each stream to cut off the flow from the jerry can. Also non return valves are used to prevent a flow towards the jerry can with the demiwater. Tube number 16 is used to pump the desired flow of 3.78 m/h. The direction of the flow during the backwash is upward (counter current). After the water leaves the column it flows through the conductivity meter before it is discharged on the sewer.

For the backwash the following procedure is followed for the column(s) that is/are regenerated:

- Fill the jerry can with demiwater
- Open the valve(s) of the demiwater vessel
- Switch all the 3-way valves to the correct position
- Change the tube(s) in the pumphead(s)
- Switch the 4-way valves to the correct position (counter current)
- Start backwash with 3.78 m/h

Injection of regenerant

The regeneration is performed after the backwash is finished. In the figure below a schematic drawing of the regeneration process is given.

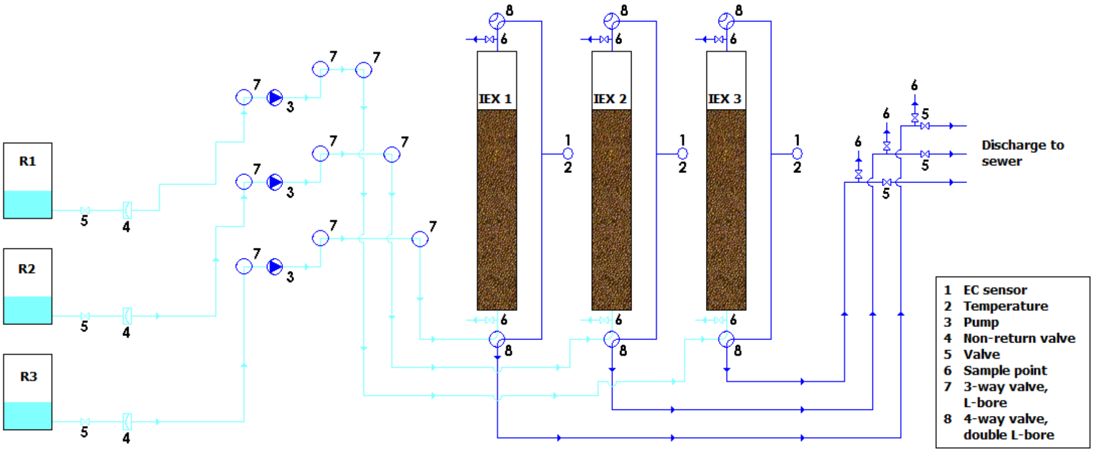


Figure 29: Schematic drawing of regeneration: Dosing of regenerant.

Each column can be regenerated with a different regenerant. The regenerant is pumped from a jerry can with a capacity of 10 l to the column. All of the columns are separated from each other. The tube of the column(s) that needs to be regenerated is placed in the pumphead. The applied non-return valves prevent the flow from the system to the vessels containing the regenerant. With the dosing of the regenerant the same tube is used as before with the backwash, tube 16. The regeneration is also performed with an upward flow direction (counter current) at a flow of 3.78 m/h. When the spent regenerant leaves the column the conductivity is measured. Before the liquid is discharged to the sewer or collected in a vessel samples can be taken. From these samples the total hardness, calcium and magnesium concentration are determined. If needed also the conductivity and the pH are measured.

For the regeneration the following procedure is followed for the column(s) that is/are regenerated:

- Fill the jerry can(s) with regenerant
- Open the valve(s) of the vessel(s) with regenerant
- To start the injection switch the 3-way valves to select the vessel(s) containing the regenerant (counter current, flow 3.78 m/h)
- The injection of regenerant is stopped by switching to the displacement when the desired amount of regenerant is dosed.

The jerry cans containing the regenerant are filled before the start of the regeneration. When the backwash is finished the 3-way valve is switched to start the regeneration. The pump is not stopped.

Displacement with demiwater

The displacement starts when the injection of the regenerant is finished. Demiwater is used to flush each column and is stored in the same jerry can as is used with the backwash. When the displacement with demiwater is started has to be taken into account that not all of the regenerant has passed the bed.
The schematic drawing of the process is the same as the drawing for the backwash, see Figure 28. For the description of the system is also referred to the backwash with demiwater. The displacement is finished when the all of the regenerant has been flushed out of the bed. That is measured with the conductivity, when the value is low enough the displacement is stopped.

For the displacement the following procedure is followed for the column(s) that is/are regenerated:

- Fill the jerry can with demiwater
- Check if the valve(s) are open
- To start the displacement switch the 3-way valves to select the vessel containing the demiwater (counter current, flow 3.78 m/h)
- Close the valves of the vessel(s) with regenerant
- The pump is stopped when the conductivity of the effluent is low enough

The first two steps are done during the backwash.

Downward rinse with demiwater

This flush is to move the bed back into place and to get the ion exchanger back into operation. In the figure below a schematic drawing is given.

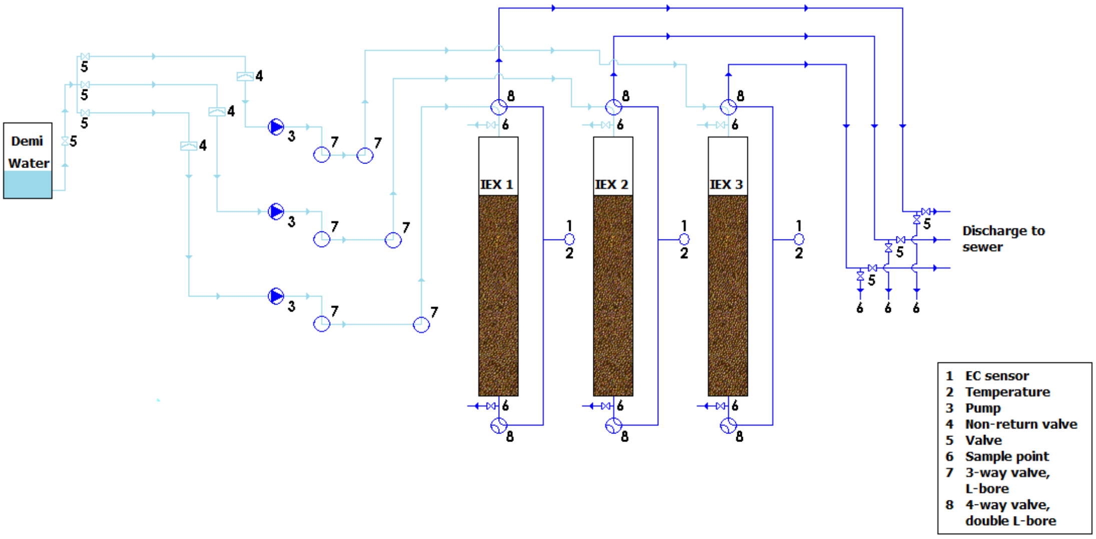


Figure 30: Schematic drawing of regeneration: Downward rinse with demiwater.

For the downward rinse demiwater is used from the same jerry can as before. Valves are placed after the jerry can with demiwater to be able to rinse only 1 or 2 columns. Non-return valves are applied to prevent flow from the setup to the jerry can with demiwater. The rinse is performed during 1 minute with a flow velocity of 25.82 m/h. For that velocity tube number 17 is used. The demiwater is pumped from the jerry can to the top of the column. The demiwater passes through the bed and the bed is pushed back into place. The demiwater leaves the column and is discharged to the sewer. No measurements are performed during this step.

For the displacement the following procedure is followed:

- Fill the jerry can with demiwater
- Close the valve(s) of the stream(s) from the demiwater vessel leading to tube 16 for the columns that was/were regenerated
- Change the tube in the pump head
- Open the valve(s) of the stream(s) from the demiwater vessel leading to tube 17 for the column(s) that is/are regenerated
- Switch all the 3-way valves to the correct position (co-current)
- Switch the 4-way valves to the correct position (co-current)
- Start the pump with 25.82 m/h
- Pump is stopped after 1 minute
- Close the valve(s) of the stream(s) from the demiwater vessel leading to tube 17 for the column(s) that is/are regenerated
- Remove the tube(s) from the pumphead(s)

5.2.6 Preparation of the solutions

For the experiment the following solutions are needed:

- Tap water with increased extra hardness
- Regenerants

Tap water with increased hardness

As mentioned before a hardness level of 6 and 8 mmol/l is used for the loading of the resin. For the solutions tap water is used and calcium and magnesium are added. In tap water already hardness is present and has to be taken into account. The average values of the hardness measured by the drinking water company Evides are given in the table below.

Table 8: Hardness of drinking water (Evides).

	Average Berenplaat [mg/l]	Average Berenplaat [mmol/l]	Average Brielse Meer [mg/l]	Average Brielse Meer [mmol/l]
TH	-	1.51	-	2.50
Ca^{2+}	47	1.18	75	1.875
Mg^{2+}	7.9	0.33	15	0.625

In the table also the values of the hardness in the water from Brielse Meer is given. Because that water is used for the loading of the resin at DWPB the same proportion of calcium and magnesium is used in the tap water with the increased hardness. So for total hardness of 6 mmol/l 3.32 mmol/l of calcium and 1.17 mmol/l of magnesium is added. And for total hardness of 8 mmol/l 4.82 mmol/l of calcium and 1.67 mmol/l of magnesium is added. The solubility is exceeded with both hardness values. In order to be able to solve these amounts of hardness without precipitation hydrochloric acid is added. With stimela is calculated that 0.486 mmol/l of HCl needs to be dosed for a solution with a TH of 6 mmol/l. And for a solution with a TH of 8 mmol/l 0.618 mmol/l needs to be added.

For the preparation of the solution in the vessel a so called stock solution is used. With a stock solution is guaranteed that each solution has the same concentration.

The chemical solution for solving calcium chloride in demi water is:

$$CaCl_2(s) \rightarrow Ca^{2+} + 2Cl^- \qquad (18)$$

The chemical solution for solving magnesium chloride in demi water is:

$$MgCl_2(s) \rightarrow Mg^{2+} + 2Cl^- \qquad (19)$$

It has to be taken into account that both reactions are exothermal and therefore, precautions have to be taken when solving these salts. In the table below the amount of chemicals that are needed for the loading are given.

Table 9: Chemicals needed for the preparation of the tap water with increased hardness.

	TH = 6 mmol/l		**TH = 8 mmol/l**	
	[mg/l]	**[mmol/l]**	**[mg/l]**	**[mmol/l]**
CaCl	368.52	3.32	535.02	4.82
MgCl	111.15	1.17	158.65	1.67
HCl	17.74	0.486	22.56	0.618

When the stock solution is only made with the calcium chloride and magnesium chloride a check has to be made that the solubility is not exceeded. Also when the stock is added to the tap water thorough mixing has to be applied to prevent precipitation. Although hydrochloric acid is dosed precipitation can occur due to the fact that a high concentration is added at one place. To prevent this, the hydrochloric acid is dosed in the stock solution.

To create the stock solution the following procedure is followed:

- Clean a bottle with a capacity of 2 l
- Determine the number of loadings for which the stock has to be created
- Calculate the amount of CaCl, MgCl and HCl needed
- Weigh the amount of CaCl, MgCl and HCl and add to the bottle
- Fill the bottle up to 2 litres with tap water.

To prepare the solution in the vessel the following procedure is followed:

- Determine the volume that is still present in the vessel
- Calculate the amount of tap water and stock solution that is needed to fill the vessel up to 150 l.
- Add the amount of tap water
- Stir and add the amount of stock solution

Regenerant

The following regenerants are used for the regeneration of the resin:

- 10% NaCl
- 3.45% NaCl
- Artificial seawater
- Water from Brittanniё harbour
- RO concentrate DWPB:
  - With 1% NaCl added
  - With 1% NaCl added and increased pH
  - With 1% NaCl added and gradient increased pH
  - With $CaCO_3$
  - With $CaCO_3$ and increased pH
  - With 10% NaCl

The regenerant with 10% NaCl, 3.45% NaCl and artificial seawater are prepared with demiwater. In the table below the amount of chemicals needed to prepare the different regenerants are given.

Table 10: Amount of chemicals needed to prepare the regenerants.

		NaCl [g/l]	**Sea salt [g/l]**	**NaOH [g/l]**	**$CaCO_3$ [mg/l]**
10% NaCl		105.7	-	-	-
3.45% NaCl		35.1	-	-	-
Artificial seawater		-	32.5	-	-
Water Brittannië harbour		-	-	-	-
RO concentrate DWPB with:	1% NaCl	10	-	-	-
	1% NaCl and increased pH	10	-	0.8	-
	1% NaCl and gradient increased pH	10	-	0.4 /0.8	-
	$CaCO_3$	-	-	-	(1)
	$CaCO_3$ and increased pH	-	-	0.8	(1)
	10% NaCl	103.2	-	-	-

(1) The amount of calcium carbonate cannot be determined exactly. An amount of calcium carbonate is added to 1 l of concentrate and waited for settlement. The liquid with the suspended calcium carbonate is added to a volume of concentrate.

With the determination of the amount of sodium chloride that needs to be added to the RO concentrate is taken into account that the concentrate contains 42.5 mmol/l of sodium (Table 18).

To prepare the regenerants the following procedure is followed:

- Clean a jerry can with a capacity of 10 l
- Add the amount of chemicals needed for the specific regenerant
- Fill the jerry can up to 10 l with demiwater, water from the Brittannië harbour or RO concentrate
- Mix the solution

When the pH is increased in gradient, a gradient mixer is used and the procedure to prepare the regenerant is than as followed:

- Clean both containers (1 and 2) of the gradient mixer
- Determine the needed number of bed volumes
- Add the amount of chemicals to container 1 / 2
- Fill container 1/2 up to the required level with RO concentrate
- Stir the solution in container 1 / 2

5.2.7 Measurements

Only the electro conductivity (EC) of the effluent of the columns is measured with an inductive conductivity sensor from Bürkert. The output of this sensor is from 4 to 20 mA. In order to be able to log the data that the signal is converted with a resistor from mA to V. The measured data is stored on a computer. The conductivity of the other liquids is measured with an EC sensor and multi-meter from WTW.

The pH is also measured with the same multi-meter, only then a probe for the pH is connected.

To measure the total hardness, calcium and magnesium concentration the total hardness cell test from Merck is used. With that test a differentiation measurement is done. The total hardness and the magnesium concentration are measured; the calcium concentration is the difference between the total hardness and the magnesium. The measuring range of the test is from 5 to 215 mg/l Ca^{2+} (0.12 – 5.38 mmol/l Ca^{2+}). While conducting the differentiation measurement this is the measuring range for the total hardness. For the measurement is important to know the sodium chloride concentration. If the concentration is higher than 2% NaCl interference can occur, the sample has to be diluted.

With the sample the following procedure is followed:

- Check if the hardness is in the measuring range of the test. When the concentration is higher the sample has to be diluted
- Check if the pH is within the range 3-9

- Pipette 1.0 ml of sample into a reaction cell, close the cell and mix.
- Add 1.0 ml of the reagent H-1K, close the cell and mix.
- Wait 3 minutes and place the cell into the photometer.
- The result is the total hardness
- Add 3 drops of reagent H-2K, close the cell and mix.
- Place the cell in the photometer, the result is the magnesium concentration.
- Press enter, the calcium and magnesium concentration are given.

For every sample the same procedure is followed.

The total amount of hardness loaded on / removed from the resin is determined with two different methods. In the experimental setup a dead volume (V_{system}) of 0.42 l is present. That is taken into account at both methods. The first method is to construct a breakthrough / elution curve with the data from the analysed samples. The total amount of hardness that is loaded on the resin is the area in the breakthrough curve between the line of the total hardness of the feed and the line of the total hardness. The area beneath a line is calculated with the trapezoid rule equation. The general form of the trapezoid rule is given by equitation 21.

$$\int_a^b f(x)dx \approx (b-a)\frac{f(a)+f(b)}{2} \tag{20}$$

Dependant on the data the area is divided in a uniform or non-uniform grid to increase the accuracy. The general formula is than converted into equitation 22 for the loading of the resin.

$$TH_{Loaded} = \int_0^b g(x)\,dx - \int_a^b f(x)dx \approx b\cdot g(a) - \frac{1}{2}\sum_{k=1}^{N}(x_{k+1}-x_k)\cdot\left(f(x_k)+f(x_{k+1})\right) \tag{21}$$

The total amount of hardness that is removed from the resin is the area beneath the line of the total hardness in the elution curve. The elution curve is constructed from the data of the analysed samples taken during regeneration. Dependant on that data the area is divided in a uniform or non-uniform grid. The general formula is than converted into equitation 23 for the regeneration of the resin.

$$TH_{Removed} = \int_a^b f(x)dx \approx \frac{1}{2}\sum_{k=1}^{N}(x_{k+1}-x_k)\cdot\left(f(x_k)+f(x_{k+1})\right) \tag{22}$$

The dead volume of the system is taken into account with the construction of the breakthrough / elution curve.

The second method is to determine the total amount of hardness with the use of a mixed sample. To get a mixed sample all of the water that normally is discharged on the sewer during loading or regeneration is collected in a vessel. After loading / regeneration is finished the volume of the collected water is determined. Then the water is stirred and a sample is taken from the vessel. That sample is called a mixed sample. From that mixed sample the total hardness concentration is measured. With the following equation the total hardness loaded on the resin is calculated.

$$TH_{Loaded} = \left(V_{collected} - V_{system}\right)\cdot\left(TH_{feed} - TH_{mixed\ sample}\right) \tag{23}$$

To determine the total hardness removed from the following equitation is used.

$$TH_{Removed} = \left(V_{collected} - V_{system}\right)\cdot TH_{mixed\ sample} \tag{24}$$

6 Results and discussion

In this chapter the results of the different experiment are presented and discussed. The results of the following experiments are given: the batch experiment and the regeneration experiment. The results of the regeneration experiment are divided into three parts:

- Regeneration with 10% NaCl
- Regeneration with seawater
- Regeneration with RO concentrate

6.1 Batch Experiment

The batch experiment is done according to the procedure given in paragraph 5.1. In the table below, Table 11 the results of the first batch experiment are given.

Table 11: Results of batch experiment 1.

Bottle / Sample description	**Amount of resin [ml]**	**pH [-]**	**T [°C]**	**TH [mmol/l]**	**Mg [mmol/l]**	**Ca [mmol/l]**
Prepared solution	-	5.82	19.6	11.30	0.60	10.70
Bottle 1	1	4.92	22.4	11.80	0.60	11.20
Bottle 2	5	4.23	22.6	7.05	0.48	6.57
Bottle 3	10	3.97	22.5	1.32	1.32	1.19
Bottle 4	20	3.80	22.6	0.26	0.13	0.13

The amount of data acquired with the first experiment is not enough to determine the capacity of the resin. Also can be seen in the table that 1 ml of resin is too low to get a reliable measurement of the hardness. Therefore is chosen to conduct the batch experiment again, only with two more bottles and different amounts of resin. The amount of resin used is 5, 10, 15, 20, 25 and 30 ml. The experiment is performed in duplicate and the results are given in Table 12.

Table 12: Results of batch experiment 2.

Bottle / Sample description	**Amount of resin [ml]**	**pH [-]**	**T [°C]**	**TH [mmol/l]**	**Mg [mmol/l]**	**Ca [mmol/l]**
Prepared solution	-	5.82	19.6	11.30	0.60	10.70
Bottle 1 (1)	5	4.36	22.9	7.34	1.88	5.51
Bottle 1 (2)	5	4.36	22.9	7.73	2.04	5.74
Bottle 2 (1)	10	4.17	23.2	3.44	1.08	2.41
Bottle 2 (2)	10	4.17	23.2	3.62	1.20	2.46
Bottle 3 (1)	15	4.05	23.3	0.89	0.20	0.73
Bottle 3 (2)	15	4.05	23.3	0.61	0.21	0.40
Bottle 4 (1)	20	4.00	25.5	0.24	0.01	0.23
Bottle 4 (2)	20	4.00	25.5	0.22	0.00	0.22
Bottle 5 (1)	25	3.95	25.7	0.20	0.00	0.20
Bottle 5 (2)	25	3.95	25.7	0.19	0.00	0.19
Bottle 6 (1)	30	3.90	24.7	0.16	0.00	0.15
Bottle 6 (2)	30	3.90	24.7	0.16	0.00	0.16

With these results the capacity of the resin can be determined. For the determination two models are used, the Langmuir and the Freundlich isotherm. For the determination of the Langmuir isotherm parameters a plot is made of C_e/q_e versus C_e. A linear regression is used for a fit of the Langmuir isotherm (see Figure 31, left). With the slope and the intercept of the linear regression the parameters is calculated.

$$\left.\begin{aligned} \frac{1}{Q_M} &= \text{slope} = 0.4268 \Rightarrow Q_M = 2.34 \\ \frac{1}{b_e Q_M} &= \text{intercept} = 0.1278 \Rightarrow b_e = 3.34 \end{aligned}\right\} \Rightarrow q_e = \frac{7.82 \cdot C_e}{1 + 3.34 \cdot C_e} \tag{25}$$

For the determination of the Freundlich isotherm parameters a log-log plot is made of q_e versus C_e. A linear regression is used for a fit of the Freundlich isotherm (see Figure 31, right). With the slope and the intercept of the linear regression the parameters is calculated.

$$\left.\begin{aligned}\frac{1}{n} &= \text{slope} = 0.4945\\ \log K &= \text{intercept} = 0.4393 \Rightarrow K = 1.24\end{aligned}\right\} \Rightarrow q_e = 1.24 \cdot C_e^{\,0.4945} \qquad (26)$$

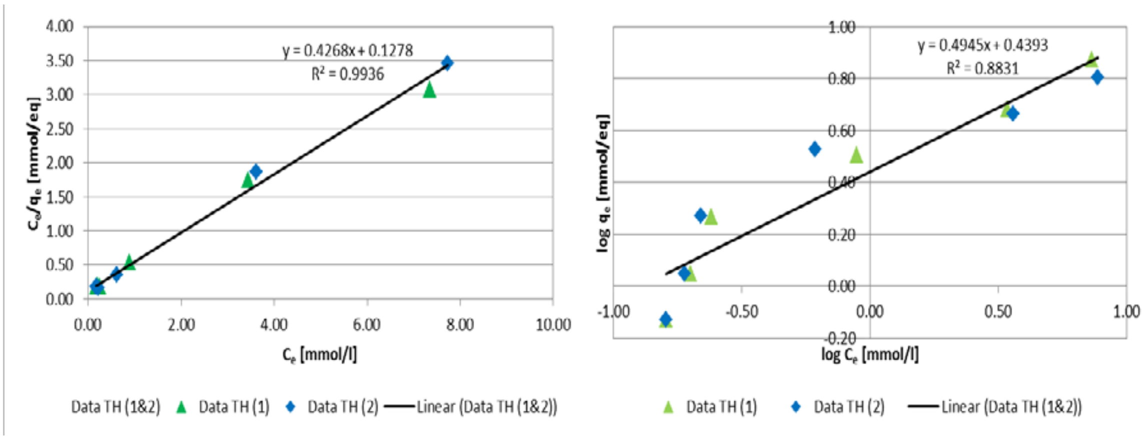


Figure 31: Parameters of the Langmuir isotherm (Left), Parameters of the Freundlich isotherm (Right).

With equitation 15 and 16 and the measured data of the total hardness from Table 12 the Langmuir and Freundlich isotherm can be drawn. The result is given in Figure 32.

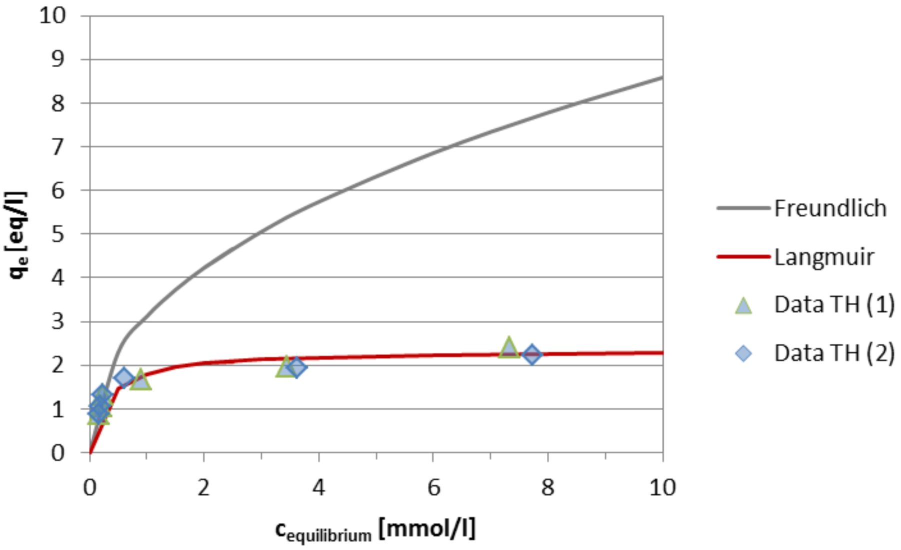


Figure 32: Langmuir and Freundlich isotherm.

In the graph can be seen that Freundlich isotherm does not go to an end value. Known from the literature is that the resin can only attach a certain amount of hardness which is dependent on the amount of functional groups on the resin, so an equilibrium value is expected. The Freundlich isotherm fits the data only at the begin of the graph, at low concentrations. When the concentration rises the Freundlich isotherm equation does not provide a good fit of the data. The Langmuir model provides a better fit of the data and develops to an end value, when the concentration of the hardness in the water raises no more hardness is loaded on the resin.

The capacity of the resin is 2.34 eq/l resin. So total hardness of 1.17 mol per litre of resin can be loaded. This value is higher than the capacity of the resin given by Lanxess, namely 2.1 eq/l. In the documentation of the resin can be found that this specification value is subject to continuous monitoring. So it is expected that a capacity of 2.1 eq/l resin is reached after 3 to 5 runs.

6.2 Regeneration with 10 % NaCl

The regeneration with 10% NaCl is conducted to have a reference where the results from the other regeneration can be compared to. Also the regeneration is done to understand and see how the experimental setup in the laboratory is performing.

In order to conduct the regeneration the bed has to be loaded first. In Figure 33 the breakthrough curve of the loading of the resin is given. The resin was loaded with tap water with increased hardness to a level of 6 mmol/l.

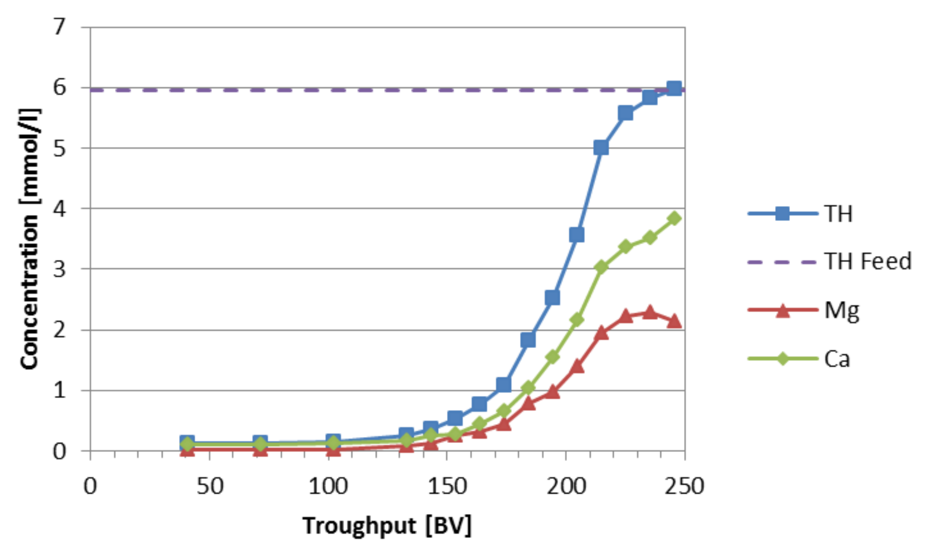


Figure 33: Breakthrough curve of column 1 at a flow of 29.7 m/h with a TH of 6 mmol/l.

In Table 13 the total amount of total hardness, calcium and magnesium that is loaded on the resin is presented. These values are determined with the trapezoid rule and the breakthrough curve according to the procedure given in the previous chapter.

The amount of regenerate that is used to regenerate the resin is normally given by the manufacturer of the resin. Only the bed is now completely loaded and not partially as the situation is at DWPB. So the given value of 100 g NaCl per litre resin cannot be used. For this regeneration is chosen to dose more bed volumes regenerant than actual is needed. The result of the measurement is given in the graph below. The flow in the column at regeneration is the same as in the column at DWPB during regeneration.

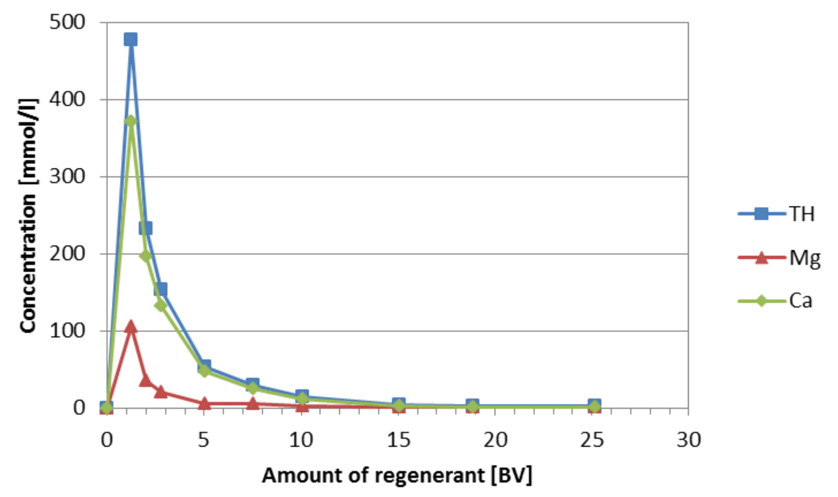


Figure 34: Elution curve column 1(Flow 3.77 m/h, 10%NaCl).

In the figure can be noticed that with the dosing of the first 5 bed volumes of regenerant, the most of the hardness is removed from the resin. With the bed volumes dosed after 5 bed volumes still hardness is removed, butt less than before. After the dosing of 15 bed volumes of regenerant no hardness is measured anymore, so all of the hardness is removed from the resin.

Table 13: Total amount of hardness loaded / removed from the resin of column 1.

	Total amount loaded [mmol]	**Total amount removed [mmol]**
TH	290.1	301.8
Mg^{2+}	58.2	56.9
Ca^{2+}	231.9	244.8

When these values are compared with the values of the loading, the conclusion can be made that more hardness is removed from the resin than is loaded. That cannot be possible, an explanation for that can be the fact that with the measurement an error is made. The absolute error that is made becomes larger when the dilution of the sample is higher. Some samples are diluted with a dilution of 2 to 100. The dilution is done because of the limitations of the cell test for the hardness concentration and the sodium concentration. With the measurement of the hardness of each sample the same error is made, but with a higher dilution the error becomes also larger. With a lower dilution another error is made, the results of the cell test for magnesium are influenced by the sodium concentration in the sample (see Appendix B.2 Results of the validation experiment). The difference between the amount removed from the resin and the amount loaded on the resin is 4%.

From the elution curve a graph can be constructed in which can be seen what capacity of the resin is expected at a certain amount of regenerant. The capacity is directly related to the amount of total hardness that is removed from the resin. This graph (Figure 35) is only valid with the use of 10% NaCl as a regenerant with a flow of 3.77 m/h. Another limitation of this graph is that the effect of tailing is not taken into account. So when for example 9 bed volumes of regenerant is used, according to the graph a capacity of 2.18 eq/l resin is expected. This number will be higher, because with the displacement of the regenerant still exchange of sodium and hardness takes place in the bed due to the dilution of the regenerant.

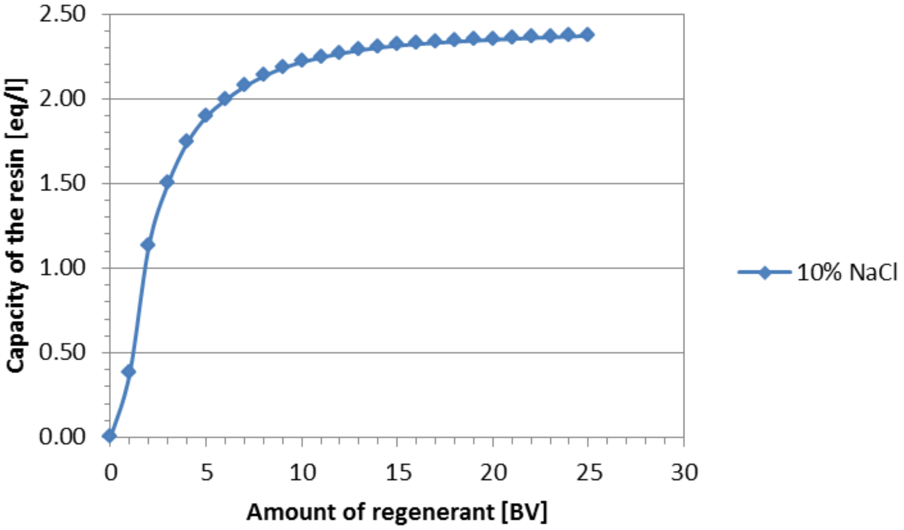


Figure 35: Capacity of the resin for the amount regenerant (determined with 10% NaCl, Flow 3.77 m/h).

Four sequential runs were performed, 1 run exists out of one loading and regeneration. After each loading the bed was completely regenerated with an excess of regenerant. For each run the breakthrough curve of loading of the resin is determined. Loading of the resin of the first three runs was done with tap water with an increased hardness level of 6 mmol/l. At the fourth run hardness was increased to 8 mmol/l. That was done because with hardness of 6 mmol/l more water was needed to load the three columns than was available in the vessel. Results of the runs are presented in appendix C.1. Breakthrough curves for the total hardness of the four runs are presented in Figure 36.

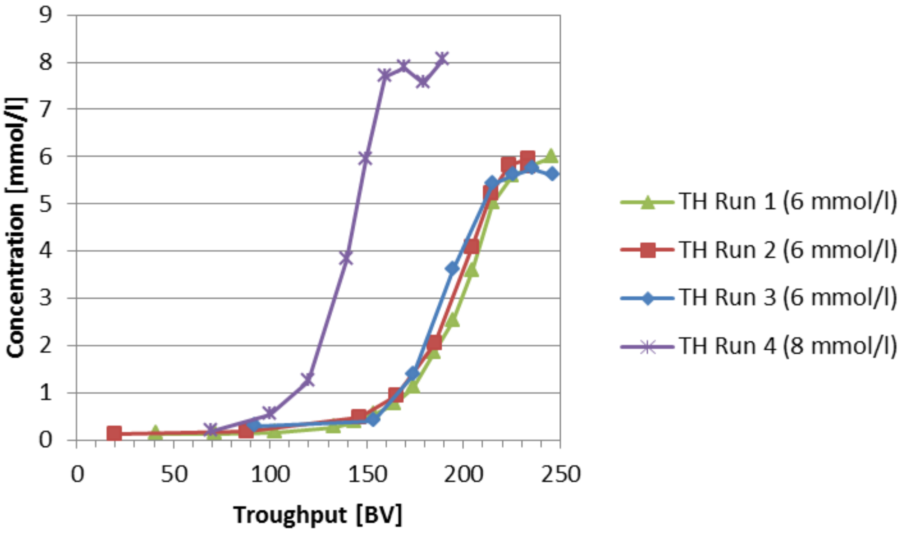


Figure 36: Breakthrough curve of 4 sequential runs (TH 6 and 8 mmol/l , Flow 29.7 m/h).

For the first three runs (TH=6 mmol/l) is noticed that the breakthrough curve is moving to the left. That was already expected, because according to literature 3 to 5 runs are needed to develop equilibrium (Crittenden, 2005). At the fourth run with tap water with an increased hardness level of 8 mmol/l the breakthrough curve is more to the left. That is explained by the fact that more hardness is present in the water and therefore less bed volumes of water are needed to load the resin. The breakthrough curve is ending at a higher level due to the increased hardness of the feed water. With the graph of the breakthrough curve no clear comparison can be made between all of the runs. In Figure 37 a histogram is given of the capacity of the resin. The capacity of the resin is determined by the amount of hardness that could be loaded on the resin.

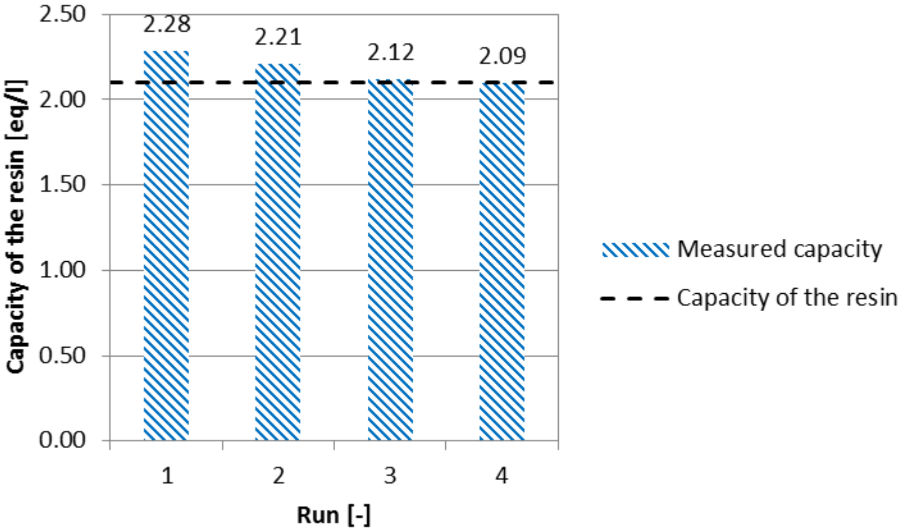


Figure 37: Capacity of the resin with four sequential runs (Run 1-3 TH= 6mmol/l, Run 4 TH = 8 mmol/l, Flow 29.7 m/h).

With the graph a comparison can be made between the four runs. Clearly now is that the capacity of the resin is higher than according to Lanxess, manufacturer of the resin. The capacity is indeed decreasing with each run, but the rate of decay also subsides with each run. The value of the capacity of the resin is going to its equilibrium as expected.

After loading of the fourth run is chosen to do a regeneration with 10 bed volumes of 10 weight percent of NaCl. From this regeneration an elution curve is drawn.

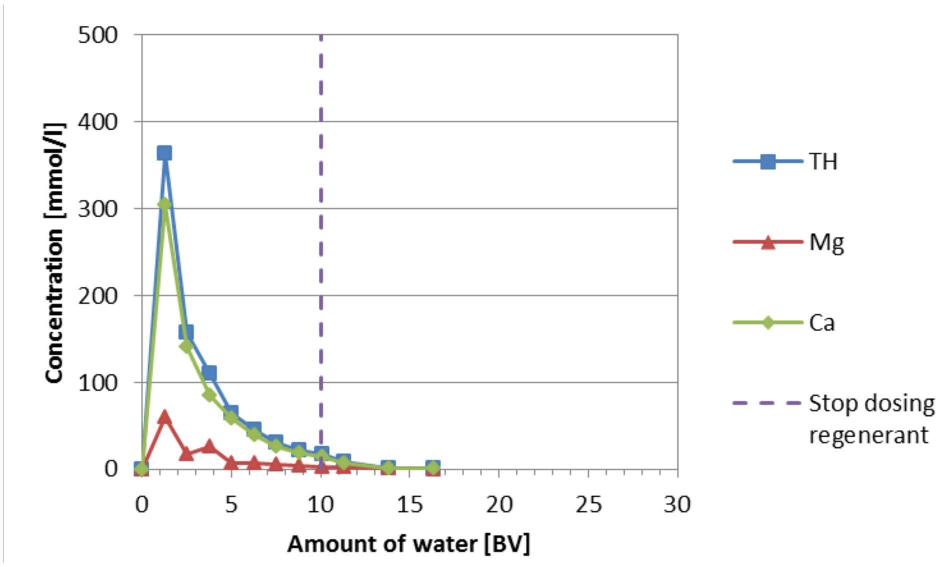


Figure 38: Elution curve of column 1 (Flow 3.77 m/h, 10 BV of 10% NaCl).

According to Figure 35 is expected that the capacity of the resin is 2.22 eq/l. When this value is related to the amount that is loaded on the resin, is expected that 93.4% of the total hardness is removed from the resin with dosing 10 bed volumes of regenerant. In the table below the total amount of hardness is given that is loaded on and removed from the resin.

Table 14: Total amount of hardness loaded / removed from the resin of column 1.

		Total amount loaded [mmol]	**Total amount removed [mmol]**
Calculated with the trapezoid rule	TH	267.6	263.4
	Mg^{2+}	40.4	41.0
	Ca^{2+}	227.2	222.4
Measured with a mixed sample	TH	266.1	268.8
	Mg^{2+}	43.3	38.4
	Ca^{2+}	222.8	230.4

The values are calculated with the trapezoid rule and the breakthrough / elution curve. During the experiment all effluent is collected and a sample (mixed sample) is taken and analysed. With the total volume of collected water and concentrations known, the total amount loaded / removed is calculated.

The total amount of hardness removed from the resin calculated with the trapezoid rule is less than the amount that is loaded on the resin. Based only on the values of the calculation of the trapezoid rule can be concluded that the regeneration was more efficient as expected. Now 98.4% of the total amount of loaded hardness on the resin was removed and not as expected 93.4%. From values of the total hardness determined with the mixed sample another conclusion can be drawn. The amount that is removed from the resin is more or less equal to the amount that is loaded on the resin, so all of the hardness is removed from the resin. The differences between these values are caused by the measuring error. The capacity of the resin is 2.11 eq/l of resin, which is lower than the expected value of 2.22 eq/l. The figure where that value is determined with is constructed with values from the first regeneration. As explained earlier in the first runs the capacity is higher and decreases to the capacity according to Lanxess. With results of the regeneration with 10 bed volumes of 10% NaCl a new graph is constructed for the capacity of the resin (Figure 39).

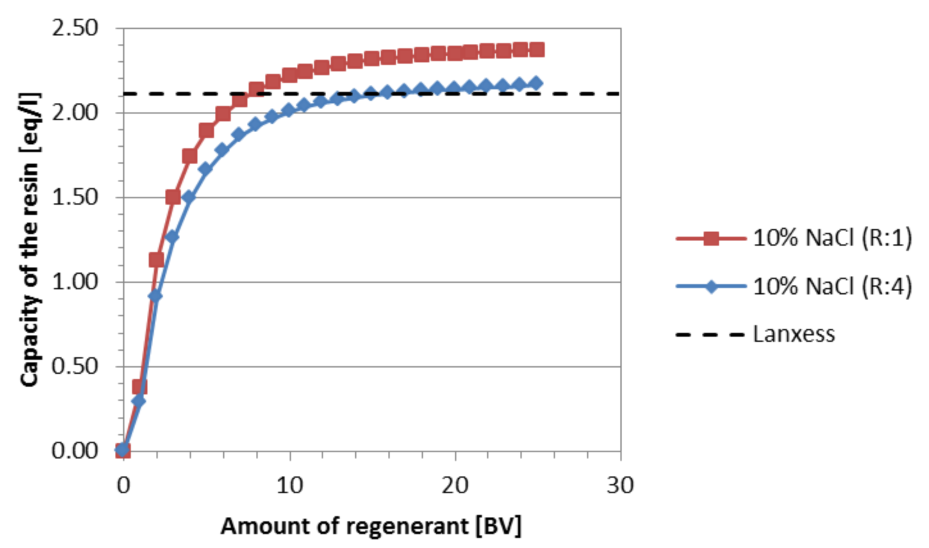


Figure 39: Capacity of the resin for the amount of regenerant of the first and fourth regeneration (determined with 10% NaCl, flow 3.77 m/h)

In the figure can be seen that the capacity of the resin is indeed decreased to almost the value of the capacity of the resin given by Lanxess, as also is seen with the loading of the resin. The line of the fourth regeneration (R:4) is used as a reference to compare the other regenerants with.

That the total amount of hardness calculated with the trapezoid rule that is removed from the resin is lower than the amount that is loaded can be explained. For that calculation also the elution curve is used. The elution curve is based on measured values of the total hardness from samples taken during regeneration. In the beginning of the regeneration a peak of hardness is expected. When a sample is taken too early or too late the peak of hardness is missed and that will be noticed in the value of the total hardness. This is checked by comparing Figure 38 and Figure 34. In Figure 34 the peak of the total hardness is higher than in Figure 38. Both regenerations were almost completely the same, only the amount of regenerant was different. So the height of the peak should be the same, because the same amount of sodium is present in the fluid. Only the width of the curve should be smaller because of the fact that only 10 bed volumes of regenerant are dosed.

Therefore an elution curve is a very good tool to understand the process during regeneration, but to determine the total amount of hardness that is removed from the resin a mixed sample is more accurate.

6.3 Regeneration with water from the Brittannië harbour.

The ultimate goal is to regenerate the resin with water from the Brittannië harbour. Because of the fact that the harbour is in connection with the sea (see Appendix A: Map of the harbour) is expected that the water is brackish and shall contain more ions than only sodium. To see what the effect of the ions are and to have a constant concentration first a regeneration is conducted with 3.45 % NaCl. Next a regeneration is done with artificial sea water. The results of the different loadings and regenerations can be found in appendix C.2.

For the experiment two columns were loaded, column 2 for the regeneration with 3.45% NaCl and column 3 for the regeneration with artificial seawater. Both columns were loaded for the first time, so it is expected that the more hardness can be loaded on the resin than given by Lanxess. In Figure 40 the breakthrough curves of the loading of both columns and the reference is presented. As a reference is taken the fourth loading of the previous paragraph; in that case the capacity of the resin given by the manufacturer of the resin is reached. The loading curves of the other loading of the resin should have the same shape. The curve could shift on the horizontal axis, which is dependent on the amount of hardness that can be loaded on the resin. If more hardness can be loaded on the resin it will shift to the right and it will shift to the left when less hardness can be loaded on the resin.

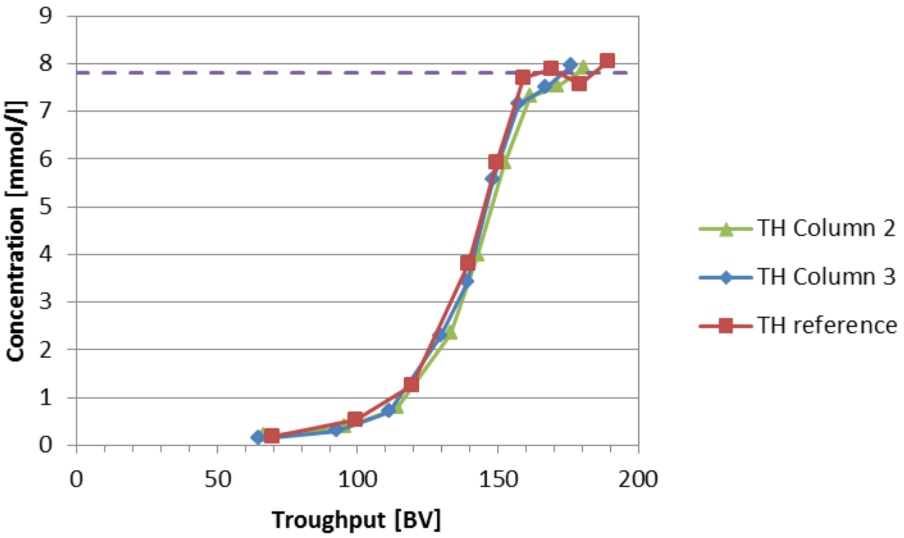


Figure 40: Breakthrough curves at a flow of 29.7 m/h with a TH of 8 mmol/l.

Both curves of column 2 and 3 are almost on top of the reference, so the capacity of the resin is almost equal to the value given by the manufacturer of the resin. Also can be seen that the shape of the curve of both columns are almost equal to each other. That can be traced back to the fact that both columns are loaded with the same liquid and have the same bed volume. The total amount of hardness that is loaded on the resin is given in Table 16. Based on these values is determined that the resin in columns 2 has a capacity of 2.16 eq/l resin and column 3 2.13 eq/l resin. According to Lanxess the resin has a capacity of 2.1 eq/l, so the capacity is indeed almost the same.

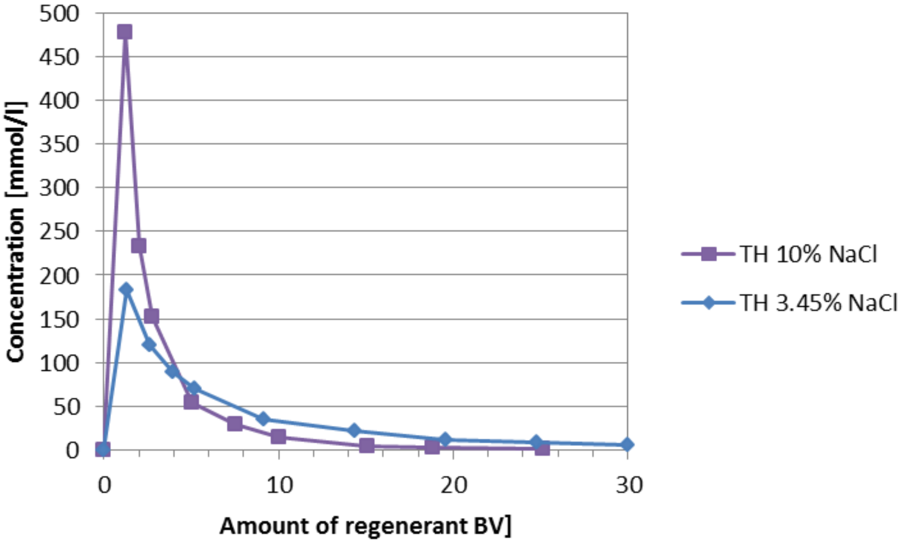


Figure 41: Elution curve for the regeneration with 3.45% and 10% NaCl (Flow 3.77 m/h).

The elution curve for the regeneration with 3.45% NaCl and 10% NaCl is compared with each other (see Figure 41). The peak in the total hardness concentration is lower than the peak for 10% NaCl. The reason for that is that the driving force of the reaction is dependent on the sodium concentration. With the use of 3.45% NaCl less sodium is available to be exchanged for the hardness on the resin. The elution curve is lower and wider because more bed volumes of regenerant is needed to remove the same amount of hardness from the resin. That can also be seen in Figure 42.

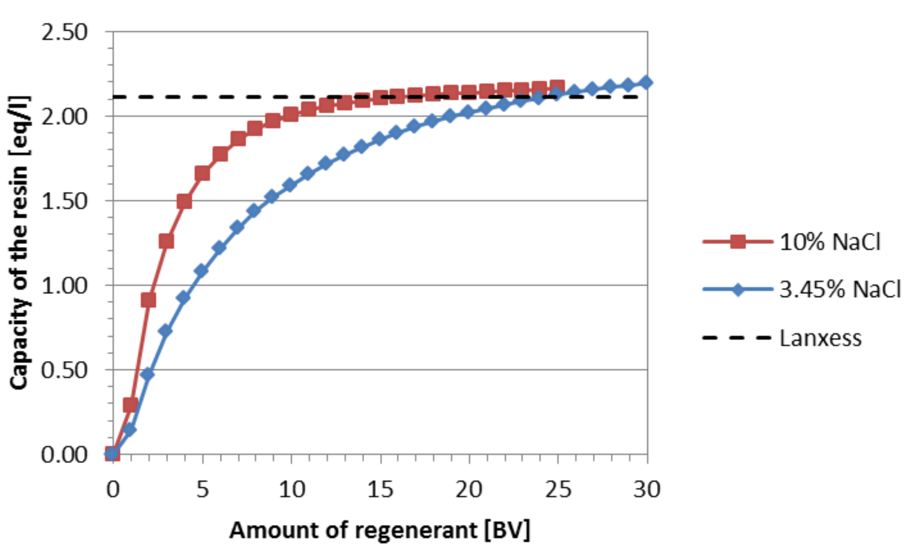


Figure 42: Percentage of TH removed from the bed for the amount of regenerant (determined with 3.45% and 10% NaCl, Flow 3.77 m/h).

Both regenerants can be compared with each other. When for example an operating capacity of 2 eq/l is needed in the figure can be deducted how many bed volumes of both regenerants are needed. For 10% NaCl (= 107.07 g/l) 10 bed volumes and for 3.45% NaCl (= 44.71 g/l) 20 bed volumes are needed. The setup in the laboratory has a bed volume of 254 ml. The total amount of salt for the regeneration is:

- 10 BV 10% NaCl: 272.0 g NaCl
- 20 BV 3.45% NaCl: 227.3 g NaCl

With a lower salt concentration 2 times more regenerant and time (if both regenerants are used at the same flow) is needed for the regeneration. With the use of 3.45% NaCl 16.4% less salt is needed for the regeneration.

For the regeneration with artificial seawater is chosen to use 30 bed volumes of the regenerant. In that case a good comparison can be made between the results of the regeneration with 3.45% NaCl and artificial seawater. The elution curve of the regeneration is given in the figure stated below.

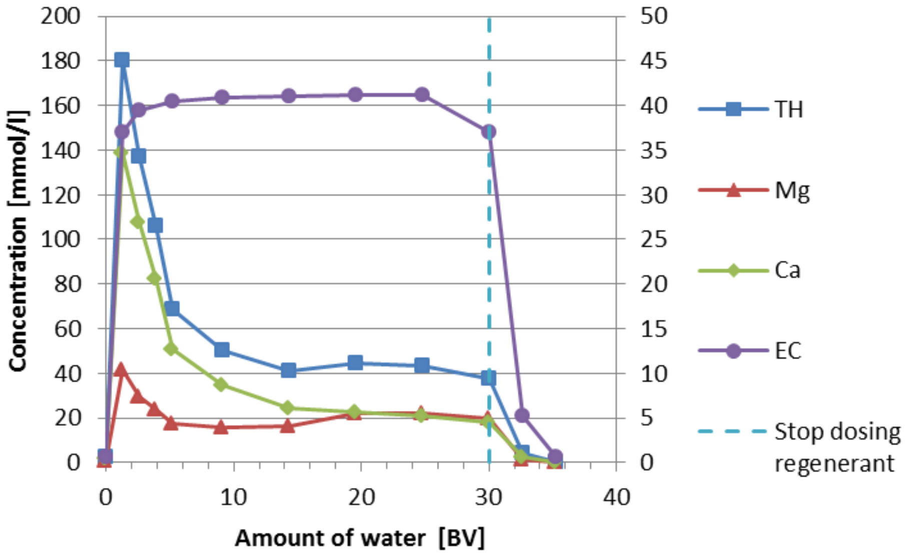


Figure 43: Elution curve of column 3 (Flow 3.77 m/h, 30 BV of artificial seawater).

In the graph of the elution curve can be seen that the line of the total hardness is going to a value of 40 mmol/l. That value is only decreasing when the supply of the regenerant is stopped. In the graph of the elution curve the line for calcium and magnesium are converging. After 14 bed volumes of regenerant the total hardness concentration is not decreasing anymore, it remains more or less constant. Expected is that the total hardness, calcium and magnesium decreases as is seen with the use of 3.45% NaCl as a regenerant. Ions in the artificial seawater that can be loaded on the resin can cause that the line is not decreasing anymore. Therefore a sample of the artificial seawater is analysed, the results are given in Table 15.

Table 15: Major ion composition of seawater [Cotruvo, 2005] and artificial seawater.

		Seawater		**Artificial seawater**	
		Total amount [mg/l]	**Total amount [mmol/l]**	**Total amount [mg/l]**	**Total amount [mmol/l]**
Chloride	Cl^-	18,980	535.40	14,555	410
Sodium	Na^+	10,556	459.16	9,706	422
Sulfate	SO_4^{2-}	2,649	27.57	2,054	21.4
Magnesium	Mg^{2+}	1,262	51.91	715	29.8
Calcium	Ca^{2+}	400	9.98	400	10.0
Potassium	K^+	380	9.72	344	8.8
Bicarbonate	HCO_3^-	140	2.29	171(3)	2.8(3)
Strontium	Sr^{2+}	13	0.15	-	-
Bromide	Br^-	65	0.81	-	-
Borate	BO_3^{3-}	26	0.44	-	-
Fluoride	F^-	1	0.05	-	-
Silicate	SiO_2	0.86(1)	0.01(1)	60(2)	1.0(2)
Iodide	I^-	<1	<0.01	-	-
Others		-	-	27.9	0.64
Total Dissolved Solids	**TDS**	**34,483**	**1,097.52**	**28,049**	**906.44**

(1)Measured as SiO_3^{2-} (2)Measured as Si (3)Measured as M-alkalinity

In the table also the major ion composition of seawater is given. From the table can be concluded that the artificial seawater looks like seawater, but deviates at some ion concentrations. The sodium concentration in the artificial seawater is enough for the regeneration of the resin, it is 2.46% NaCl. More important is that also calcium and magnesium are present in the regenerant. The total hardness of artificial seawater 39.8 mmol/l. That is the same value where the elution curve is converging to (see Figure 44). The regeneration of the resin is a process given by the following equilibrium reaction:

$$\left[2\ R^-\right]TH + 2\ Na^+ \leftrightarrow TH + 2\ \left[R^-\right]Na \qquad (27)$$

The equilibrium shifts to the left when in the regenerant hardness is present. The result of the shift is that less hardness is removed from the resin. When the amount of hardness on the resin decreases, the reaction rate is going down. In the figure below a comparison is made of 3.45% NaCl and the artificial seawater as a regenerant. The value of the total hardness of the artificial seawater is also given.

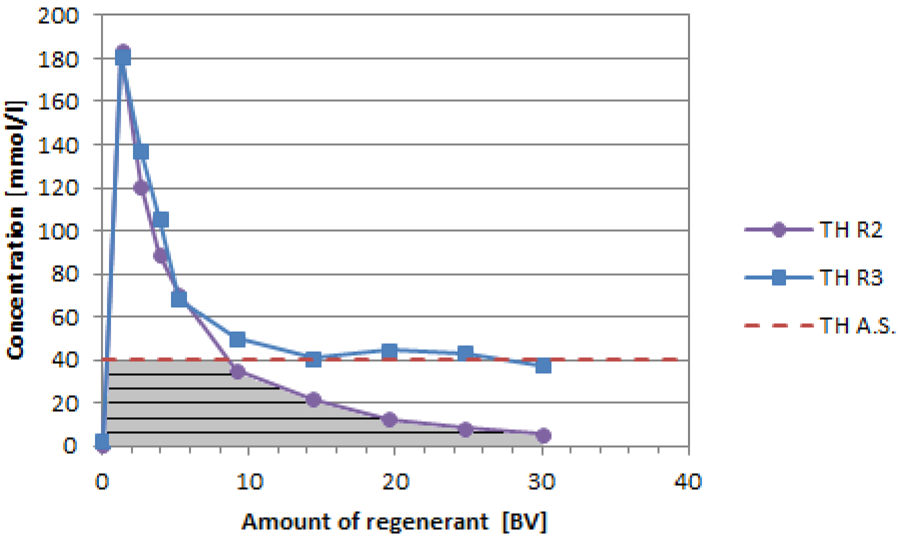


Figure 44: Comparison of R_2 (3.45% NaCl) and R_3 (artificial seawater).

The marked area in the figure is the amount of hardness that cannot be removed with the artificial seawater. That amount is 119 mmol of total hardness. So almost 44% of the hardness is not removed. The converging of calcium and magnesium in the elution curve states that more processes are occurring in the bed. In Table 16 the total amount hardness loaded and removed from the resin is presented.

Table 16: Total amount of hardness loaded / removed from the resin of column 2 and 3.

		Total amount loaded		Total amount removed	
		Column 2 [mmol]	Column 3 [mmol]	Column 2 [mmol]	Column 3 [mmol]
Calculated with the trapezoid rule	TH	275.1	271.5	281.9	152.5
	Mg^{2+}	45.3	46.3	46.7	-65.0
	Ca^{2+}	229.7	225.2	235.2	217.5
Measured with a mixed sample	TH	256.8	267.6	274.4	134.1
	Mg^{2+}	38.1	45.2	55.8	-58.4
	Ca^{2+}	218.7	222.4	218.6	192.5

With the determination of the values is taken into account that hardness is present in the regenerant. The calculated amount of magnesium that is removed from the resin is a negative value. From that can be concluded that no magnesium was removed from the resin, but in fact was loaded on the resin. That can be explained with the fact that in artificial seawater more magnesium is present then on the resin. Although the resin has a higher affinity for calcium than for magnesium, exchange of calcium and magnesium takes place. In the table can be seen that 50.1% of the amount that is loaded on the resin is removed during regeneration. When the total hardness is divided into calcium and magnesium the situation becomes different. For the amount of calcium can be seen that a total of 192.5 mmol is removed from the resin, which is 86.6% of the total amount of calcium that is loaded on the resin. The extra removal of calcium is at the cost of the removal of the magnesium. Magnesium is not removed during the regeneration, but loaded on the resin. At the end of the regeneration a total of 103.6 mmol of magnesium is attached to the resin.
In Figure 45 left a comparison is given of the following regenerants; artificial seawater, 3.45% NaCl and 10% NaCl. Also the capacity of the resin according to the analysis of Lanxess is presented. The development of the total amount of removed hardness, calcium and magnesium is given in the right graph of Figure 45.

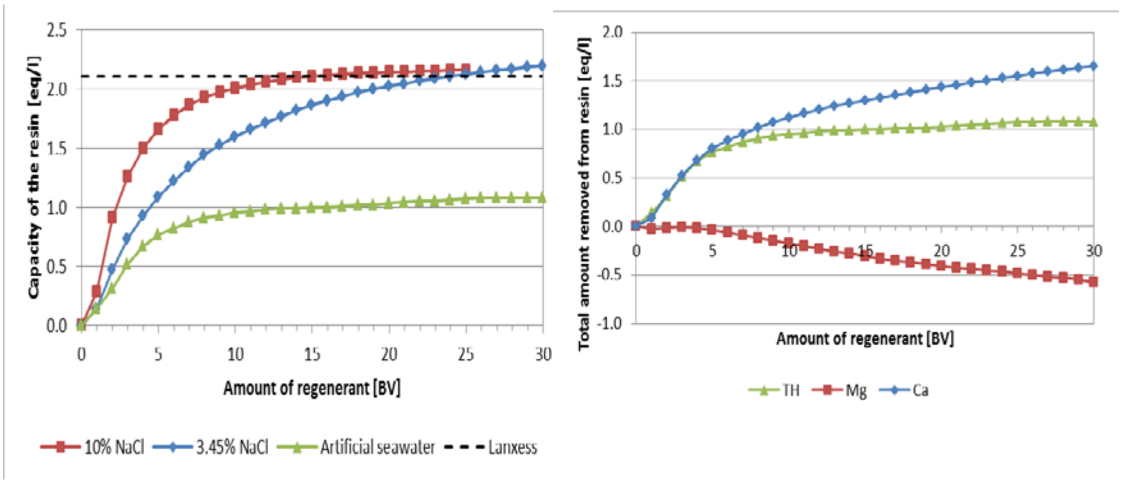


Figure 45: ***Left*** *Capacity of the resin for the amount of regenerant (determined at a flow of 3.77 m/h with artificial seawater, 3.45% and 10% NaCl)* ***Right*** *Total amount hardness, magnesium and calcium for the amount of regenerant (artificial seawater, flow 3.77 m/h).*

From the left figure can be deducted how many bed volumes of a regenerant are needed to achieve a specific capacity of the resin. For example when a capacity of 1.0 eq/l is required. Then 1.3 bed volumes of 10% NaCl, 4.5 bed volumes of 3.45% NaCl or 17 bed volumes of artificial seawater is needed. The total amount of salt needed for the regeneration is:

- 2.3 BV 10% NaCl : 62.6 g NaCl
- 4.5 BV 3.45% NaCl : 51.1 g NaCl
- 17 BV artificial seawater : 140.3 g Sea salt (=106.6 g NaCl)

In this case with the use of 3.45% NaCl the smallest amount of salt is used, 18% of sodium chloride is saved compared to the use of 10% NaCl. Only almost 2 times more time is needed for the regeneration and that time needs to be available in the process. Another disadvantage is that more water is needed, 2.2 BV. When a plant is near seawater, enough of that water is available. The important question is than if the time is available in the process which is needed for the regeneration with seawater. Another possibility is to increase the flow velocity to lower the time needed for the regeneration, but then more bed volumes of regenerant could be needed. That was not a scope of this research and more investigation should be done if this process is considered.

In the right figure can be seen that when 17 bed volume of artificial sweater are dosed, also the exchange of calcium and magnesium takes place. As mentioned before the magnesium is not removed from the resin at all. The question now is what will happen with the magnesium concentration on the resin when several sequential runs are applied. Is the amount of the magnesium on the resin increasing until the bed is completely loaded or is equilibrium developed? Even more important is to notice that when the dosing of the artificial seawater is kept below 5 bed volumes no exchange of calcium and magnesium takes place. Only the calcium is removed from the bed. Then a capacity of 0.77 eq/l resin is expected.

In the left figure can be seen that the capacity of the resin is not increasing above 1.1 eq/l, so the bed cannot be completely regenerated with artificial seawater.

Artificial seawater can be applied as a regenerant in the case that an incomplete regeneration of the resin is desired, but attention has to be paid to leakage. In case of the process at DWPB a layer of resin at the bottom of the vessel is never loaded to ensure a good quality of softened water. When artificial seawater is applied that layer is loaded, what is not desired.

Before the regeneration of the resin with water from the Brittannië harbour is applied, first a sample of water from the harbour is analysed. The result of the analysis is given in Table 17.

Table 17: Major ion composition of water from the Brittanniё harbour and artificial seawater.

		Water Brittanniё harbour		**Artificial seawater**	
		Total amount [mg/l]	**Total amount [mmol/l]**	**Total amount [mg/l]**	**Total amount [mmol/l]**
Chloride	Cl^-	12,620	356	14,555	410
Sodium	Na^+	5,931	258	9,706	422
Sulphate	SO_4^{2-}	1,306	13.6	2,054	21.4
Magnesium	Mg^{2+}	727	29.9	715	29.8
Calcium	Ca^{2+}	253	6.3	400	10.0
Potassium	K^+	250	6.4	344	8.8
Bicarbonate	HCO_3^-	171(2)	2.8(2)	171(2)	2.8(2)
Strontium	Sr^{2+}	-	-	-	-
Bromide	Br^-	-	-	-	-
Borate	BO_3^{3-}	-	-	-	-
Fluoride	F^-	-	-	-	-
Silicate	SiO_2	<6(1)	<0.1(1)	60(1)	1.0(1)
Iodide	I^-	-	-	-	-
Others		18.9	0.63	27.9	0.64
Total Dissolved Solids	**TDS**	**21,280**	**673.73**	**28,049**	**906.44**

(1)Measured as Si (2)Measured as M-alkalinity

In the table can be seen that the ion composition of the artificial seawater and the water of the Brittanniё harbour are almost the same. In the water from the harbour also calcium and magnesium are present. The magnesium concentration is almost the same as in the artificial seawater, the calcium concentration is lower. More important is that the sodium concentration in the water from the harbour is lower than in the artificial seawater. The result of this is that the driving force in the reaction of the regeneration is lower. The process of regeneration will develop even worse than with the use of artificial seawater.

The desire of Evides is that the resin layer at the bottom of the vessel should not be loaded. Also a fact is that hardness and a lower sodium concentration are present in the water from the harbour. Based on these facts is decided that water from the Brittanniё harbour is not suited to be used as a regenerant at DWPB.

6.4 Regeneration with RO concentrate

The regeneration with concentrate from the RO unit of DWP is performed with different variants of the concentrate. A division is made in three different types:

- RO concentrate with the addition of 1% NaCl
- RO concentrate with the addition of $CaCO_3$
- RO concentrate with 10% NaCl

Within these types variations in parameters as the pH and the flow velocity were applied. Before regeneration with RO concentrate was performed a sample of the RO concentrate from DWPB was analysed. The result of that analysis is given in the table below with the major ion composition of seawater [Cotruvo, 2005].

Table 18: Major ion composition of seawater [Cotruvo, 2005] and RO concentrate of DWPB.

		Seawater		RO Concentrate	
		Total amount [mg/l]	**Total amount [mmol/l]**	**Total amount [mg/l]**	**Total amount [mmol/l]**
Chloride	Cl^-	18,980	535.40	500	14.1
Sodium	Na^+	10,556	459.16	977	42.5
Sulphate	SO_4^{2-}	2,649	27.57	307.4	3.2
Magnesium	Mg^{2+}	1,262	51.91	<0.24	<0.01
Calcium	Ca^{2+}	400	9.98	1.25	0.03
Potassium	K^+	380	9.72	11.7	0.3
Bicarbonate	HCO_3^-	140	2.29	1,134.9⁽³⁾	18.6⁽³⁾
Strontium	Sr^{2+}	13	0.15	-	-
Bromide	Br^-	65	0.81	-	-
Borate	BO_3^{3-}	26	0.44	-	-
Fluoride	F^-	1	0.05	-	-
Silicate	SiO_2	0.86⁽¹⁾	0.01⁽¹⁾	30⁽²⁾	0.5⁽²⁾
Iodide	I^-	<1	<0.01	-	-
Others		-	-	96.6	1.67
Total Dissolved Solids	**TDS**	**34,483**	**1,097.52**	**3,048**	**81.07**

(1) Measured as SiO_3^{2-} (2) Measured as Si (3) Measured as M-alkalinity

In the table can be seen that the available sodium concentration in the concentrate is almost ten times lower than in seawater. And compared to the regenerant that is used at DWPB (10% NaCl) the sodium concentration is more than 42 times lower. So when only is looked at the sodium concentration and the same amount of hardness needs to be removed from the resin, more than 42 times of bed volumes of regenerant is needed. That is a lot of regenerant that then is used. At the current flow velocity that amount of regenerant result in a longer regeneration period. Therefore is chosen to add salt to the regenerant to increase the sodium concentration. At least 1% NaCl needs to be added; in that case 8 times more regenerant and time is needed for the regeneration compared to the use of 10% NaCl. Also another effect can have a major contribution in the regeneration process. In the concentrate bicarbonate was measured. The value given is the total of carbonate and bicarbonate measured as the M-alkalinity. The pH of the concentrate was 9.38 and then 14.6 mmol/l of bicarbonate and 2.0 mmol/l of carbonate is present. The carbonate reacts with the hardness to calcium- or magnesium carbonate. As a consequence of that the reaction shifts and more hardness can be removed with the same amount of sodium.

Important to realize is that with the use of the concentrate, the solubility product can be exceeded resulting in the formation of calcium / magnesium carbonate. The solubility products for both salts are given by the following equations.

$$\begin{aligned} &\text{Calcium carbonate, 20°C:} && K_s = \left[Ca^{2+}\right]\cdot\left[CO_3^{2-}\right] = 8.7\cdot10^{-9} \\ &\text{Magnesium carbonate, 20°C:} && K_s = \left[Mg^{2+}\right]\cdot\left[CO_3^{2-}\right] = 1.0\cdot10^{-8} \end{aligned} \tag{28}$$

In case of calcium the concentration has to be above 0.093 mmol/l to get precipitation of calcium carbonate. For the formation of insoluble magnesium carbonate the magnesium concentration has to be above 3.16 mmol/l. Also in both cases the concentration of carbonate has to be above the same values in order to have precipitation.

6.4.1 RO concentrate with 1% NaCl added

As was the case with the other experiments, the resin was loaded first before the regeneration with the concentrate with 1% NaCl added ($R_{5\text{-}1}$) was conducted. The breakthrough curve of the loading of the resin is given in the figure below.

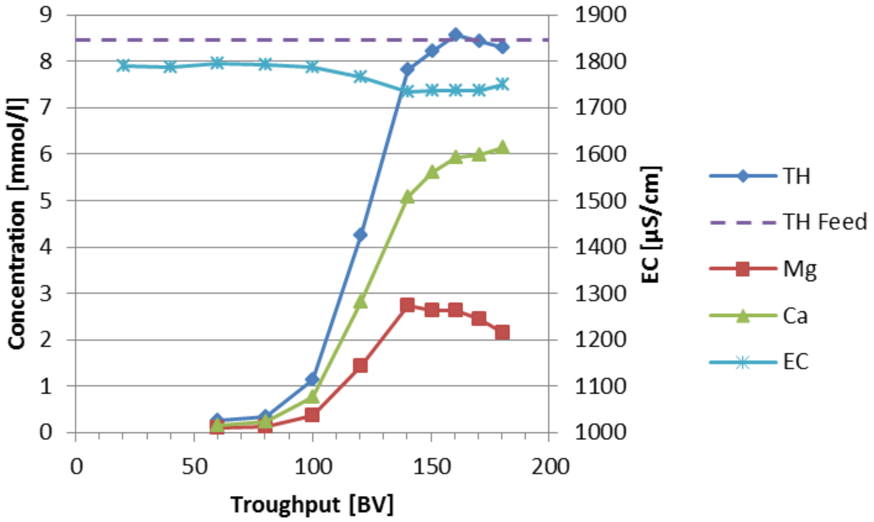


Figure 46: Breakthrough curve of column 2 at a flow of 30.09 m/h with a TH of 8 mmol/l.

In the introduction of the RO concentrate as a regenerant already was mentioned that the formation of calcium and magnesium carbonate can occur. With the previous regenerations samples were taken from which the hardness, calcium and magnesium concentrations were determined. If the same procedure is followed during this regeneration, the values that are determined with the cell test will be to low. That is caused by the fact that with the cell test only the calcium and magnesium ions are measured. So the part that has reacted with the carbonate is not measured with the test. During the regeneration still samples are taken, but only to determine the pH and conductivity. The capacity of the resin is calculated with the amount of hardness that is loaded on the resin before and after the regeneration of the resin. In the figure below the pH and conductivity during the regeneration are given. Also the values of the pH and conductivity of the regenerant ($R_{5\text{-}1}$) are displayed in the figure.

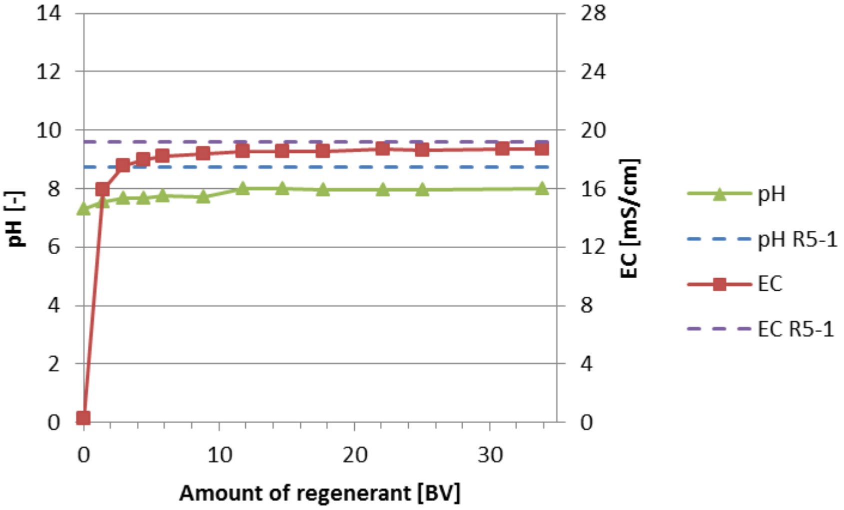


Figure 47: pH and conductivity during the regeneration with $R_{5\text{-}1}$ (Flow 4.19 m/h).

For the regeneration RO concentrate with 1% NaCl added is used as a regenerant. A higher flow velocity is used than with the previous regenerants. The higher flow velocity of 4.19 m/h is chosen because the formation of calcium carbonate was expected. With a higher flow velocity is tried to achieve that the formed calcium carbonate is flushed out of the bed. In the graph can be seen that the conductivity is very low at the start of the dosing. That is caused by the flush of the bed with demi water, conducted before the start of the regeneration. The conductivity rises towards the value of the conductivity of the regenerant. No clear distinction can be made when more hardness is removed from the bed. An explanation for that can be that when the exchange takes place of a hardness ion (calcium or / and magnesium) for 2

sodium ions the same amount of ions is present in the solution. In the graph can also be seen that the pH of the effluent is lower than the pH of the regenerant. But also at the start of the dosing of the regenerant the pH of the effluent is even a little bit lower. That suggests that a reaction is taking place in which an ion is released or removed that causes a decrease in pH.
Known from the analysis is that the concentrate contains bicarbonate and carbonate. During the regeneration calcium is exchanged from the resin in high concentrations. The calcium and the carbonate together form calcium carbonate. Because of the high concentrations the calcium carbonate is oversaturated, and precipitation will take place (positive SI). A result of that is that the pH decreases. The formation of calcium carbonate is an equilibrium reaction, and with the increase of the calcium concentration a new equilibrium will develop. The possibility is that not all of the carbonate is used.
In the graph can be seen that in the beginning of the regeneration, the pH drops more because then more calcium is exchanged from the resin. When less calcium is released from the resin the pH increases and remains constant, a new equilibrium has been developed. The magnesium concentration in the liquid is also important in the formation of calcium carbonate. With the regeneration also magnesium is released from the resin which can cause impurities in the formation of calcium carbonate. That causes that the growth of the calcium carbonate particles is slowed down or stopped because of the fact that the contact surface is disturbed by the magnesium carbonate.
The pH gives besides a visual inspection a good indication if calcium is converted to calcium carbonate. From the drop in the pH also can be seen when the more calcium is released from the resin and if the calcium released during the entire dosing of the regenerant. Which is the case in this run, the pH at the end is still lower than the pH of the regenerant.
With the determination of the total amount of hardness removed from the bed the breakthrough curve of the second run is used. The amount that can be loaded on the resin after regeneration is the same amount that is removed during the regeneration. Both breakthrough curves are given in Figure 48.

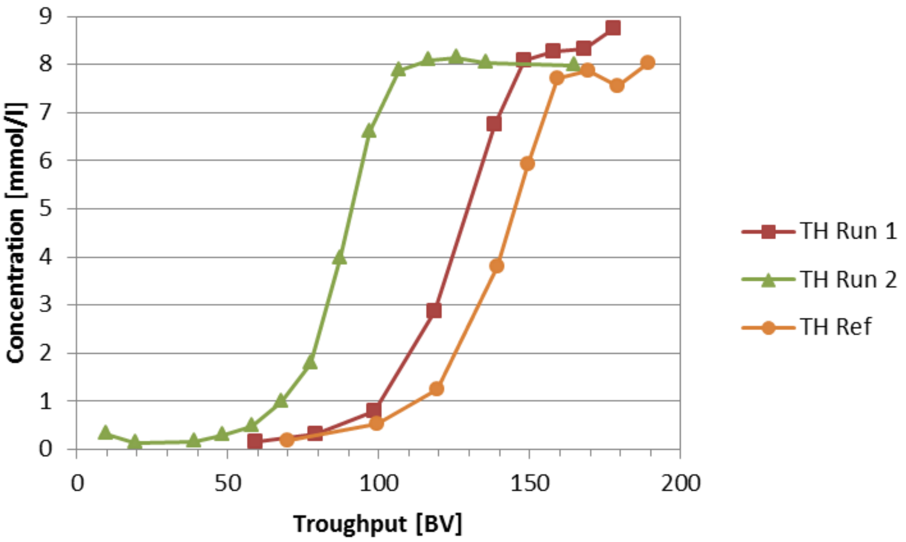


Figure 48: Breakthrough curve of the first and second run (loaded with TH = 8 mmol/l).

The total amount of hardness loaded on / removed from the resin is given in the table below.

Table 19: Total amount of hardness loaded / removed from the resin with the use of R_{5-1}.

		Total amount loaded [mmol]	**Total amount removed [mmol]**
Calculated with the trapezoid rule	TH	253.8	182.2
	Mg^{2+}	33.3	30.0
	Ca^{2+}	220.5	152.2
Measured with a mixed sample	TH	256.8	184.3
	Mg^{2+}	38.6	30.6
	Ca^{2+}	218.2	153.7

From the table can be concluded that only 71.8% of the loaded hardness is removed from the resin. After the regeneration a capacity of the resin is achieved of 1.45 eq/l with the use of 35 bed volumes of regenerant. Expected was that 8 times more regenerant was needed than with the use of 10% NaCl. With 10% NaCl 4 bed volumes are needed to get an operating capacity of 1.45 eq/l. Expected was that with the use of the concentrate with 1% NaCl added as a regenerant 32 bed volumes were needed. So the regeneration was performing worse than expected. The amount of carbonate that is present in the water is not giving that effect on the performance of the regeneration that is expected. Therefore also other configurations were investigated in the experimental setup.

During the experiments with this regenerant the pH was changed and the flow velocity. The following configurations were used (all with RO concentrate from DWPB and a flow velocity of 4.19 m/h unless mentioned otherwise):

- (1) 1% NaCl added (R_{5-1})
- (2) 1% NaCl added and the pH increased to 11.77 (R_{5-3})
- (4) 1% NaCl added and the pH increased in a gradient from 9.14 to 11.83 (R_{5-6})
- (6) 1% NaCl added and the pH increased in a gradient from 10.04 to 11.92 at a flow velocity of 7.07 m/h (R_{5-6})

The pH was increased to have a higher concentration of carbonate present in the regenerant. Also two regenerations (3 and 5) with 10% NaCl were conducted in order to compare the capacity with values determined earlier.

To compare the performance of the variations in regenerant the breakthrough curves of all runs are given in one figure. The different runs are:

- Run 1: loading after regeneration with R_1 (10%NaCl)
- Run 2: loading after regeneration with R_{5-1}
- Run 3: loading after regeneration with R_{5-3}
- Run 4: loading after regeneration with R_1
- Run 5: loading after regeneration with R_{5-6} (pH from 9.14 to 11.83)
- Run 6: loading after regeneration with R_1
- Run 7: loading after regeneration with R_{5-6} (pH from 10.04 to 11.92)

The breakthrough curves of these runs are given in Figure 49; also the reference curve is given. The results of the loadings and regeneration of each of these runs is given in appendix C.3. In the table below the amount of bed volumes used of each regenerant is given.

Table 20: Amount of regenerant used for each regeneration

Regeneration	**[-]**	**1**	**2**	**3**	**4**	**5**	**6**
Regenerant	[-]	R_{5-1}	R_{5-3}	R_1	R_{5-6}	R_1	R_{5-6}
Amount	[BV]	33.5	21	5.5	25	6	21

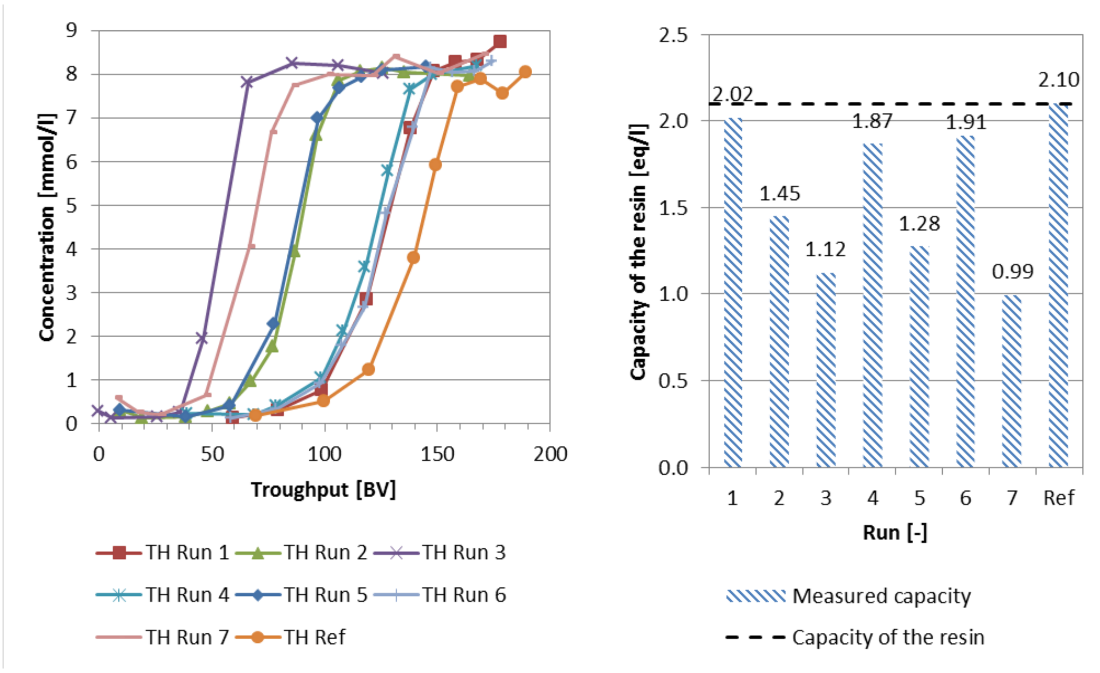


*Figure 49: **Left** Breakthrough curves of the 7 runs related to the regeneration with concentrate with 1% NaCl added. **Right** Capacity of the resin for each run.*

In the figure can be seen that the breakthrough curve of the first run is left from the reference, less amount of hardness could be loaded on the resin. Which can also be seen in the right figure. The capacity of the resin at run 1 is 0.08 eq/l resin lower than the reference. That can be due to the fact that some of resin is damaged (attrition) after the previous loadings or to a measurement error that is made with the determination of the hardness. While performing the 7 runs was noticed that the flow velocity in the bed was decreasing, which was caused by the clogging of the filter plates. After the run 2 and 5 the filter plates were removed from the system and cleaned with hydrochloric acid. In that case the formed calcium carbonate was dissolved and the holes were open again.

Table 21: Flow velocity in the bed during the loading of the resin for the seven runs.

Run	**[-]**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Flow velocity	[m/h]	30.09	29.05	29.6	29.59	29.12	29.44	29.32

In the left graph can be seen that the breakthrough curve of the loading of the resin after regeneration with concentrate with 1% NaCl and a pH of 11.77 is the one that is the farthest to the left. That indicates that the regeneration is performing the worst of all. Already with the regeneration was seen that almost all of the resin became one lump due to the formation of calcium carbonate in the bed. No exchange can take place anymore with the resin that is inside that lump. The amount of hardness that can be removed from the resin is less, and therefore the capacity of the resin is also decreased. The regeneration with no addition of caustic soda (NaOH) to increase the pH was performing better (run 2). In that case less carbonate was present in the regenerant and therefore, less calcium carbonate is instantly formed. The formation of calcium carbonate still occurs but more gradually, and no lump of resin was formed.

The high amount of carbonate causes problems with precipitation in the bed. In the beginning of the regeneration more hardness is released from the bed, at that moment the carbonate concentration should be lower to prevent the formation of a large amount of calcium carbonate. To achieve a lower concentration of carbonate at the start and a high concentration at the end of the regeneration, a gradient mixer was used. In the gradient mixer two vessels are present which both contain RO concentrate with 1% NaCl added. Only at one vessel (vessel 2) the pH is higher than at the other, and both vessels are connected to eachother. The regenerant is pumped from the vessel with the lowest pH. Regenerant is than flowing from the second vessel (with higher pH) to the first. As a result of that flow the pH of the regenerant in the first vessel is increasing. Development of pH in the regenerant with a gradient mixer is given in Figure 50 for regeneration with R_{5-6} (pH from 10.04 to 11.92).

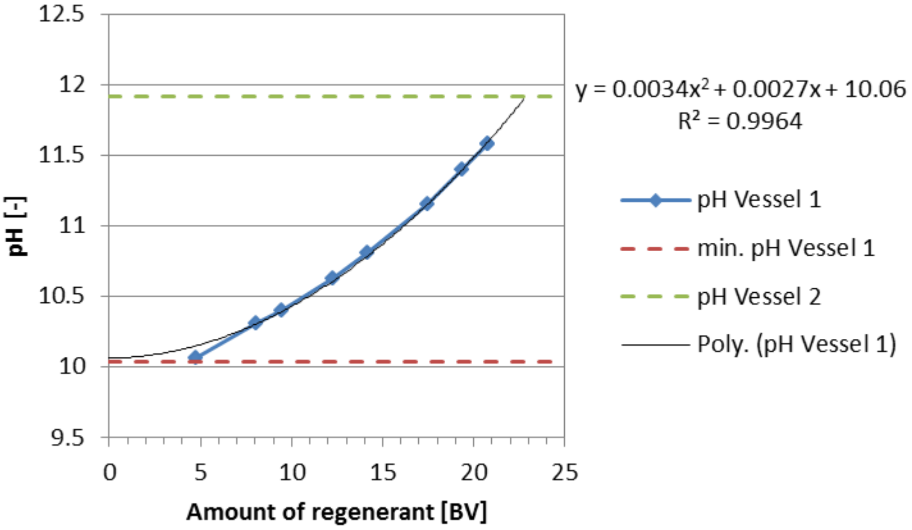


Figure 50: pH increase with the gradient mixer for the regeneration with R_{5-6} (pH from 10.04 to 11.92).

Two regenerations were performed with gradient increased pH. The first was with regenerant that had a pH level from 9.14 (concentrate with only 1% NaCl added) to 11.83. The second was with a regenerant that had a pH level from 10.04 to 11.92, and in that case also the flow velocity was increased to 7.07 m/h. During the first gradient regeneration was noticed that again precipitation was taking place in the bed. Noticed was that not one but two smaller lumps of resin were formed. When the result of this experiment is compared to the result of the regeneration with the increased pH is noticed that the capacity of the resin is higher. But with the first gradient regeneration more bed volumes of regenerant is used (25 against 21). When that is taken into consideration, the performance of both regenerations are almost the same. The intended result with the gradient increased pH is not achieved. The concentration of carbonate is still too high whereby precipitation and lump formation in the bed occur. With the second gradient regeneration the flow velocity in the bed was increased to get a fluidized bed. In that way is tried to prevent the precipitation in the bed. To have enough sodium present is determined that 21 bed volumes of regenerant were needed. With that determination is also taken into account that more bed volumes are needed because of the higher flow velocity (less contact time). Because of the higher flow velocity is expected that a lower concentration of hardness is released; therefore, the pH at the start of the regeneration is already elevated. During the regeneration the bed was constantly fluidized, and no lump formation was present. Only a front of calcium carbonate could be seen travelling through the bed. At the end of the regeneration the bed was completely white of formation of calcium carbonate on the resin.

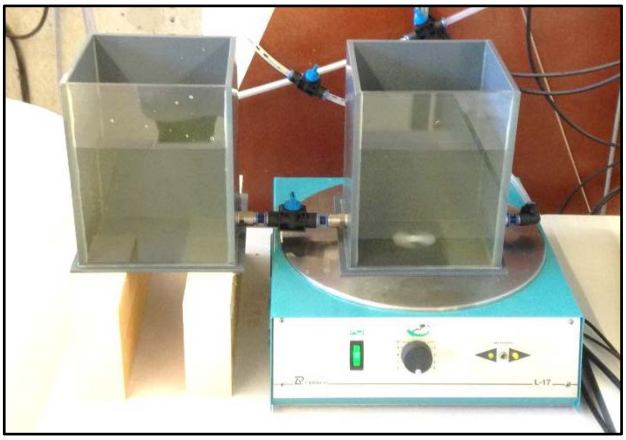


Figure 51: Gradient mixer.

After dosing of regenerant the bed was flushed according to the procedure of the regeneration. At normal flow velocity the precipitated calcium carbonate was not removed from the bed. To remove precipitation the flow velocity was increased to 13 m/h and much more bed volumes of flush water were used. The lumps that were formed did not break up at higher flow velocity; therefore, air and a combination of air and water was injected in the bed. With several injections it was possible to break up the lumps. With enough flush water also visible deposit on the resin was removed. Only with the last gradient regeneration it was not possible to remove any deposit from the resin. After both gradient regenerations the loading was performed with still calcium carbonate present in the bed. That was noticed by the formation of bubbles in the bed with the loading, than calcium carbonate dissolves in the lime aggressive water and CO_2 is formed. When the loading of the resin was finished, the bed expanded because of the CO_2 (Figure 52).

Known is that the deposit exists out of calcium carbonate or / and magnesium carbonate. To remove that from the filter plates hydrochloric acid was used before. That is also dosed to the column. The result was that all of the deposit was removed from the resin. That was noticed by the colour of the resin and also that carbon dioxide was escaping from the bed. A side effect was that the resin was not anymore in the sodium form but in the hydrogen form. To convert that caustic soda was dosed to the column. Then hydrogen is exchanged for sodium and is neutralized by OH^-. Also was noticed that with dosing of hydrochloric acid the colour of the bed was changing, it became very light. With dosing of caustic soda the colour of the resin was changed again to very dark brown. The colour of the bed depends on the pH. The colour of the resin goes from very light at a low pH to very dark at a high pH.


Figure 52: Gas formation in the bed during the loading of the resin.

The breakthrough curves of loading of the resin after regeneration with 10% NaCl are almost on top of the curve of the first run. When than is looked at the capacity of the resin can be noticed that the capacity is lower. That is explained by the fact that 5.5 and 6 bed volumes of 10% NaCl were used. According to Figure 42 a capacity of 1.72 / 1.77 eq/l is expected. The capacity of the resin is now above that value, so precipitation of calcium carbonate in the bed does not cause a permanent effect on the capacity of the resin.

From the results can be concluded that the addition of only 1% NaCl to the concentrate is to low to be used as a regenerant. With the pH increase to improve the efficiency of the amount of sodium that is used for the exchange of hardness from the resin several side effects occur. Deposit of calcium / magnesium carbonate occurs in the bed, which also causes lump formation. Also clogging of the filter plates occur. When it is not possible to remove all of the deposit from the bed it will dissolve again with loading of the resin. That is because of the fact that water that is used for loading is lime aggressive. The amount of hardness that can be loaded on the resin is then lower than the capacity of the resin. With each run an amount of the hardness that is removed from the bed is loaded again. The process is than not very efficient.

With these experiments is tried to control the formation of calcium carbonate with pH. That is proven to be very difficult. There is also another option to control the formation, namely to adjust release of calcium and magnesium from the resin. Than can be achieved by increasing the sodium concentration in gradient. At the start of the regeneration a low concentration of sodium is present and less hardness is exchanged from the resin. Then also less precipitation is formed even when an excess of carbonate is available.

The flow velocity in the bed is changing with the different runs. That is explained by the fact that resistance is increased in the column. The increase in resistance is caused by the formation of calcium carbonate during regeneration. The calcium carbonate causes two things, namely that pores of the filter plates were clogged. And also that when calcium carbonate is formed in the bed lumps of resin are formed.

6.4.2 RO concentrate with $CaCO_3$

With use of RO concentrate as a regenerant calcium carbonate is added. That is done with the consideration that when formation of calcium carbonate is occurring deposit is not taking place on the resin but on the calcium carbonate particles. Also pH of the regenerant is increased (R_{5-4}) in order to have a higher carbonate concentration to enhance the formation of calcium carbonate.

For this experiment also the columns need to be loaded before regeneration can be performed. With loading of the resin was also seen that the velocity was decreasing with the different runs. After inspection of the filter plates it became clear that clogging was occurring of the filter plates. The flow velocities during the different runs are given in the table below.

Table 22: Flow velocity in the bed during the loading of the resin for the four runs.

Run	**[-]**	**1**	**2**	**3**	**4**
Flow velocity	[m/h]	29.64	28.93	29.60	28.92

To compare the performance of the different variations in regenerant breakthrough curves of all runs are given in one figure. The different runs are:

- Run 1: loading after regeneration with R_1 (10%NaCl)
- Run 2: loading after regeneration with R_{5-2}
- Run 3: loading after regeneration with R_{5-4}
- Run 4: loading after regeneration with R_1

Breakthrough curves of these runs are given in Figure 53; also the reference curve is given. Results of the loadings and regeneration of each of these runs are given in appendix C.3. The amount of bed volumes used of each regenerant is given in the table below.

Table 23: Amount of regenerant used for each regeneration.

Regeneration	**[-]**	**1**	**2**	**3**
Regenerant	[-]	R_{5-2}	R_{5-4}	R_1
Amount	[BV]	33.4	20.8	8.5

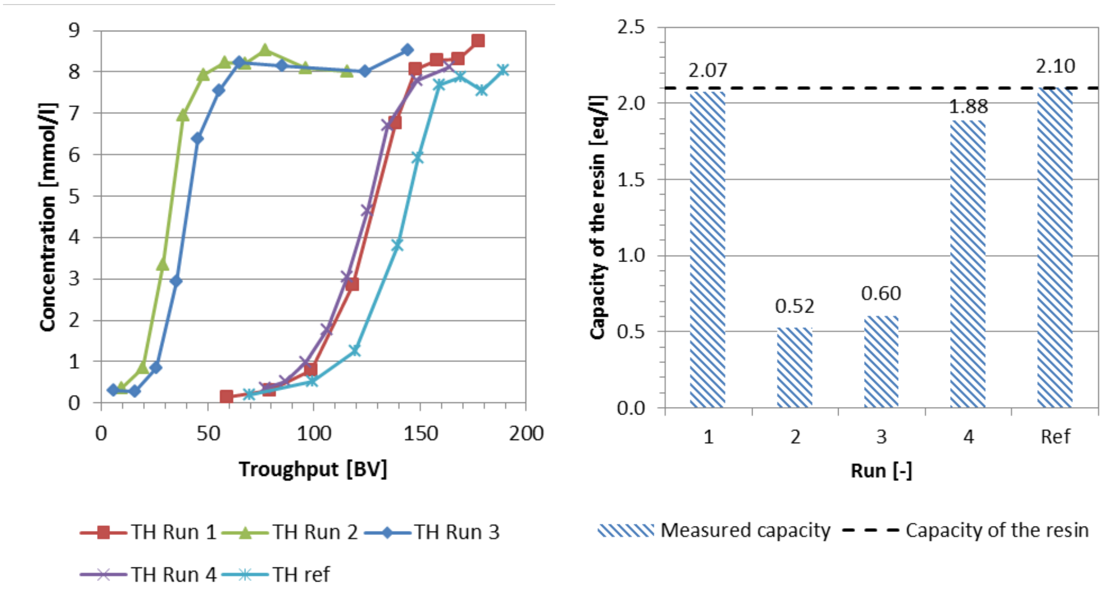


*Figure 53: **Left** Breakthrough curves of the 4 runs related to the regeneration with concentrate with $CaCO_3$ added. **Right** Capacity of the resin for each run.*

In the left figure can be seen that all of the breakthrough curves are to the left from the reference. That indicates that less amount could be loaded on the resin than according to Lanxess. Only when now is looked at the right figure it can be noticed that capacity of the resin with the first run is only 0.03 eq/l resin lower. That is because loading of the resin was performed with water with hardness of 8.46 mmol/l. The other loadings were done with tap water with total hardness of 8 mmol/l. When a closer look is taken at the breakthrough curve of run 1 it can be seen that the curve is a little bit higher, which is caused by the higher hardness.

With the application of concentrate with $CaCO_3$ (R_{5-2}) added as a regenerant was noticed at the start of the regeneration that indeed a white cloud of particles was formed above the bed. That was the calcium carbonate that was added to the concentrate with calcium carbonate from the resin. Only directly was noticed that the solution coming from the bed contained fewer particles than the regenerant that was pumped into the setup. So particles were staying in the bed. After some time the number of particles present above the bed was decreasing. It could be seen that deposit on the resin was taking place, the resin was turning white. Lump formation occurred, due to deposit. As a result of the lump formation short circuit flow was occurring in the bed. That a part of the calcium carbonate particles that were added to the concentrate were not leaving the bed could be seen with displacement with demi water. In this case also air injection was needed to remove particles and deposit form the bed. During the injection with air was noticed that a large amount of calcium carbonate was present in the bed, see Figure 55.

Figure 55: Suspended calcium carbonate during the displacement with demi water.

The second regeneration was also done with concentrate with $CaCO_3$ added, but now pH was increased to 11.9 (R_{5-4}). In that case more carbonate is present in the water and therefore more precipitation is expected. Now also a white cloud of calcium carbonate particles was leaving the bed. But when compared to regeneration with no pH increase the cloud had a lower density, it was less white. In the bed more deposition was taking place, and more particles stayed in the bed. Also more calcium carbonate was formed, which can be concluded from Figure 54. The pH drop is larger with the regenerant with increased pH, more carbonate is converted in calcium carbonate which cause the drop in pH. More significant is to conclude that more calcium carbonate is formed in the first part of the regeneration than in the last. That was also noticed during the experiment. With the other regenerant (R_{5-2}) the drop in pH is lower and also the value is not increasing towards the pH of the regenerant as with R_{5-4}. That indicates that with no pH increase, calcium carbonate is formed almost evenly spread over the entire regeneration. In the beginning a little bit more calcium carbonate is formed which causes the pH to drop a little bit more. When regenerations are compared can be seen that in spite of extra formation of calcium carbonate the regenerant with increased pH is performing better. Difference between the operating capacities that is reached after the regenerations is small, but also has to be

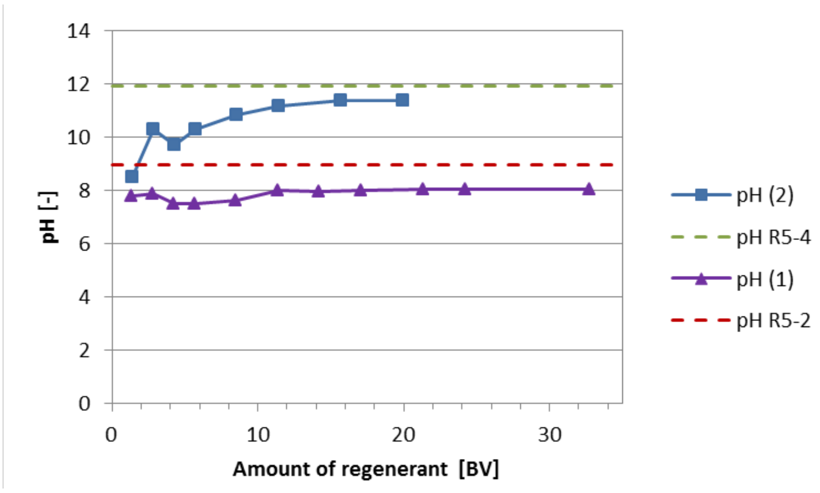


Figure 54: pH during the regeneration with R_{5-2} and R_{5-4}.

taken into account that in the case of the use of regenerant with a higher pH also less bed volumes are used. In that case 20.8 bed volumes are used instead of 33.4 BV. But still both regenerants are performing very badly; capacity of the resin is only 0.52 / 0.60 eq/l after regeneration.

After regeneration with both regenerants with calcium carbonate, regeneration was performed with 8.5 bed volumes of 10% NaCl. According to Figure 42 than an operating capacity of 1.95 eq/l resin is expected. In Figure 53 right can be seen that the measured capacity of the resin after regeneration with 10% NaCl (4) was 1.88 eq/l resin. That is less than expected, but the capacity is only decreased with 2.1%. A part of the difference between the values can be explained by the fact that an error is made with the determination of the total hardness with the cell test. Another explanation is that the some of the resin can be damaged after the regeneration. Less exchange or no exchange of ions can take place on a damaged resin. Then a lower capacity is measured.

6.4.3 RO concentrate with 10 % NaCl

For this regeneration also RO concentrate is used only now with a sodium chloride concentration of 10% NaCl. As was valid for the previous regeneration now still is, before the regeneration can be performed the resin has to be loaded first. To see if the regeneration with this regenerant is possible the first regeneration is conducted with 24.5 bed volumes of concentrate with 10% NaCl at a flow of 4.19 m/h. In the figure below the loadings before and after the regeneration are given with the reference.

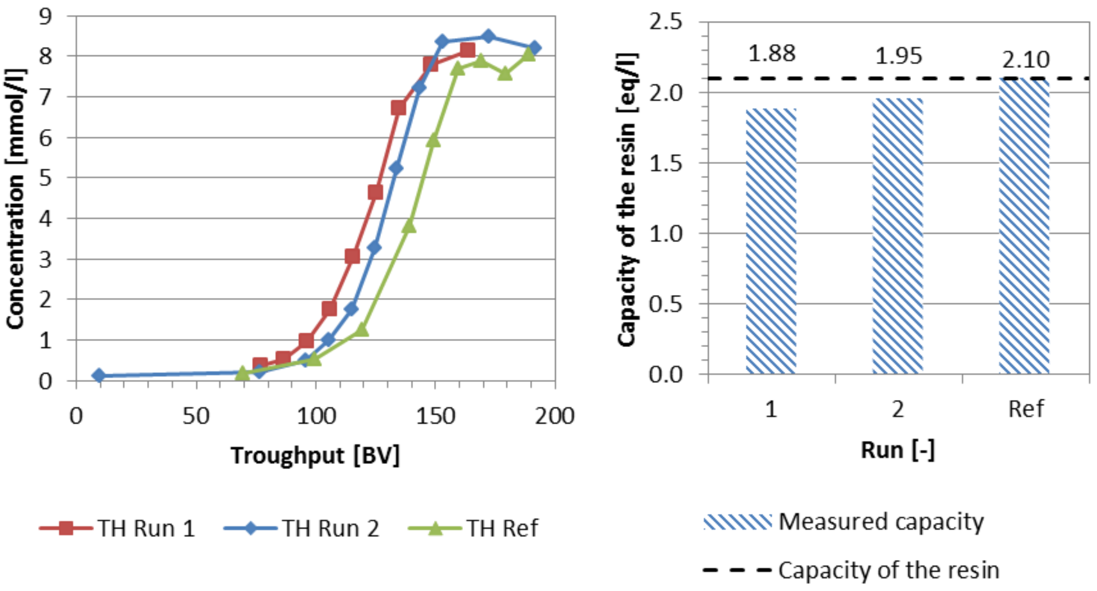


*Figure 56: **Left** Breakthrough of the loadings before and after the regeneration of column 3 with a TH of 8 mmol/l. **Right** Capacity of the resin for each run.*

The first loading was conducted at a velocity of 28.92 m/h, because of a slight increase in resistance the second loading was performed at a velocity of 28.71 m/h. In the right figure can be seen that the capacity of resin before the regeneration was 1.88 eq/l. According to Figure 42 an operating capacity is expected of 2.16 eq/l with the use of 24.5 bed volumes of 10% NaCl as a regenerant. After the regeneration an operating capacity was measured of 1.95 eq/l, which is less than expected.

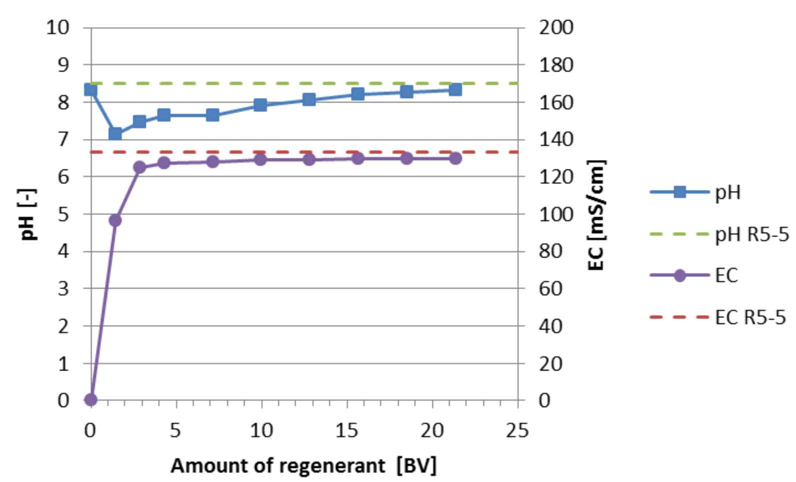


Figure 57: pH and conductivity during the regeneration.

Figure 58: Deposit formation in the top of the bed.

In Figure 57 can be seen that the pH of the effluent of the column first is decreasing and then increases to the pH of the regenerant. This process is already seen before and is an indication for the formation of calcium carbonate. During the regeneration was seen that in the top layer of the bed deposition was taking place. With the displacement all of the visual deposit was flushed away. The lower capacity can be explained by the fact that the resin is deteriorated, and less resin is available for exchange. Another option is that still some calcium carbonate is present in the bed. The resin is loaded with water that is lime aggressive and causes that the calcium carbonate dissolves again. That calcium is than loaded on the resin and results in a lower operating capacity. An indication for this process is that carbon dioxide is leaving the bed. During the loading after the regeneration some bubbles were seen, but not much.

To determine if the regenerant does not have a permanent side effect on the resin 5 runs were performed. With these runs can be seen if the deposition of the calcium carbonate does not cause a decrease in operating capacity with each run. All of the regenerations were conducted at a flow of 3.77 m/h, which is the same flow as used at DWPB. During the loading of the resin was noticed that the flow slightly decreased at some runs. Therefore after loading 3 the filter plates at the top of the column were cleaned. That can be seen from the values in the table below; at loading 4 the flow was higher than before.

Table 24: Flow velocity in the bed during the loading of the resin for the six runs.

Run	**[-]**	**1**	**2**	**3**	**4**	**5**	**6**
Flow velocity	[m/h]	29.55	29.77	29.44	30.61	29.57	29.05

In the figure below all of the breakthrough curves of the six loadings are given.

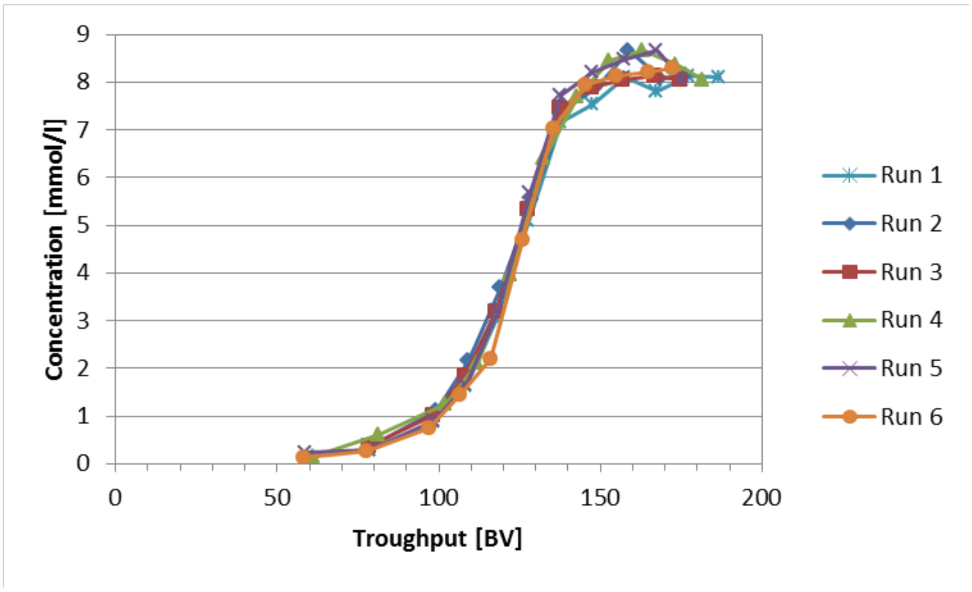


Figure 59: Breakthrough curve for 6 sequential runs.

In the figure can be seen that the curves are almost on top of each other. So can be concluded that the regeneration with 10 BV of concentrate with 10% NaCl is performing well. With the data form the figure and from the analysed mixed samples can be determined what the operating capacity of the resin is after each regeneration. The results of that calculation are presented in Figure 60.

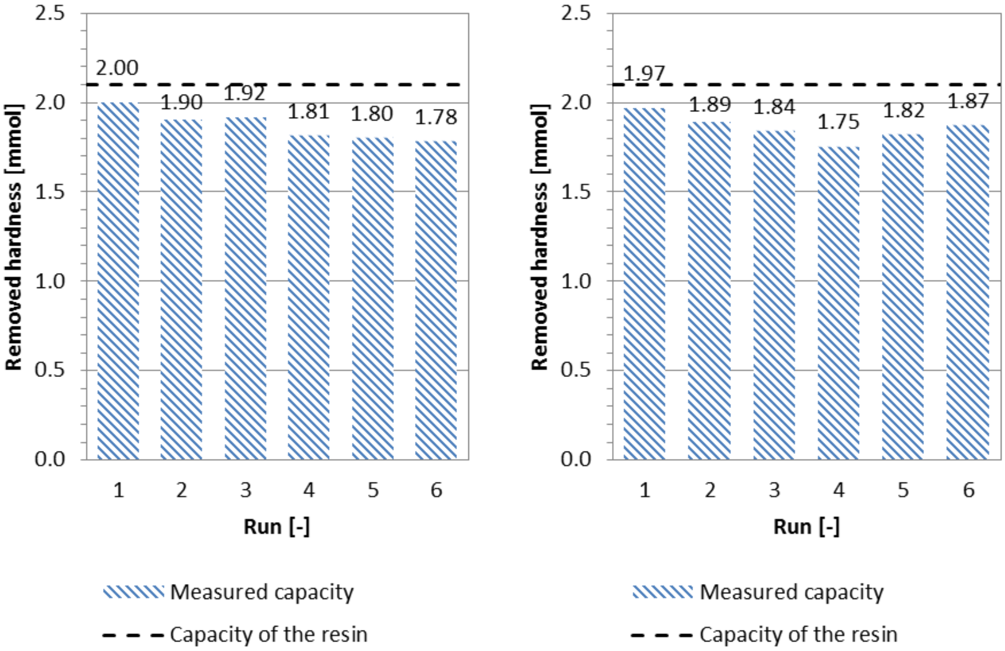


Figure 60: Removed hardness from the resin for 6 runs based on the measured values of the mixed samples (Left) and the trapezoid rule (Right).

There is some difference between values of the calculation with the trapezoid rule and values from the mixed sample. That can be explained by the fact that with both methods, measurement errors are made and the results can get higher or lower. The difference between the results of both methods is 0.09 eq/l, which is acceptable.

While performing these runs no visible deposit was noticed anymore, but during loading still some bubbles escaped from the bed. Since the system was watertight the only explanation for the bubbles is that calcium carbonate is dissolving in the bed. As a consequence of that reaction carbon dioxide is released. From both graphs can be concluded that in the first three runs, the operating capacity is decreasing and then goes to equilibrium.

In practice the resin is not completely loaded and regenerated, so more data is needed to determine the amount of bed volumes of regenerant for a lower operating capacity. For that purpose 5 additional regenerations were done. The column was regenerated with 8, 6, 4, 2 and bed volume(s) of regenerant; also data from the last run with 10 bed volumes were used. With the retrieved data a graph is made in which can be seen what amount of bed volume is needed to reach a certain operating capacity.

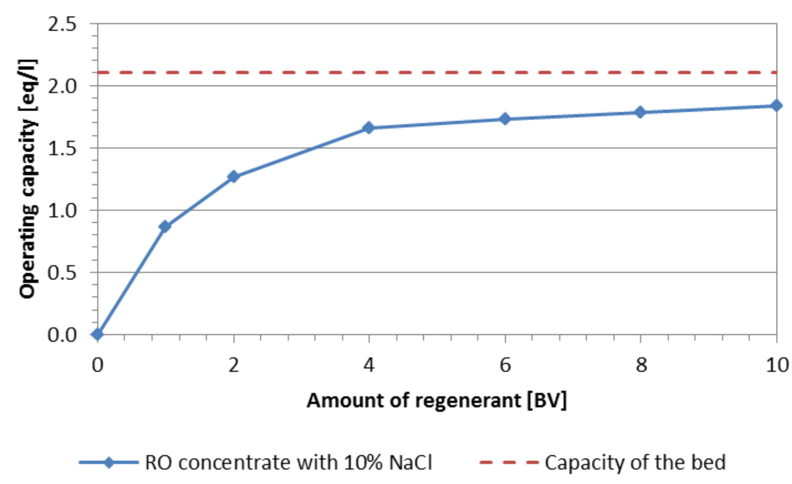


Figure 61: Capacity of the resin for different amount of regenerant ($R_{5\text{-}5}$)

A remark with this graph is that it is only valid with RO concentrate with 10% NaCl at a flow of 3.77 m/h. Also needs to be realized that this graph is determined with data from a small scale experimental setup. The parameters are not all the same as in a full scale installation. Therefore this graph can be used as an indication, but still more research should be done to validate the data.

6.5 Discussion of results of the experiments

6.5.1 Regeneration with 10 % NaCl

The figure below is constructed with data retrieved from experimental research with 10% NaCl as regenerant. In the presented figure, the value is given of regeneration of the softener at DWPB according to the manual of Lanxess, 0.82 BV is used to obtain an operating capacity of 0.95 eq/l. With use of 10% NaCl different flow velocities were present in the bed. The flow is basically kept the same as at DWPB, with 1 run the velocity was decreased to see what effect that has on capacity of the resin. The other flow velocities are explained by the fact that they were conducted after use of other regenerants, which were dosed at a higher flow velocity. In the figure it can be seen that the experimental setup has a lower operating capacity with use of 0.82 bed volume of regenerant than at DWPB or that more bed volumes are needed to reach the same operating capacity. Furthermore, also that at DWPB 9% NaCl is used and in the setup 10% NaCl, so expected was that the setup would perform better. Based on these data however it can be concluded that the experimental setup is performing worse with regeneration than the softener at DWPB. Given the information from chapter 3 it can be concluded that this is due to the effect of use of a small bed height.

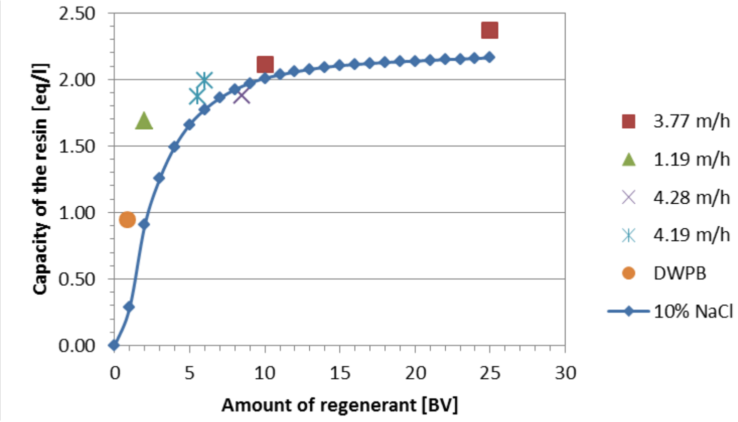


Figure 62: Results of the regenerations with 10% NaCl.

Optimization of the flow velocity was not a part of the scope of the research, but from the figure can be concluded that the flow velocity is important in regeneration of an ion exchanger. With a lower flow velocity and same amount of regenerant a higher operating capacity is reached.

During regeneration a peak of hardness is released form the resin, in order to measure that peak exactly the moment on which a sample is taken has to be determined. While performing the experiments this proved to be difficult, but in most cases realizable as can be seen from the data when it is compared with results of the mixed sample. So in order to have a good determination mixed samples are better to use, but to understand the process that is happening during regeneration an elution curve tells much more than only values of the analysis of mixed samples. Therefore it can be concluded that to understand the process of regeneration both techniques have to be used. Elution curve to understand the process, and mixed sample to check the results of the elution curve.

6.5.2 Water from the Brittanniё harbour as a regenerant

Ultimate goal was to regenerate resin with water from the Brittanniё harbour. To understand effect of other ions in water from the harbour first 3.45% NaCl and artificial seawater were used as regenerants. Regeneration with 3.45% was performed at the same flow velocity as at DWPB, 3.77 m/h. From Figure 42, a comparison of the different regenerants for amount of bed volumes used, can be concluded that with use of 3.45% NaCl as regenerant more bed volumes are needed to reach the same operating capacity as with 10% NaCl. Bed volumes are important for the amount of water needed and also the time needed for regeneration. But also important to compare is the amount of salt needed for regeneration. In the figure below can be seen that with use of 3.45% NaCl less salt per litre resin is used to reach the same operating capacity as with use of 10% NaCl.

A reduction of 16.4% is possible on the amount of salt needed for regeneration. Only in that case more water is used and also more time is needed for regeneration. Therefore can be concluded that reduction of the amount of salt is only possible when enough time and water is available for regeneration.

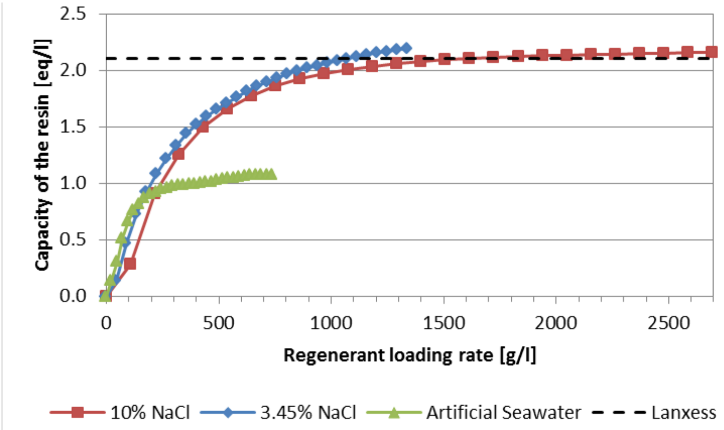


Figure 63: Capacity of the resin for the regenerant loading rate with 10% NaCl, 3.45% NaCl and Artificial seawater.

From results of regeneration with artificial seawater and analysis of water from the Brittanniё harbour can be concluded that it is not possible to use water from the Brittanniё harbour as regenerant. In artificial seawater and water from the Brittanniё harbour calcium and magnesium are present. The magnesium concentration is high (almost 30 mmol/l) in both waters which causes that during regeneration no magnesium is removed from the resin. In fact magnesium is exchanged for calcium. With regeneration with artificial seawater was seen that until the dosage of 5 BV of regenerant, no magnesium was loaded on the resin. With 5 BV an operating capacity of 0.77 eq/l can be reached. Evides aims with regeneration of their softeners at 0.95 eq/l, so more regenerations are needed. More important is to conclude that with regeneration with a regenerant containing calcium and magnesium the layer at the bottom of the vessel is loaded as well. So after regeneration leakage can be expected and no safety is present anymore. When breakthrough of the bed is taking place, concentration of calcium and magnesium ions will be much higher.

6.5.3 RO concentrate as a regenerant

With use of RO concentrate as a regenerant also different variants were applied in the experimental research. A division is made in three different types: RO concentrate with addition of 1% NaCl, RO concentrate with addition of $CaCO_3$ and RO concentrate with 10% NaCl. Within these types variations in parameters as pH and flow velocity were applied. In both graphs all results of the experiments are presented. Distinction is made in shape of the marker for the three different types; within the types the filling is different for the variants. In Table 25 a description is given of the different variants.

Table 25: Description of the different regenerants.

Regenerant	Variant	Description
RO concentrate + 1% NaCl	R_{5-1}	Concentrate with 1% NaCl added
	R_{5-3}	Concentrate with 1% NaCl added and increased pH
	R_{5-6}	Concentrate with 1% NaCl added and gradient increased pH
RO concentrate + $CaCO_3$	R_{5-2}	Concentrate with $CaCO_3$
	R_{5-4}	Concentrate with $CaCO_3$ and increased pH
RO concentrate with 10% NaCl	R_{5-5}	Concentrate with 10% NaCl
DWPB		9% NaCl, used at DWPB

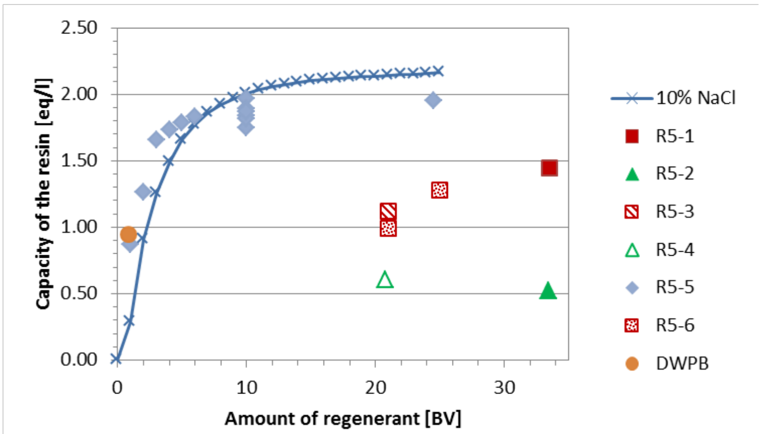


Figure 64: Results of the experiments with variants of RO concentrate as regenerant with regard to the amount of regenerant.

From the presented figure it can be concluded that the only regenerant that is suitable to be used as regenerant is concentrate with 10% NaCl. In that case the operating capacity is in the vicinity of the line of 10% NaCl. The other regenerants give with a larger amount of bed volumes a lower operating capacity, so more water is used in these cases. Lower operating capacity is caused by a lower sodium concentration and formation of calcium carbonate. Based on stoichiometry 30.7 bed volumes of R_{5-1} should be needed to get an operating capacity of 1.45 eq/l. So lower sodium concentration causes that more bed volumes of regenerant are needed to reach the same operating capacity. In fact 33.5 bed volumes of R_{5-1} are used, more than calculated. That is caused by the formation of calcium carbonate. On resin and in the bed deposition is taking place, but also lump formation is occurring. Due to these processes there is no contact between regenerant and resin. It causes that the resin is not regenerated resulting in a lower operating capacity.

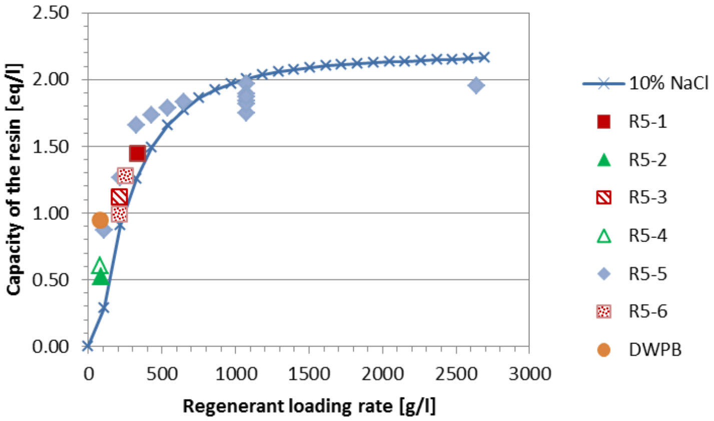


Figure 65: Results of the experiments with variants of RO concentrate as regenerant with regard to the regenerant loading rate.

From both graphs can be concluded that use of a higher velocity combined with concentrate with 10% NaCl added as regenerant is performing worse than at the lower velocity as used at DWPB.

From Figure 65 it can be concluded that with regard to the regenerant loading rate all the regenerants are performing well, all the results are on almost on the line or to the left. So with less salt a higher operating capacity is reached. Therefore, it can be concluded that the amount bed volumes of regenerant used in these situations play a decisive role. Also important in this case is the effect of the regenerant on the resin. In all of the experiments besides the ones with $R_{5\text{-}5}$ severe calcium carbonate formation occurred. That led to deposition and lump formation, which in almost all of the cases could be removed with flush water and air injection. The side effect was that much more flush water was needed. But also after inspection of the pipes of the setup was noticed that precipitation occurred in the system. That are effects that are not desirable in a full scale installation, therefore can be concluded that these regenerants are not suited for regeneration of softeners at DWPB.

6.5.4 Comparison

In this paragraph results of the experiments with 10% NaCl, 3.45% NaCl, artificial seawater and concentrate with 10% NaCl are compared. From the graph below it can be concluded that with regard to the amount of regenerants used concentrate with 10% NaCl is performing the best. After dosing of 5 bed volumes of concentrate with 10% NaCl the operating capacity is becoming lower than with dosing of the same amount of softened water with 10% NaCl. Now can be concluded that until a dosing of 5 bed volumes of regenerant, RO concentrate is the best regenerant to use with regard to the amount of bed volumes used. After 5 bed volumes the regenerant of softened water with 10% NaCl is performing better.

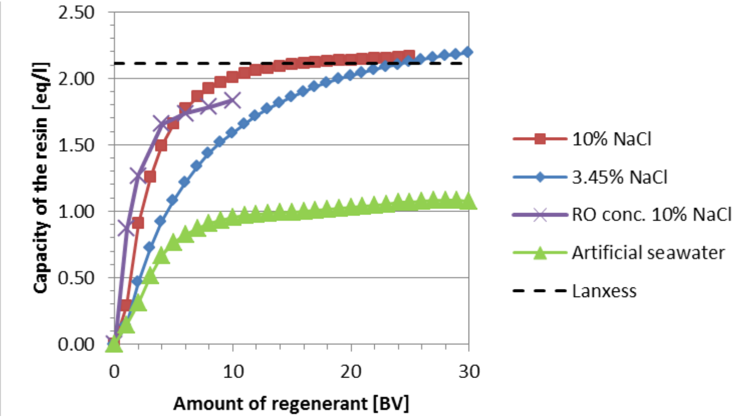


Figure 66: Capacity of the resin for the amount of regenerant with 10% NaCl, 3.45% NaCl, artificial seawater and RO concentrate with 10% NaCl.

Also a comparison can be made based on the amount of salt that is used with regeneration. In the figure to the right the operating capacity is given with regard to the regenerant loading rate for the different regenerants. From that graph it can be concluded that concentrate with 10% NaCl is also performing the best with regard to the regenerant loading rate until 540 g/l. After

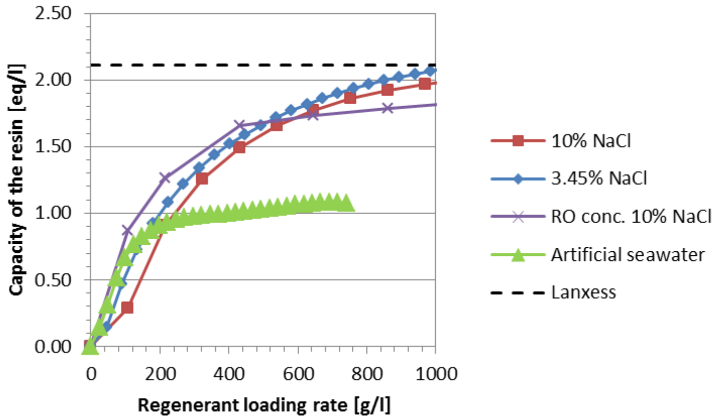


Figure 67: Capacity of the resin for the regenerant loading rate with 10% NaCl, 3.45% NaCl, artificial seawater and RO concentrate with 10% NaCl.

540 g/l softened water with 3.45% NaCl is performing the best. Also can be concluded that artificial seawater despite disadvantages is performing well to achieve low operating capacities with regard to the amount of salt used per litre of resin.
Taken into consideration that Evides does not completely load and regenerate the softeners a more specific conclusion can be given. Evides wants to achieve an operating capacity of 0.95 eq/l. Given that operating capacity and both figures can be concluded that concentrate with 10% NaCl added as regenerant the less amount of bed volumes are needed and that also the less amount of salt is used per litre of resin. In fact even more salt is saved because in the figure the total amount of salt that is present in the regenerant is used, not the total added amount of salt.

7 Design

With results of chapter 6 a design with different variants are made which can be applied to the plant of DWPB. The different variants are:

- Variant 1: Production of regenerant with RO concentrate.
- Variant 2: Concentration of RO concentrate.

The designs are elaborated in the paragraphs of this chapter.

In chapter 2 is shown that for regeneration with 9% NaCl a total of 111 m^3 of softened water is needed. That amount is divided into two parts, an amount needed as flush water and an amount needed for production of regenerant.
For the design is taken that 93 m^3 of flush water is needed for 1 regeneration. Evides wants to reach an operating capacity of 0.95 eq/l resin after regeneration of the resin. With Figure 61 is determined that 1.2 BV of RO concentrate with 10% NaCl is needed. One bed volume at DWPB is 21.9 m^3, so a total of 26.3 m^3 of regenerant is used. For one regeneration a total of 119.3 m^3 of RO concentrate is needed. In chapter 2 is already determined that at maximum production of the softeners, 12 regenerations will take place in 1 day.
With concentrate as flush water and regenerant no longer any softened water is used. That amount could be used for production of extra demi water, but production of the RO unit is already at maximum capacity. Therefore is chosen to lower the production of softened water. In the current situation of DWPB 7 softeners are in production. Flow is lowered from 325 m^3/h to 269.5 m^3/h. Runtime of a softener becomes longer and less regenerations are needed, 10 regenerations per day. So the total number of regenerations per day decreases with two. With that decrease 3470 kg of sodium chloride is saved with a value of € 3.47. In total over one day the production is lowered with 1332 m^3, which gives a benefit of € 133.20. The values are summarized in the table below.

Table 26: Savings from no longer using softened water.

	Total amount [per day]	**Savings [€/day]**
Softened water	1332 m^3	133.20
NaCl	3470 kg	347.00
Total		**480.20**

Total amount of flush water and regenerant needed for 1 regeneration is still the same, but the flow is less because of decrease in regenerations per day. In the table below values used with the design are summarized.

Table 27: RO concentrate needed for regeneration.

	Total amount* [m^3]	**Flow [m^3/h]**
Flush water	93	38.75
Regenerant	26.3	10.96
Total	**119.3**	**49.71**

*Needed for regeneration of one softener.

7.1 Production of regenerant with RO concentrate

From results of the previous chapter can be concluded that RO concentrate with extra sodium chloride added can be used as a regenerant. For this solution a design of the process is made. In the process scheme is given which steps are needed to use RO concentrate as flush water and to produce regenerant with RO concentrate. Difference with the current process at DWPB is that now RO concentrate is used for regeneration instead of softened water. Brine (26%) is made with the RO concentrate and NaCl and is diluted in a static mixer with RO concentrate to create a 10% NaCl solution. No softened water is used anymore, and less water is discharged on the harbour. The process scheme of the design is given in the figure below.

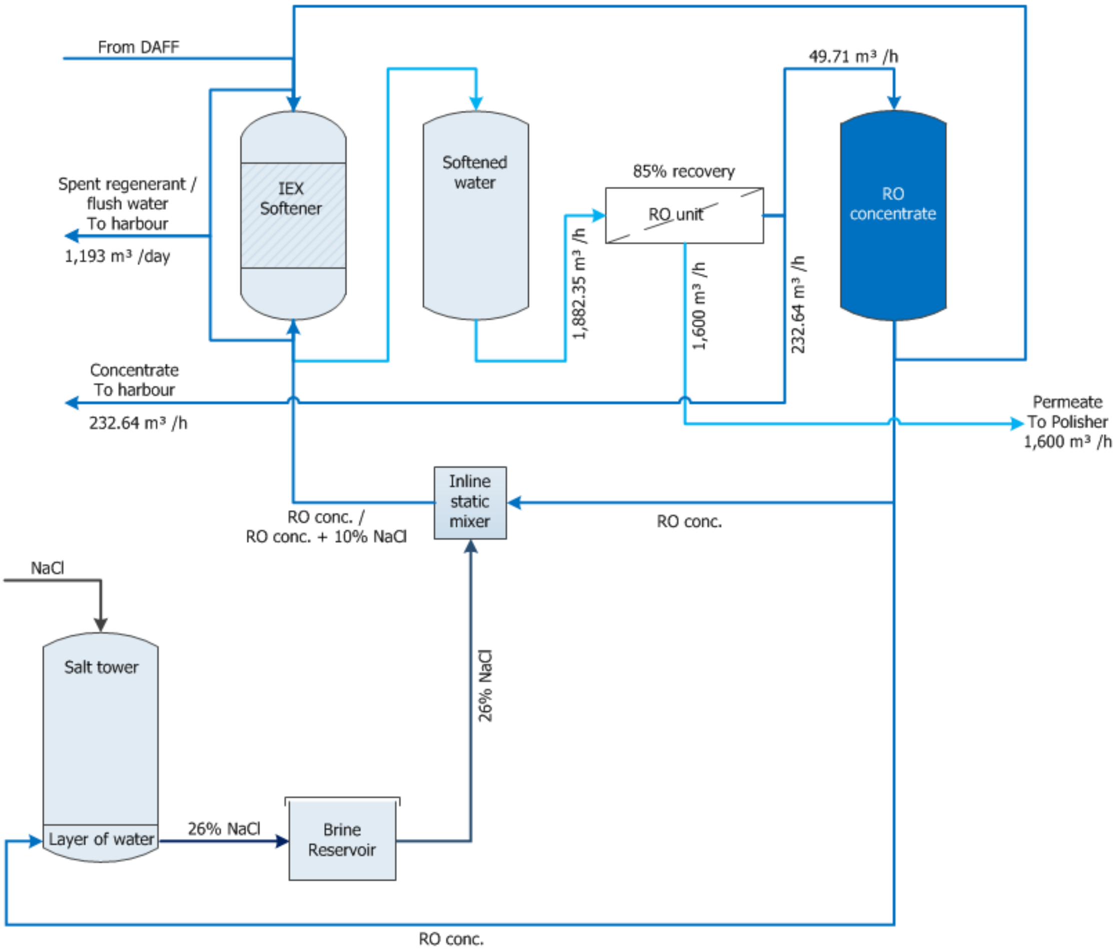


Figure 68: Process scheme of design 1.

In the process scheme can be seen that no significant changes are necessary. Only one storage vessel is needed to store RO concentrate for regeneration. The part of the concentrate that is not needed is still discharged into the harbour. Also some pipes need to be rearranged, or new pipes need to be added. In this design pipes that are going from the storage tank of softened water towards the softeners and the production unit of regenerant are not needed anymore. These pipes can stay in the process as a backup when RO concentrate cannot be used. In that case new pipes have to be installed to transport RO concentrate. If is decided that a backup of softened water is not needed, pipes can be rearranged to the storage tank of RO concentrate. Because now instead of softened water RO concentrate is used for regeneration less softened water is needed. So production of the softened water can be lowered, which also causes that run times of the softeners increase and less regenerations are needed. Another benefit of use of concentrate is that according to the analysis sodium is present, so less sodium chloride is dosed.

From this design also can be determined what the costs of discharge are and what is saved with a lower production of softened water. Also the amount of water and sodium chloride that is needed can be calculated.
The amount of RO concentrate that is used for the flush of the resin is 93 m^3 for 1 regeneration. To produce the regenerant two different streams of concentrate are needed, one for production of brine and on for dilution of brine. From analysis of the RO concentrate is known that it contains 42.5 mmol/l of sodium. So RO concentrate has a salt concentration of 0.25% NaCl. With production of brine a natural equilibrium is created of 26% NaCl. That equilibrium does not change with use of another type of water. Therefore with use of RO concentrate the amount of salt that is needed is reduced with almost 1%. The produced brine is diluted in a static mixer with RO concentrate to create the desired 10% NaCl solution.

Because of the fact that concentrate is used with 0.25% NaCl more saving of sodium chloride takes place with dilution of brine.

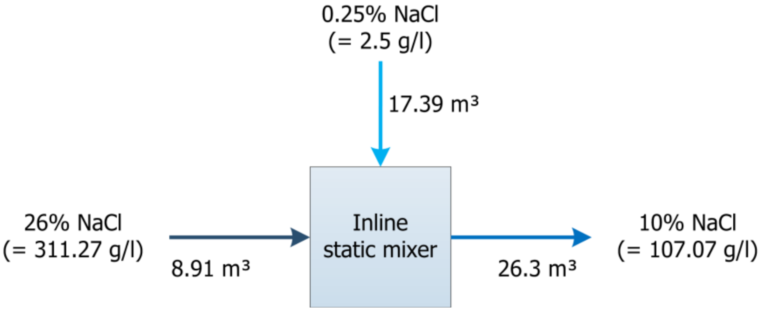


Figure 69: Representation of different streams of the static mixer.

With the figure and knowledge that brine is produced with concentrate can be deducted that for 1 regeneration, a total of 2751.1 kg of NaCl is needed to produce 1.2 BV of regenerant. In the table below the amount sodium chloride needed for 1 day is given with the costs.

Table 28: Cost and amount of salt needed for regeneration.

	Total amount [kg]	**Total amount [kg/day]**	**Costs [€/day]**
NaCl	2751.1	27511	2751.10

In the table below values are summarized related to discharge into the Brittanniё harbour.

Table 29: Cost and amounts for discharge into the Brittanniё harbour.

	Total amount [m^3/day]	**Costs [€/day]**
RO concentrate	5583.4	41.87
Spent regenerant	263	1.97
Flush water	930	6.98
Total	**6876**	**50.82**

So on an annual basis € 18,549.30 has to be paid for discharge into the Brittanniё harbour.

With kostencalculator from RHDHV is calculated what the investment costs are to build the storage tank for RO concentrate. The volume of the storage tank is based on knowledge that for 1 regeneration 119.3 m^3 of concentrate is needed. For calculation of the cost is calculated with a gross volume of 149.13 m^3. Total investment costs for the storage tank are € 87,460.

7.2 Concentration of the RO concentrate

With the previous design still a lot of water is discharged into the harbour, namely 232.64 m^3/h. In this design an extra RO unit is added to concentrate the concentrate of the existing RO unit to lower discharge into the harbour. With addition of an extra RO unit more permeate is produced. When with design of the unit attention is paid to the quality of the permeate it can be used to produce more demi water. Within the design two different variants are developed. In the first variant concentrate that is produced with the second RO unit is discharged into harbour. So with that design only reduction of discharge on the harbour takes place. In the second variant a part of the concentrate of the second RO unit is used for regeneration, the other part is discharged into the harbour. Within that design can be chosen if extra sodium chloride is added to the concentrate or not.

7.2.1 Production of regenerant with RO concentrate from unit 1

In this design RO concentrate is fed to the second RO unit. Permeate is transported to the polishers, and concentrate is discharged into the harbour. The regeneration in this design is exactly the same as at the design in chapter 7.1. The process scheme is given in the figure below.

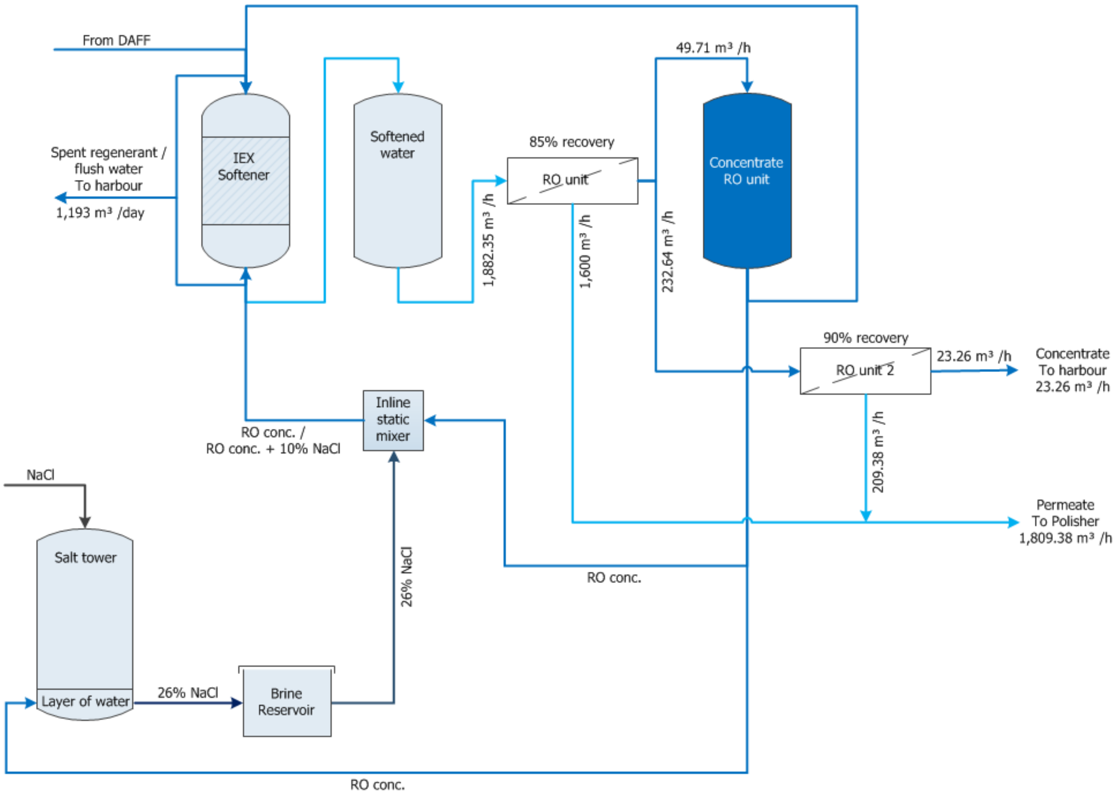


Figure 70: Process scheme of design 2a: concentrating the concentrate.

Values from Table 28 are also valid for this design. For the added RO unit a design is made. Because feed water to the RO unit already contains sodium and a recovery of 90% wants to be reached is chosen for seawater membranes. These types of membranes have a higher salt rejection. Membranes that are chosen are SW30XHR-440i (salt rejection of 99.82%) from DOW. With ROSA a simulation is made to determine the amount of membranes that are needed and in which configuration. Results of the simulation are in appendix D.1 Production of regenerant with RO concentrate from unit 1. For the feed water data, the analysis of RO concentrate is used. With ROSA is determined that 3 stages are needed for a recovery of 90%. In the first stage 16 pressure vessels (PV) are applied, in the second stage 8 PV and the third stage 3 PV. Each pressure vessel contains 7 membrane elements. So in total 189 membrane elements are applied in the RO unit.

Between stage 1 and 2 a booster pump is added to increase the pressure with 5 bar. That is also done between stage 2 and 3, only then the pressure is increased with 12 bar. Total power needed for the unit is 493.88 kW.

Table 30: Concentrations in feed, concentrate and permeate of the second RO.

	Feed [mg/l]	**Concentrate [mg/l]**	**Permeate [mg/l]**
Na	977	9759.43	1.98
Mg	0.24	2.40	0.00
Ca	1.25	12.51	0.00
CO_3^{2-}	100.32	1100.03	0.00
HCO_3^-	1034.58	10144.06	2.97
SiO_2	30.05	299.85	0.10
TDS	**3058.21**	**30685.10**	**7.68**

In the feed also silica (SiO_2) is present. When concentration becomes too high scaling can occur on membranes. Silica scaling is an irreversible process; it cannot be removed from membranes. From results of the simulation can be deducted that silica concentration reaches a level of 299.85 mg/l SiO_2 in the concentrate. In RO units it is possible to go up to 150 mg/l SiO_2 (Bremere et all, 2000 and Gill, 1992). With dosing of antiscalants it is even possible to go to concentrations of 300 mg/l SiO_2 (Freeman et all, 1995 and Darton, 1999). So this design is possible with dosing of antiscalants. According to Haidari 2011 it is also possible that in absence of antiscalants and divalent ions a silica concentration of about 280 mg/l in the concentrate can be reached without declining of mass transfer through membranes. With previous known can be concluded that dosing of antiscalants is only necessary at the third stage. In that case only to a flow of 22.32 m^3/h antiscalants need to be added.

In the table above also concentration in the permeate is presented. Total hardness is 0 mmol/l, which is below the value that Evides desires (0.04 mmol/l). Only silicate concentration is higher; Evides desires a concentration of 0.064 mg/l SiO_2 at the customer. The values are determined with a simulation, the order of magnitude is correct. For more accurate values a measurement should be conducted.

Table 31: Flow regarding both RO units.

	Unit	**RO unit 1**	**RO unit 2**
Feed	[m^3/h]	1882.35	232.64
Concentrate	[m^3/h]	282.35	23.26
Permeate	[m^3/h]	1600	209.38
Recovery	[%]	85	90
Overall Recovery	[%]	99	

The amount of water that is discharged into the harbour is decreased, instead of the 232.64 m^3/h now 23.26 m^3/h is discharged. In the table below the total amount that is discharged into the harbour is given with the costs.

Table 32: Cost and amounts of discharge into the Brittanniё harbour.

	Total amount [m^3/day]	**Costs [€/day]**
RO concentrate	558.24	4.18
Spent regenerant	263	1.97
Flush water	930	6.98
Total	**1751.28**	**13.13**

So on an annual basis € 4,792.45 has to be paid for discharge into the Brittanniё harbour.

Parts of the design that have to be build are the storage tank and the second RO unit. Volume of the storage tank is the same as with the previous design, 149.13 m^3. With kostencalculator from RHDHV is calculated what the investment costs are. For the second RO unit also exploitation costs are determined. The costs are presented in the table below.

Table 33: Investment and exploitation costs for design 2a.

	Investment costs	**Exploitation costs**	
	[€]	**[€/year]**	**[€/m^3]**
Storage tank	87,460	-	-
Second RO unit	4,294,859	964,485	59.16
Total	**4,382,319**	**946,485**	**59.16**

With the exploitation cost is taken into account that membranes will break down, and are replaced. The following is also taken into account with calculating of the costs with kostencalculator:

- Membranes
- Pressure vessels, regulating equipment included
- Pipes and fittings
- Pumps and candle filters
- Cleaning facilities (backwash pump, buffer etc.)
- Building volume
- Energy facilities
- General facilities (lighting, heating, cooling, ventilation)

Not included in the calculation is:

- Pre- and after treatment
- Treatment of the concentrate, discharge or injection in the ground

In this case pretreatment is not necessary, concentrate from the first RO unit can directly be fed to the second RO unit. After treatment of the permeate could be needed with the use of the existing polisher. That can result in decrease of runtime and increase in use of chemicals needed for the regeneration of the polisher, costs that are involved are not taken into account. The costs for discharge of concentrate are calculated separately.

7.2.2 Production of regenerant with RO concentrate from unit 2

In the previous design RO concentrate from the second RO unit was discharged into the harbour. In this design that concentrate is applied as a regenerant. With the design also a possibility to dose sodium chloride is taken into account. Difference between the two designs is that now an extra storage vessel is needed for the amount of water that is used for production of regenerant. Also pipes need to be rearranged or to be installed to transport concentrate from the second storage vessel to the static mixer and production unit of brine. Process of the regeneration is still the same as at design 1 in chapter 7.1. Values from Table 28 are also valid for this design. In the figure below the process scheme of the design is presented.

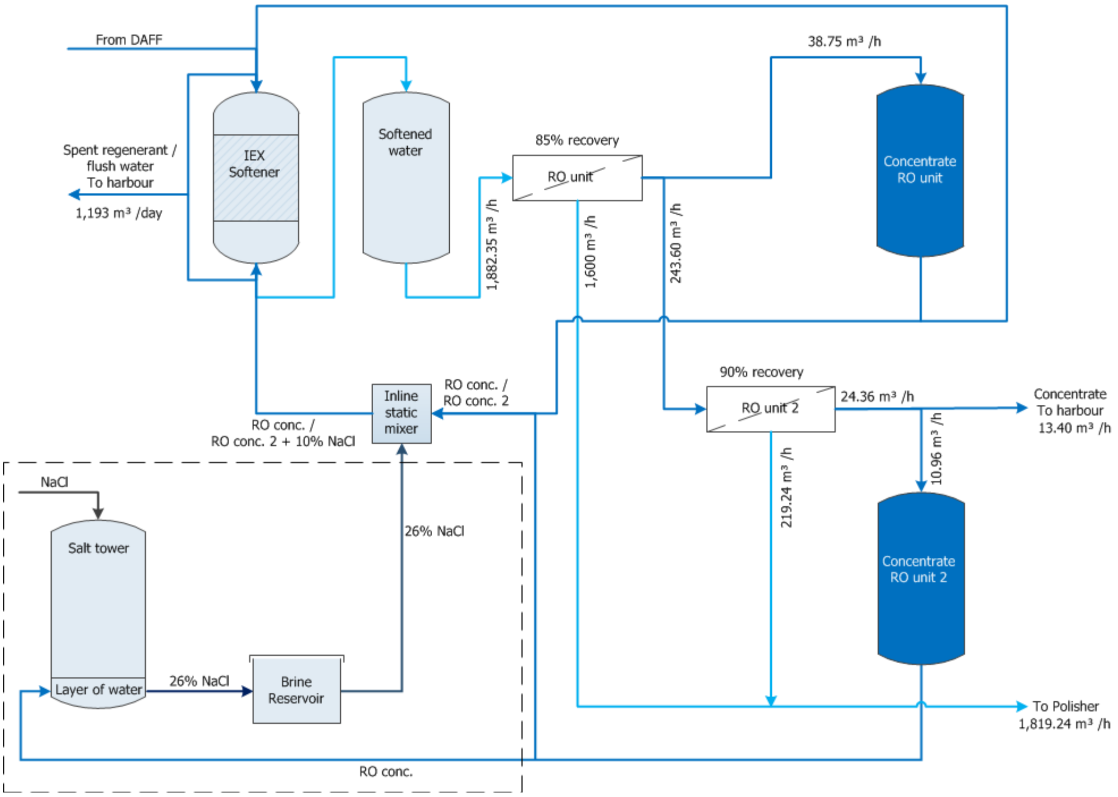


Figure 71: Process scheme of design 2b.

Configuration of the second RO unit is the same as at design 2a. Only the amount of feed water is changed. For production of regenerant or as a regenerant a part of the concentrate of the second RO unit is used. As a consequence less concentrate from the existing RO unit is stored in the first vessel. Flow towards that vessel is now 38.75 m^3/h. Another consequence is that flow to the second RO unit is increased. With ROSA is checked if the configuration is able to handle that amount of water. Results are given in appendix D.2. From results of the simulation can be concluded that the configuration can handle that amount of water. Also has to be checked if the amount of silica is not exceeding the limits. With use of antiscalants a silica concentration of 300 mg/l is possible. In the table below can be seen that now a concentration of 300.09 mg/l is present in the concentrate. That is on the limit and possible, but no safety is present. So concentration of silica in the feed water needs to be monitored very carefully. In case of a higher silica concentration in the feed water, that water needs to be discharged into the harbour and not fed to the second RO unit. Another possibility is that water is fed to the RO unit and discharged after the second stage, then also a reduction of concentrate is achieved.

Table 34: Concentrations in feed, concentrate and permeate of the second RO.

	Feed [mg/l]	**Concentrate [mg/l]**	**Permeate [mg/l]**
Na	977	9766.86	1.90
Mg	0.24	2.40	0.00
Ca	1.25	12.52	0.00
CO_3^{2-}	100.32	1100.92	0.00
HCO_3^-	1034.58	10151.64	2.87
SiO_2	30.05	300.09	0.09
TDS	**3058.21**	**30708.65**	**7.40**

Also, a higher carbonate concentration is present in the RO concentrate, 18.3 mmol/l. Beside that also 0.31 mmol/l of calcium and less than 0.1 mmol/l of magnesium is present. So when concentrate is used for regeneration has to be taken into account that precipitation and deposition of calcium carbonate can occur in the column. DOC in water from Brielse Meer is 2.84 mg/l and concentrate of the second RO unit has a DOC of 189 mg/l. When concentrate is used for regeneration has to be investigated if the performance is not influenced. In the table above also concentrations in the permeate are presented. The total hardness is 0 mmol/l, which is below the value that Evides desires (0.04 mmol/l). Only silicate concentration is higher; Evides desires a concentration of 0.064 mg/l SiO_2 at the customer. Values are determined with a simulation, the order of magnitude is correct. For more accurate values a measurement should be conducted.

The amount of RO concentrate for the flush of the resin is 93 m^3 for 1 regeneration. To produce regenerant two different streams of concentrate are needed, one for production of brine and one for dilution of brine. From data of the simulation with ROSA is known that concentrate from the second RO unit contains 424.6 mmol/l of sodium. So RO concentrate has a salt concentration of 2.5% NaCl. With production of brine a natural equilibrium is created of 26% NaCl. That equilibrium does not change with use of another type of water. Therefore with use of the RO concentrate the amount of salt that is needed is reduced with almost 10%. Produced brine is diluted in a static mixer with RO concentrate to create the desired 10% NaCl solution. Brine is diluted with concentrate, 2.5% NaCl saving of sodium chloride is achieved.

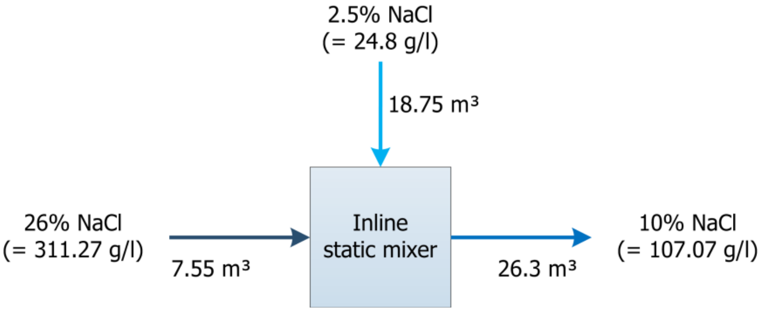


Figure 72: Representation of the different streams of the static mixer.

With the figure and knowledge that brine is produced with concentrate can be deducted that for 1 regeneration a total of 2,162.8 kg of NaCl is needed to produce 1.2 BV of regenerant. In the table below the amount sodium chloride needed for 1 day is given along with the costs.

Table 35: Cost and amount of salt needed for regeneration.

	Total amount [kg]	**Total amount [kg/day]**	**Costs [€/day]**
NaCl	2,162.8	21,628	2,162.80

In the table below values are summarized related to discharge into the Brittanniё harbour.

Table 36: Cost and amounts for discharge into the Brittanniё harbour.

	Total amount [m^3/day]	**Costs [€/day]**
RO concentrate	312.6	2.41
Spent regenerant	263	1.97
Flush water	930	6.98
Total	**1,514.6**	**11.36**

So on an annual basis € 4,146.4 has to be paid for discharge into the Brittanniё harbour.

Parts of the design that have to be build are the two storage tanks and the second RO unit. Volume of the storage tanks is based on the knowledge that for 1 regeneration 93 m^3 of concentrate is needed as flush water and 26.3 m^3 for production of regenerant. The first storage tank is for flush water and the second for concentrate that is used for the production of regenerant. For calculation of the cost is calculated with a gross volume of 149.13 m^3 for the first and 32.89 m^3 for the second storage tank. Investment costs are calculated with kostencalculator of RHDHV. For the second RO unit also is determined what the exploitation costs are. Costs are presented in the table below.

Table 37: Investment and exploitation costs for design 2a.

	Investment costs	**Exploitation costs**	
	[€]	**[€/year]**	**[€/m^3]**
Storage tank 1	68,179	-	-
Storage tank 2	19,281	-	-
Second RO unit	4,294,543	1,014,965	59.45
Total	**4,382,003**	**1,014,965**	**59.45**

Another option is that concentrate (2.5% NaCl) from the second RO unit is directly used as regenerant without dosing sodium chloride. Two things are important for that, if there is enough concentrate available and if the sodium concentration high enough is for regeneration. With experiments was determined that 3.45% NaCl is performing well as a regenerant, so lower sodium chloride concentrations are possible. That situation is used to determine if enough concentrate is available for regeneration. In that case to reach an operating capacity of 0.95 eq/l 4.15 bed volumes of regenerant are needed and addition of 0.95% NaCl. Translated to the design with 10 regenerations per day results in 910 m^3 of concentrate for the production of regenerant. In order to have enough for regeneration 37.92 m^3/h of concentrate needs to be produced. The second RO unit gives a concentrate flow of 24.36 m^3/h, so not enough concentrate is available for regeneration with 3.45% NaCl. To use only concentrate even more bed volumes of concentrate are needed because of the lower sodium chloride concentration, and therefore is not possible.

An option to create enough flow is to lower the recovery, but then sodium chloride concentration in the concentrate decreases. And also permeate production decrease and less water is available to be sold to customers. So lowering of the recovery gives more disadvantages than advantages.

7.3 Comparison of the designs

First is noticed that with decrease of regenerations needed per day the total amount of water that is discharged into the harbour does not change in design 1. The amount of concentrate that is saved with regeneration is discharged as concentrate from the RO unit. Only in the second design the amount of discharge into the harbour is influenced by the number of regenerations. When less regenerations are needed more water is fed to the second RO unit and also more permeate is produced. So the total amount of water discharged into the harbour decreases. The total amount of salt used with designs 1, 2a and 2b and current situation (0) are given in the table below. Also the amount that is discharged into the harbour is given. Values of the current situation are determined from results of experiments with 10% NaCl as regenerant at the same flow velocity as at DWPB. In that case 2.1 BV is required to achieve an operating capacity of 0.95 eq/l.

Table 38: Total amount of resources used for regeneration for the different designs.

		Amounts per design			
	Unit	**0**	**1**	**2a**	**2b**
Number of regenerations	[-]	12	10	10	10
Softened water	[m^3]	1668	-	-	-
NaCl	[kg/day]	59,090	27,511	27,511	21,628

Table 39: Amounts discharged into the harbour for the different designs.

		Amounts per design			
	Unit	**0**	**1**	**2a**	**2b**
RO concentrate	[m^3/day]	6776.4	5583.4	558.2	321.6
Spent regenerant	[m^3/day]	552	263	263	263
Flush water	[m^3/day]	1116	930	930	930
Total amount of liquid	**[m^3/day]**	**8,444.4**	**6,876**	**1,751.2**	**1,514.6**

From the table can be concluded that with design 2b the less amount of water is discharged into the harbour. With that design also the lowest amount of salt is needed. In the design is handled in a sustainable way with available resources. The amount of salt of the current situation is larger than the amount used with regeneration at DWPB. That is due to the fact that the values are determined with the experimental setup and 10% NaCl is used instead of 9% NaCl. The designs can also be compared on the costs. In the table below a comparison of the cost are given with regard to discharge into the harbour, amount of softened water and amount of salt.

Table 40: Costs per design regarding to operation.

		Costs per design			
		0 **[€/day]**	**1** **[€/day]**	**2a** **[€/day]**	**2b** **[€/day]**
Discharge on harbour	RO concentrate	50.82	41.87	4.18	2.41
	Spent regenerant	4.14	1.97	1.97	1.97
	Flush water	8.37	6.98	6.98	6.98
	Softened water	166.80	-	-	-
	NaCl	5,909.00	2,751.10	2,751.10	2,162.80
Total		**6,139.13**	**2,801.92**	**2,764.23**	**2,174.85**

In Table 41 investment and exploitation costs of the designs are compared.

Table 41: Investment and exploitation costs of the designs.

	Investment costs **[€]**	**Exploitation costs** **[€/day]**	**[€cent/m^3]**
Design 1	87,460	-	-
Design 2a	4,382,319	2,642.42$^{(1)}$	59.16$^{(1)}$
Design 2b	4,382,003	2,780.73$^{(1)}$	59.45$^{(1)}$

(^{1}) These values are without the cost for the use of antiscalants.

From Table 40 can be concluded that also with design 2b the lowest costs with regard to operation are made. The benefit compared to the current situation is € 3964.28 per day. So on an annual basis at least € 1,446,962.20 is saved. For design 1 only investment cost are needed for a storage tank. Savings with that design is € 3337.21 per day. So on an annual basis € 1,218,081.65 is saved. With the design where the concentrate is concentrated (design 2a and 2b) also demiwater is produced. For 1 m^3 of demi water 0.80 euro has to be paid. In the table below the profit of the second RO unit of design 2a and b is compared.

Table 42: Profit of the second RO unit for the designs.

	Production **[m^3/h]**	**Costs** **[€/day]**	**Turnover** **[€/day]**	**Profit** **[€/day]**
Design 2a	209.38	2972.86	4020.10	1047.24
Design 2b	219.24	3128.12	4209.41	1081.29

Before the second RO unit no pre-treatment is necessary, concentrate from the existing RO unit is directly fed to the second RO unit. No additional costs are made; profit is the difference between turnover and exploitation costs. With these values is determined that it takes 11.5 years for design 2a and 11.1 years for design 2b to earn back the investment based on the profit. When also the saving is taken into account, design 2a has a payback period of 2.7 years and 2b of 2.4 years.

Table 43: Comparison of the concentrations in the concentrate and permeate for design 2a and 2b.

	Feed	**Concentrate**		**Permeate**	
		2a	**2b**	**2a**	**2b**
	[mg/l]	**[mg/l]**	**[mg/l]**	**[mg/l]**	**[mg/l]**
Na	977	9759.43	9766.86	1.98	1.90
Mg	0.24	2.40	2.40	0.00	0.00
Ca	1.25	12.51	12.52	0.00	0.00
CO_3^{2-}	100.32	1100.03	1100.92	0.00	0.00
HCO_3^-	1034.58	10144.06	10151.64	2.97	2.87
SiO_2	30.05	299.85	300.09	0.10	0.09
TDS	**3058.21**	**30685.10**	**30708.65**	**7.68**	**7.40**

From the table above can be concluded that water composition of concentrate for both designs is almost the same. Both concentrates are similar to seawater, only with less hardness. Permeate of both design is also almost the same, permeate of design 2b is slightly better.

When is looked at the amount of resources used and to operating cost, design 2b is the best solution. That design is not the most expensive one, but exploitation costs are the highest. With that design also the highest amount of demi water is produced. Time needed to earn back the investment is therefore the shortest.

From comparison of the designs can be concluded that if extra demiwater is needed the best solutions is to treat the concentrate. In that case the amount of water that is discharged into the harbour is reduced. With application of the design also is saved on the amount of salt that is used for regeneration of the softeners and more important on the amount of softened water.

When there is no necessity to produce more demiwater, design 1 is the best solution. In that case € 3337.21 is saved compared to the current situation. So in 27 days the investment of the extra storage tank is earned back.

8 Conclusions and recommendations

In this chapter the main results of the research are summarized. Also conclusions are drawn towards effects of different regenerants on the resin. Parameters focussed at are operating capacity of the resin, amount of bed volumes of regenerant, precipitation in the bed and applicability to DWPB.

8.1 The use of other regenerants

The main objective of this research is to investigate possibilities of decreasing the amount of resources (sodium chloride and softened water) needed for regeneration of the softeners. From a literature review it was concluded that only two solutions are suitable to further investigation. The two solutions in this study both aiming at the use of another regenerant, namely water from the Brittannië harbour and RO concentrate. Also 10% NaCl was used as a reference regenerant.

8.1.1 Regeneration with 10% NaCl

- Accuracy of determination of hardness mass balance with the elution curve and trapezoid rule is dependent on the moment of sampling. The peak of release of hardness from the bed is easily missed.

- Mass balances (hardness loaded on/ hardness removed from) are more accurate with the use of mixed samples from both softened water and spent regenerant solution. The elution curve is used to understand the regeneration process.

8.1.2 Water from the Brittannië harbour as a regenerant

- Reduction of the use of salt is only possible when enough time and water is available for regeneration. With use of 3.45% NaCl less salt per litre resin is used to reach the same operating capacity as with use of 10% NaCl. The regeneration period was longer, because more bed volumes were needed.

- It is not possible to use water from the Brittannië harbour as regenerant. Only a part of the hardness is removed from the resin due to the high hardness (mainly magnesium) in the regenerant.

8.1.3 RO concentrate as a regenerant

- RO concentrate with 1% NaCl or $CaCO_3$ added is not suitable as regenerant in a fixed ion exchange column. Carbonate in the regenerant result in the formation of calcium carbonate in the bed during regeneration. As a consequence deposit and lump formation is taking place, and the operating capacity decreases.

- With RO concentrate (with 10% NaCl) as a regenerant the least amount of bed volumes and addition of salt is needed to reach an operating capacity of 0.95 eq/l.

8.2 Design

- The amount of water saved on with the first design, concentrate as regenerant, is 1332 m^3/day. Also 18.6% less water is discharged to the harbour. The investment costs of this design is low (€ 87.460).

- With the second design, concentration of the concentrate, the concentrate of the secondary RO can be used as a regenerant because the salt concentration is about 2.5%. The largest reduction of discharge into the harbour is reached, 82%. In this design the used amount of salt is reduced with 63.3%. The investment costs are 1.4

million. With the sales of produced permeate the investment can be earned back in 2.5 years.

8.3 Recommendations

Recommendations for further research:

- With the RO-concentrate regeneration at higher pH calcium carbonate clogging of the fixed bed can be avoided by a regulated release of calcium in a fluidized bed. This is still a possibility that can be investigated. It is probably not possible to have a calcium carbonate-free resin after regeneration. So probably the method might be useful for softening. But is not useful for producing water with very low calcium concentrations.

- Pilot plant research of design 2 to investigate effect of hardness in the concentrate to the resin. Also can be investigated if increased DOC has an fouling effect on the resin.

- Any change in regeneration should be monitored over long periods of time and will require pilot-scale testing.

List of references

Books

[1] Binnemans, Koen, **Analytische Chemie, Scheidingsmethoden.** K.U. Leuven, Leuven, 2003.

[2] Crittenden, John C, **Water treatment: Principles and design**, Wiley, 2005.

[3] Degremont, **Water treatment handbook**, Lavoisier, 2007 (2-7430-0970-5)

[4] Van Dijk, J.C., Rietveld, L.C., Verberk, J.Q.J.C., **Drinking water supply I – Technology.** Delft University of Technology, Sanitary Engineering section, faculty of Civil Engineering and Geosciences, September 2004.

[5] Water desalting committee, **Water desalting planning guide for water utilities**, 2004.

[6] Wachinski, Anthony M., **Ion exchange treatment for water**, Denver, American Water Works Association, 2006 (1-58321-322-8)

Articles

[7] Bremere, Ingrida; Kennedy, Matia; Mhyio, Sahar; Jaljuli, Abdulfattah; Witkamp, Geert-Jan; Schippers, Jan. **Prevention of silica scale in membrane systems: removal of monomer and polymer silica.** Desalination 132 p337-344, 2000.

[8] Cotruvo, Joseph A, **Water desalination processes and associated health and environmental issues**, Water conditioning & purification, p13-17, January 2005.

[9] Darton, E.G., **RO plant experiences with high silica waters in the Canary Islands.** Desalination 124, p33-41, 1999.

[10] Freeman, Scott D.N.; Majerle, Randall J.; **Silica fouling revisited**. Desalination 103, p113-115, 1995.

[11] Gill, J.S., **Inhibition of silica-silicate deposit in industrial waters.** Physicochemical and Engineering Aspects, 74, December 1992.

[12] Haidari, Amir, **High silica concentration in RO concentrate and magnesium-silica polymers formation.** Delft University of Technology, Sanitary Engineering section, faculty of Civil Engineering and Geosciences, March 2011

[13] Lanxess, **Engineering information softening**, Data for co-current and counter-current operation (S1467, S1468 and MonoPlus SP112)

[14] Lanxess, **Product information Lewatit S 1428**, Leverkusen, October 2011

[15] Pathema, Limeteq Converter 5-300 m^3/h

[16] "**Stevige basis voor efficiënte watervoorziening**", Constant Gras, Europoort Kringen, Maart 2010

[17] Seok-Jun Seo, Hongrae Jeon, Jae Kwang Lee, Gha-Young Kim, Daewook Park, Hideo Nojima, Jaeyoung Lee, Seung-Hyeon Moon, **Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications**, water research 44, p2267–2275, 2010.

Internet

[1] www.evides.nl
[2] www.dwp-botlek.nl
[3] www.logisticon.com
[4] www.wetsalt.nl
[5] www.excelwater.com
[6] www.eurowater.nl
[7] www.gewater.com
[8] www.lenntech.com
[9] www.ediwater.com
[10] www.watertechonline.com
[11] www.dowwaterandprocess.com/products/edi
[12] http://www.dowwaterandprocess.com/applications/chem_petrochem/brine_soft.htm
[13] http://apps.awwa.org/waterlibrary
[14] http://www.voltea.com/technology/introduction/

Appendix A: Map of the harbour

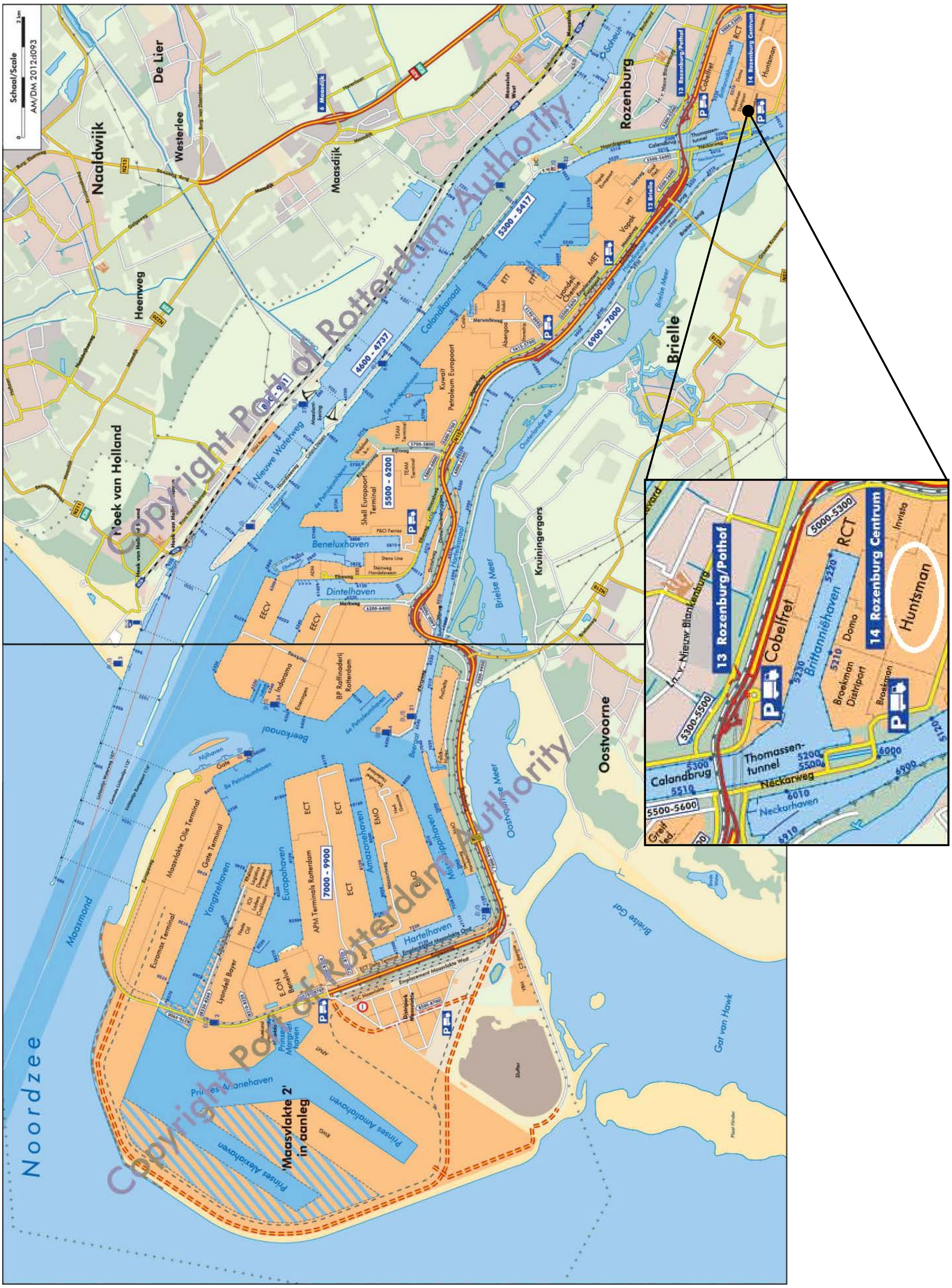


Figure 73: Map of a part of the harbour (Port of Rotterdam Authority).

Appendix B: Validation of the hardness cell test

This experiment is conducted to evaluate the results of the test with known calcium and magnesium concentrations. A stock solution with a known calcium and magnesium concentration is used with the test in order to compare the measured value with the known values. The test is also conducted with the addition of sodium chloride to see if the measurement is influenced by these ions. First the experimental approach and methods are elaborated. Next the results of the experiment are given.

In the table below the results of the total hardness cell test of Merck for the prepared solution, demi water with a calcium concentration of 420 mg/l are given.

Table 44: Results of the total hardness cell test.

Bottle / Sample description	pH [-]	T [°C]	Dilution [-]	TH [mg/l Ca]	Mg [mg/l]	Ca [mg/l]
Prepared solution	6.03	19.2	3	149	-	149
			3	149	-	149
			3	148	-	148

In order to be able to determine the calcium concentration, the sample was three times diluted to meet the requirements of the test for the calcium concentration. Because of the dilution the test should give a calcium concentration of 140 mg/l. In the prepared solution only calcium is added to demi water, so there is no magnesium present in the solution and total hardness equals the calcium concentration. According to the manual of the test the total hardness is expressed as mg/l Ca. As can be seen in the table the measured value is 148-149 mg/l. The values between the different tests of the same sample are in the confidence interval (±4 mg/l) given by the manufacturer of the test. The value measured with the test is a little bit higher than the actual calcium concentration. According to the manufacturer the accuracy of a measurement value is max. ±7 mg/l. With this fact known now can be concluded that the test is applicable for the experiments.
The values of the hardness measured by the drinking water company Evides are given in the table below.

Table 45: Hardness of drinking water (Evides).

	Min		Max	
	[mg/l]	[mmol/l]	[mg/l]	[mmol/l]
TH	-	1.46	-	1.72
Ca^{2+}	45.1	1.13	54.5	1.36
Mg^{2+}	7.9	0.33	8.7	0.36

The settings of the photo spectrometer were changed from mg/l to mmol/l in order to be able to perform a differentiation measurement. With the correct settings and the use of two photo spectrometer (both Nova60) the results stated in the table below were measured.

Table 46: Results of the total hardness cell test.

Bottle / Sample description	Photo Spectrometer	pH [-]	T [°C]	TH [mmol/l]	Mg [mmol/l]	Ca [mmol/l]
Drinking water	Nova 60-2	7.65	17.6	2.02	16	-
	Nova 60-3			2.06	0.42	1.64

Now can be concluded that the first photo spectrometer is not functioning in a proper way, the measured magnesium concentration is too high. The magnesium concentration can never be higher than the total hardness. Calcium and magnesium are still higher than the values of Evides. The deviation between the measured calcium and magnesium concentration and the values of Evides is higher than the accuracy according to the manufacturer of the test. Before this test can be used a validation has to be conducted.

B.1 Validation experiment: approach and methods

B.1.1 Objective

The objective of this experiment is to validate the hardness cell test.

B.1.2 Materials

The materials used for this experiment are:

- *Measurement devices*
    - 1 thermometer
    - 1 pH meter
    - Photometer Nova 60, version 3
    - Pipette for a pipetting volume of 1.0 ml
- *Test kits*
    - Total harness cell test of Merck (1.00961.0001)
- *Chemicals*
    - Calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$) or Calcium chloride anhydrous ($CaCl_2$)
    - Magnesium chloride ($MgCl_2$)
    - Sodium chloride ($NaCl$)
- *Liquids*
    - Demi water
- Storage vessels
    - 1 bottle with a capacity of 2 l
    - 1 small jar

B.1.3 Stock solution

For each measurement an amount is taken from a so called stock solution. In this way is guaranteed that each solution that is made has the same start concentration, only the dilution is different. For a stock solution a larger amount of calcium and magnesium chloride can be taken, that is easier to weigh.
For the stock solution calcium chloride is needed, but for this experiment calcium chloride dehydrate is used. Important to know is that calcium chloride is used in dehumidifiers and attracts water very easy. To be certain that no water is present in the calcium chloride, it is dried in an oven at 104 °C. According to literature the drying time has to be at least 2 hours [Binnemans, 2003]. The chemical equation for drying calcium chloride dehydrate is:

$$CaCl_2 \cdot 2H_2O(s) \rightarrow CaCl_2(s) + 2H_2O(g) \tag{29}$$

The chemical solution for solving calcium chloride in demi water is:

$$CaCl_2(s) \rightarrow Ca^{2+} + 2Cl^- \tag{30}$$

The chemical solution for solving magnesium chloride in demi water is:

$$MgCl_2(s) \rightarrow Mg^{2+} + 2Cl^- \tag{31}$$

It has to be taken into account that both reactions are exothermal and therefore precautions have to be taken when solving these salts.

To create a stock solution the following procedure is followed:

- 3858.86 mg of calcium chloride dehydrate is weighed
- The calcium chloride dehydrate is dried in an oven at 104 °C for at least 2 hours
- 1195.4 mg of calcium chloride is weighed and added to the bottle
- 344 mg of magnesium chloride is weighed and added to the bottle
- The bottle is filled up to 2 litres with demi water.

If calcium chloride is available, the step of drying is not necessary anymore and the right amount can be weight directly. The stock solution is stored in a refrigerator, available to use when needed.

B.1.4 Experimental Setup

In a neutral solution calcium and magnesium ions react with phthalein purple to form a violet dye that is determined photometrically. With the use of a selective masking agent it is possible to determine the differentiation between calcium and magnesium. The measuring range of the test is from 5 to 215 mg/l Ca (0.12 – 5.38 mmol/l Ca). Each sample is 10 ml, only a different amount of stock solution is used and then demi water is added. In Table 47 the different amount of stock solution that are used to create the samples are given with the known values for calcium and magnesium concentration and the total hardness. With the determination of the amount of stock that is needed for each sample the measuring range is taken into account.

Table 47: Amount of calcium and magnesium chloride with different amounts of stock solution.

Stock solution [ml]	$[Ca^{2+}]$ [mg/l]	$[Ca^{2+}]$ [mmol/l]	$[Mg^{2+}]$ [mg/l]	$[Mg^{2+}]$ [mmol/l]	TH [mmol/l]
0.3	6.45	0.16	1.31	0.05	0.22
0.5	10.75	0.27	2.18	0.09	0.36
1.0	21.50	0.54	4.36	0.18	0.72
2.0	43.01	1.08	8.72	0.36	1.44
3.0	64.51	1.61	13.07	0.54	2.16
4.0	86.02	2.15	17.43	0.73	2.88
5.0	107.52	2.69	21.79	0.91	3.60
6.0	129.03	3.23	26.15	1.09	4.32
7.0	150.53	3.76	30.51	1.27	5.03
8.0	172.04	4.30	34.86	1.45	5.75
9.0	193.54	4.84	39.22	1.63	6.47
10.0	215.05	5.38	43.58	1.82	7.19

Before the measurement can be done, in the menu of the photometer has to be checked if the device is set to perform a differentiation measurement.

With the prepared sample the following procedure is followed:

- Check if the hardness is in the measuring range of the test. When the concentration is higher the sample has to be diluted
- Check if the pH is within the range 3-9
- Pipette 1.0 ml of sample into a reaction cell, close the cell and mix.
- Add 1.0 ml of the reagent H-1K, close the cell and mix.
- Wait 3 minutes and place the cell into the photometer.
- The result is the total hardness, measured in mmol/l.
- Add 3 drops of reagent H-2K, close the cell and mix.
- Place the cell in the photometer, the result is the magnesium concentration (mmol/l).
- Press enter, the calcium and magnesium concentration are given (in mmol/l).

For every sample the same procedure is followed. With the results of the measurements a curve can be drawn.

B.2 Results of the validation experiment

The results of the validation experiment can be divided into three parts:

- The validation of the cell test for the total hardness
- The validation of the cell test for calcium
- The validation of the cell test for magnesium

B.2.1 Results of the validation for total hardness

In Table 48 the measured values for the total hardness are given. The experiment is done with two types of solution, one with 2% of sodium chloride and one with no addition of sodium chloride.

Table 48: Total hardness, measured and known values for each sample.

Known concentration	Measured concentration	
TH [mmol/l]	**TH [mmol/l]**	**TH 2% NaCl [mmol/l]**
0.22	0.20	0.64
	0.21	
0.36	0.31	0.70
	0.33	
0.72	0.68	0.95
	0.66	
1.44	1.45	1.39
	1.39	
2.16	2.10	1.88
	2.14	
2.88	2.84	2.42
	2.81	
3.60	3.59	2.85
	3.46	
4.32	4.23	3.36
	4.24	
5.04	4.73	3.82
	4.68	
5.75	5.55	4.19
	5.71	

A visualisation of the data can be made by displaying the measured concentrations of the total hardness against the known concentration. With the visualisation can be seen what the deviation is of the measured values. Also can be noticed what the effect of sodium chloride is on the results of the cell test for the value of the total hardness. The result of the visualisation is presented in Figure 74.

On the data points in the figure a linear regression is conducted. For both datasets also the formulas of these regressions are given in the figure. The given R^2 coefficient of is a statistical measure of the degree in which the regression line approximates the real data points. An R^2 of 1 indicates that the regression line perfectly fits the data. In this case both

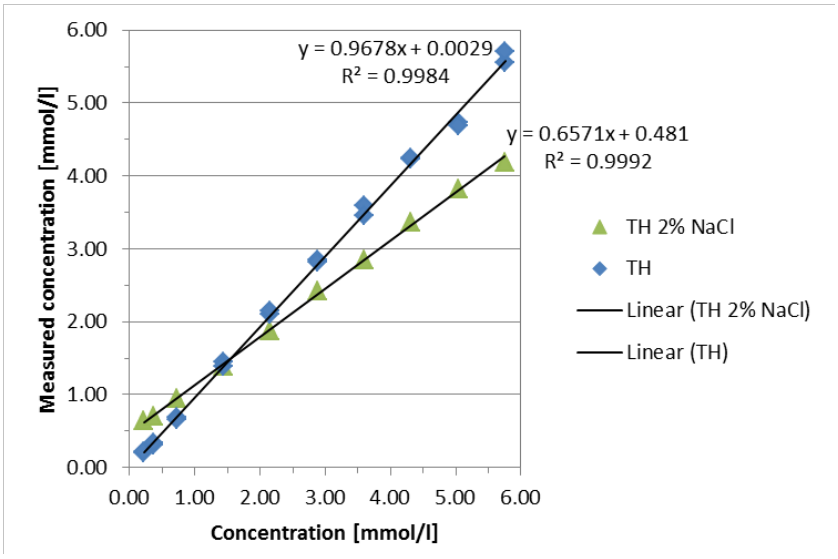


Figure 74: Validation curve for the total hardness.

values are very close to 1, so it can be concluded that linear regression is a good fit. In case of no addition of sodium chloride the measured total hardness is almost equal to the known concentration. The cell test gives a reliable result. According to the manual of the cell test the maximum value for sodium chloride to which the result of the measurement is not influenced is 2% NaCl. In the graph can be seen that the result of the cell test is influenced by the sodium chloride. When the total hardness is below 1.5 mmol/l the measured value is too high, when the total hardness is above 1.5 mmol/l the measured value is too low. For both sides is valid that when the concentration is decreasing / increasing the deviation of the known values becomes larger. So when the cell test is used the sodium chloride (NaCl) concentration has to be taken into account.

B.2.2 Results of the validation for calcium

In Table 49 the measured values of the calcium concentration are given. The experiment is conducted with two types of solution, one with 2% of sodium chloride and one with no addition of sodium chloride. The calcium concentration is the difference between the total hardness and the magnesium concentration.

Table 49: Calcium concentrations; measured and known values for each sample.

Known concentration	**Measured concentration**	
Ca^{2+} [mmol/l]	**Ca^{2+} [mmol/l]**	**Ca^{2+} 2% NaCl [mmol/l]**
0.16	0.18 0.20	0.26
0.27	0.25 0.27	0.37
0.54	0.52 0.52	0.59
1.08	1.18 1.07	1.02
1.61	1.61 1.71	1.47
2.15	2.20 2.20	1.96
2.69	2.85 2.71	2.39
3.23	3.25 3.28	2.86
3.76	3.55 3.55	3.27
4.30	4.14 4.34	3.66

A visualisation of the data can be made by displaying the measured calcium concentrations against the known concentrations. With the visualisation can be seen what the deviation is of the measured values. Also can be noticed what the effect of sodium chloride is on the results of the cell test for the value of the calcium concentration. The result of the visualisation is presented in Figure 75.

On the data points in the figure a linear regression is conducted. For both datasets also the formulas of these regressions are given in the figure. The given R^2 coefficient of is a statistical measure of the degree in which the regression line approximates the real data points. An R^2 of 1 indicates that the regression line perfectly fits the data. In this case both values are also very close to 1, so it can be concluded that linear regression is a good fit. The results of the cell test for the samples with no addition of sodium chloride are almost the same as the known concentrations. In the figure can be seen that the measured calcium concentration is influenced by the addition of the sodium chloride, but not that so much as the total hardness.

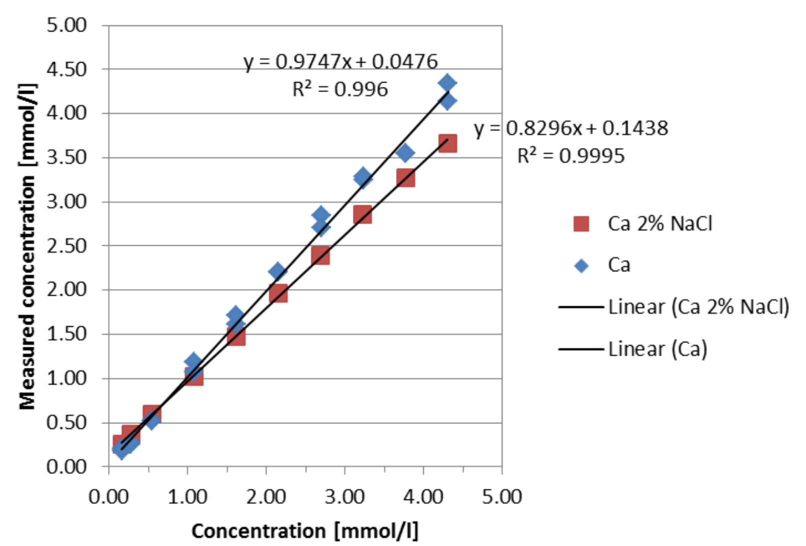


Figure 75: Validation curve for calcium.

B.2.3 Results of the validation for magnesium

The validation is conducted with two types of solution, one with 2% of sodium chloride and one with no addition of sodium chloride. In Table 50 the measured values of the magnesium concentration are given.

Table 50: Magnesium concentrations; measured and known values for each sample.

Known concentration Mg^{2+} [mmol/l]	Measured concentration Mg^{2+} [mmol/l]	Measured concentration Mg^{2+} 2% NaCl [mmol/l]
0.05	0.02 0.01	0.38
0.09	0.06 0.06	0.33
0.18	0.16 0.14	0.36
0.36	0.27 0.32	0.37
0.54	0.49 0.43	0.41
0.73	0.64 0.61	0.46
0.91	0.74 0.75	0.46
1.09	0.98 0.96	0.50
1.27	1.18 1.13	0.55
1.45	1.41 1.37	0.53

A visualisation of the data can be made by displaying the measured magnesium concentrations against the known concentrations. With the visualisation can be seen what the deviation is of the measured values. Also can be noticed what the effect of sodium chloride is on the results of the cell test for the magnesium concentration. The validation curve for magnesium is given in Figure 76.

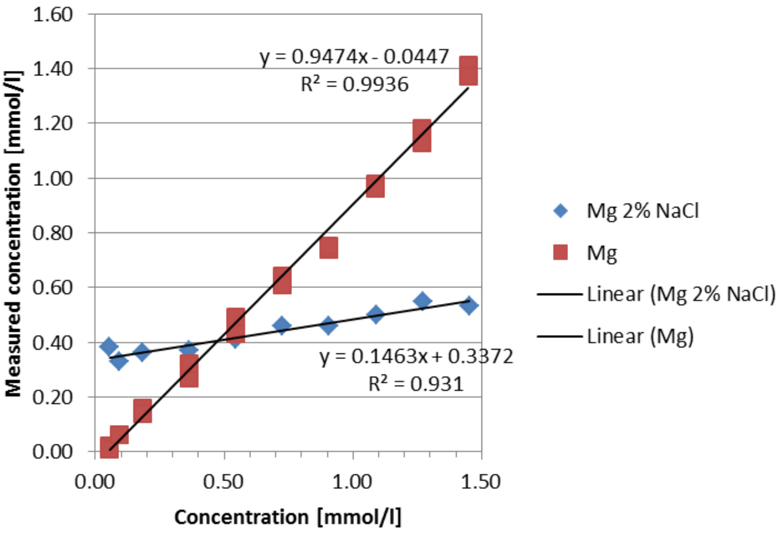


Figure 76: Validation curve for magnesium.

In this case also on both data sets a linear regression is applied and the result is given in the figure. For both regressions also the formulas are presented in the figure. An R^2 of 1 indicates that the regression line perfectly fits the data. In this case both values are very close to 1, so it can be concluded that linear regression is a good fit. But the linear regression fits the data of the samples with no addition of sodium chloride better than the one with sodium chloride. In the figure can also be seen that the determination of the magnesium concentration is sensitive for the amount of sodium chloride that is present in the solution. So with the use of the cell test it is very important to realize what amount of sodium chloride is present in the sample.

B.3 Conclusion

From the validation of the total hardness cell test some conclusions can be drawn. First it is important to check if the setting of the photo spectrometer is correct. That is because the differentiation measurement is only possible when the values are measured in mmol/l. Also it is important to check if the photo spectrometer can handle the differentiation measurement. With that differentiation measurement only two values are measured, the total hardness and the magnesium concentration. The calcium concentration is calculated as the difference between the total hardness and the magnesium. That is only valid when strontium and barium are only present in the water as traces. In this situation demiwater was used, so the calculation is valid. The measurement is also influenced by the concentration of sodium chloride. The calcium concentration is the one that is less influenced by the sodium concentration. The determination of the magnesium concentration was influenced on a large scale by the presence of sodium chloride in the water. Therefore when the total hardness cell test is used it is very important to realize this, especially in the case that the test is used in samples from the regeneration of the ion exchange resin. In that case the samples are diluted when the concentration of the hardness is too high. But when the concentration of the hardness decreases the dilution of the samples also decreases and the sodium chloride concentration increases. Then it becomes important to realize the effect of the sodium concentration on the results of the test and to ensure that the samples are diluted enough to be able to use the cell test. When these limitations are kept in mind the cell test is a good tool to be used for the determination of the total hardness.

Appendix C: Results of the regeneration experiment

In this appendix the results of the conducted regeneration experiments are presented. First results of the regeneration with 10% NaCl are given. After that the results of the regeneration with 3.45% NaCl and artificial seawater is presented. Finally, the results of the regenerations with RO concentrate are given.

C.1 Regeneration with 10 % NaCl

C.1.1 Regeneration with 10 % NaCl (R_1) at 3.77 m/h

In Figure 33 the breakthrough curve is given of the loading of resin. The resin was loaded with tap water with increased hardness to a level of 6 mmol/l.

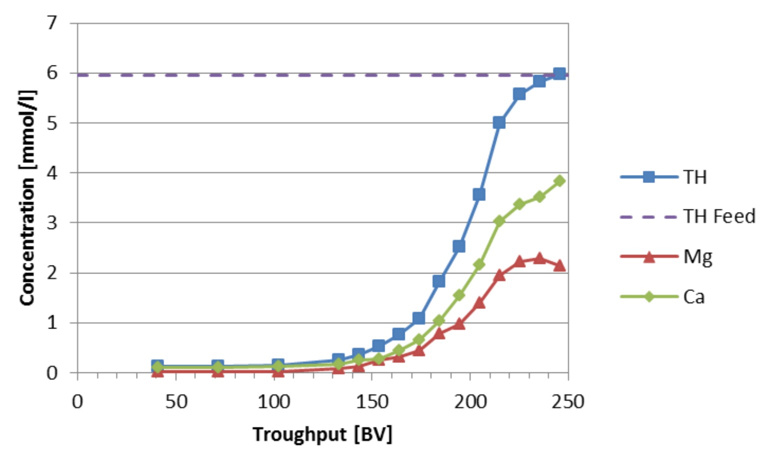


Figure 77: Breakthrough curve of column 1 at a flow of 30.71 m/h with a TH of 6 mmol/l.

The area between the line of the total hardness and the line of the total hardness of the feed is the amount of total hardness that is loaded on the resin. In the figure below the elution curve based on the data of the regeneration is given. For the regeneration 25 bed volumes of 10% NaCl is used at a flow velocity of 3.77 m/h.

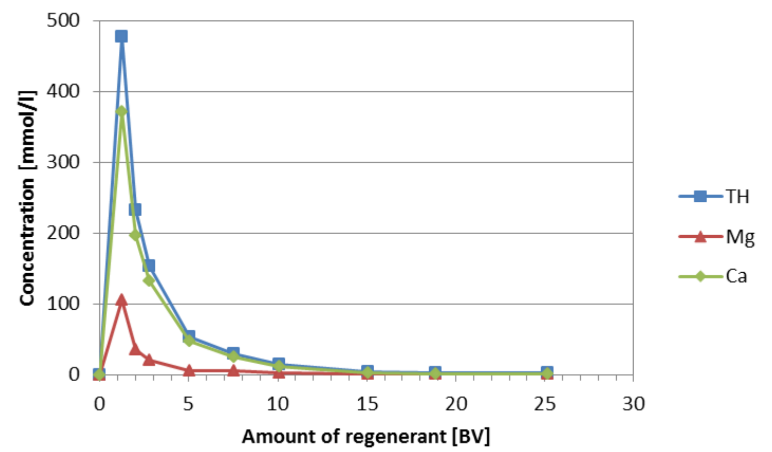


Figure 78: Elution curve column 1(Flow 3.77 m/h, 10%NaCl).

The total amount that is removed from the resin is the area beneath the line. That is calculated with the trapezoid rule. The results are given in the table below.

Table 51: Total amount of hardness loaded / removed from the resin of column 1.

	Total amount loaded [mmol]	Total amount removed [mmol]
TH	290.1	301.8
Mg^{2+}	58.2	56.9
Ca^{2+}	213.9	244.8

C.1.2 Regeneration with 2 BV 10 % NaCl (R_1) at 1.19 m / h

In order to conduct the regeneration the bed has to be loaded first. In the figure below the breakthrough curve is given.

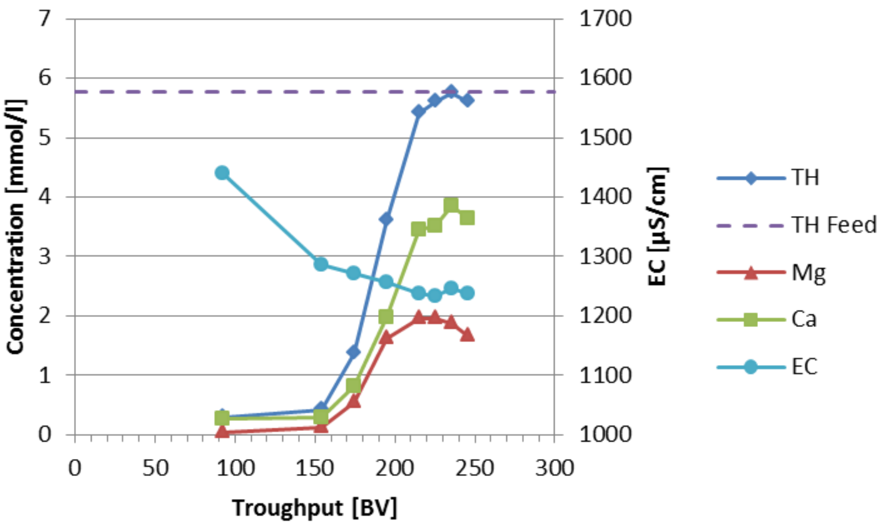


Figure 79: Breakthrough curve of column 1 at a flow of 30.74 m/h with a TH of 6 mmol/l.

The total amount that is loaded on the resin is given in Table 52. For the regeneration of the resin 2 bed volumes (BV) of 10% NaCl are used at a flow velocity of 1.19 m/h. The elution curve of the regeneration is given in the graph below.

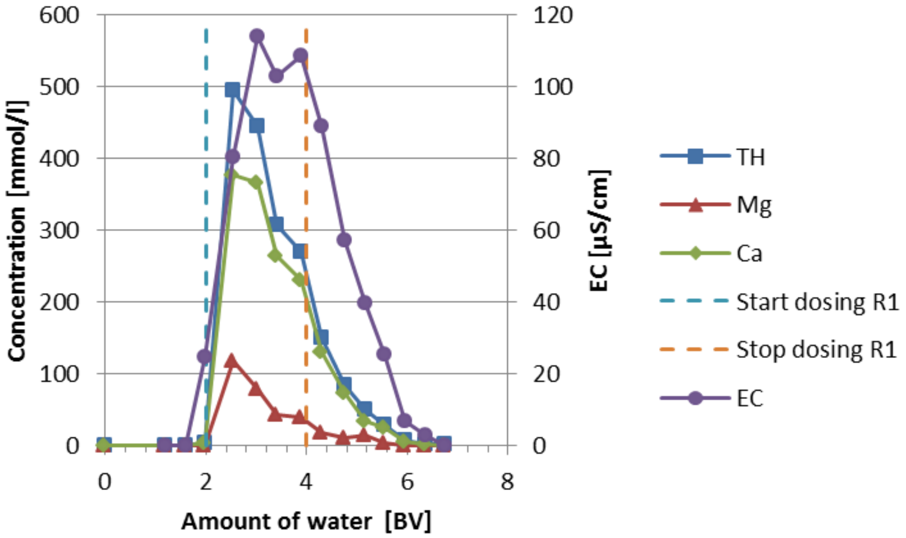


Figure 80: Elution curve of column 1 (Flow 1.19 m/h, 2 BV 10%NaCl).

In the graph also the start and the end of the regeneration is given. The total amount that is removed from the resin with the regeneration is the area beneath the line. That is calculated with the trapezoid rule. The result is given below.

Table 52: Total amount of hardness loaded / removed from the resin of column 1.

	Total amount loaded [mmol]	**Total amount removed [mmol]**
TH	269.8	214.6
Mg^{2+}	39.9	39.0
Ca^{2+}	230.6	175.6

C.1.3 Regeneration with 10 BV of 10 % NaCl (R_1) at 3.77 m/h.

The breakthrough curve of the loading of the resin is given in Figure 81.

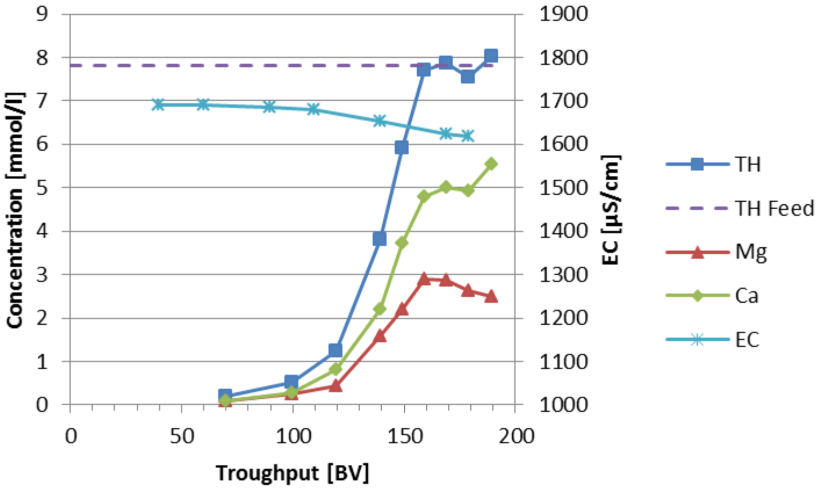


Figure 81: Breakthrough curve of column 1 at a flow of 29.86 m/h with a TH of 8 mmol/l.

In Figure 82 the elution curve for the regeneration of the resin is presented. The column is regenerated with 10 bed volumes of 10% NaCl at a flow of 3.77 m/h.

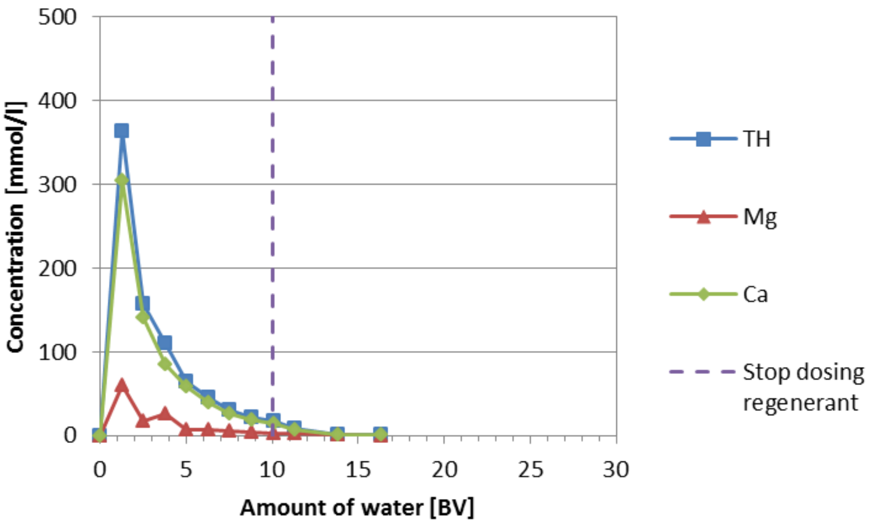


Figure 82: Elution curve of column 1 (Flow 3.77 m/h, 10 BV 10% NaCl).

The total amount of hardness that is loaded / removed from the resin is given in Table 53.

Table 53: Total amount of hardness loaded / removed from the resin of column 1.

		Total amount loaded [mmol]	**Total amount removed [mmol]**
Calculated with the trapezoid rule	TH	267.6	263.4
	Mg^{2+}	40.5	41.0
	Ca^{2+}	227.2	222.4
Measured with a mixed sample	TH	266.1	268.8
	Mg^{2+}	43.3	38.4
	Ca^{2+}	222.8	230.4

In the table also the values are given for the measurement with a mixed sample.

C.2 Regeneration with water from the Brittanniё harbour

C.2.1 Regenerant: 3.45 % NaCl (R_2)

The breakthrough curve of the loading of the resin is given in Figure 83.

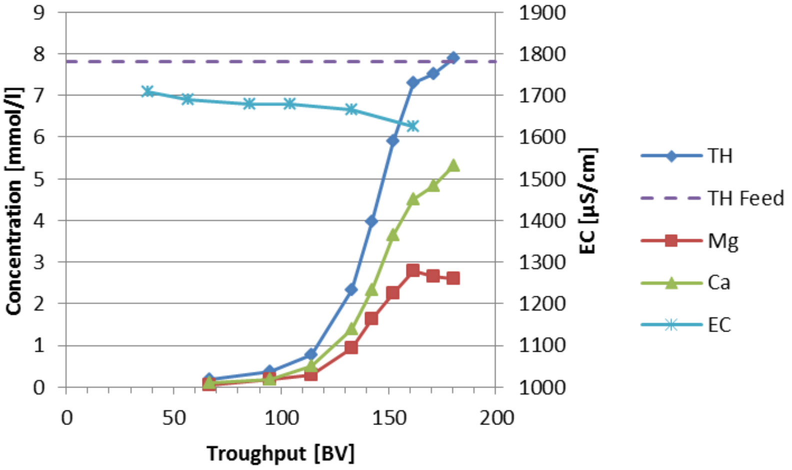


Figure 83: Breakthrough curve of column 2 at a flow of 28.51 m/h with a TH of 8 mmol/l.

In Figure 84 the elution curve for regeneration of the resin with 30 bed volumes of 3.45% NaCl at a flow of 3.77 m/h is given.

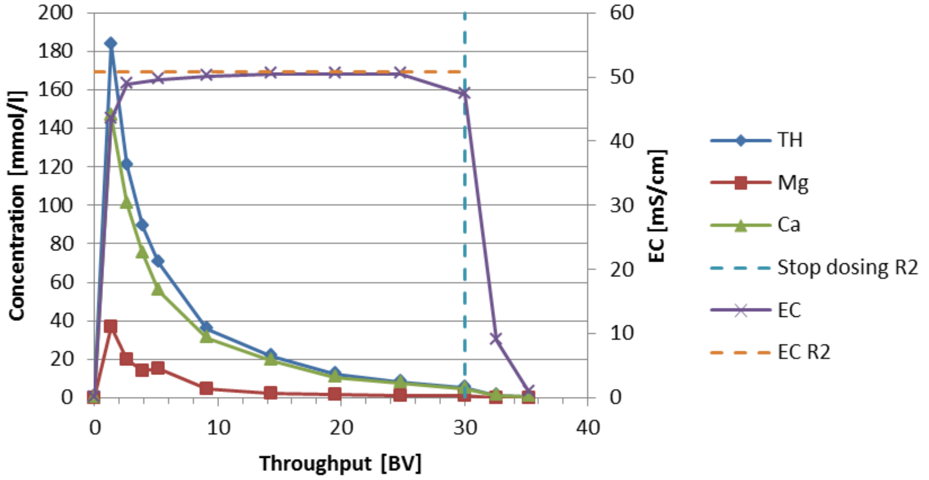


Figure 84: Elution curve of column 2 (Flow 3.91 m/h, 30 BV 3.45%NaCl).

From the elution curve the total amount that is removed from the resin is determined. The breakthrough is used for the calculation of the total amount that is loaded on the resin. Both values are also determined with the measurements from the mixed samples. The results are presented in the table below.

Table 54: Total amount of hardness loaded / removed from the resin of column 2.

		Total amount loaded [mmol]	**Total amount removed [mmol]**
Calculated with the trapezoid rule	TH	275.1	281.9
	Mg^{2+}	45.3	46.7
	Ca^{2+}	229.7	235.2
Measured with a mixed sample	TH	256.8	274.4
	Mg^{2+}	38.1	55.8
	Ca^{2+}	218.7	218.6

C.2.2 Regenerant: artificial seawater (R_3)

The breakthrough curve of the loading of the resin is given in Figure 85.

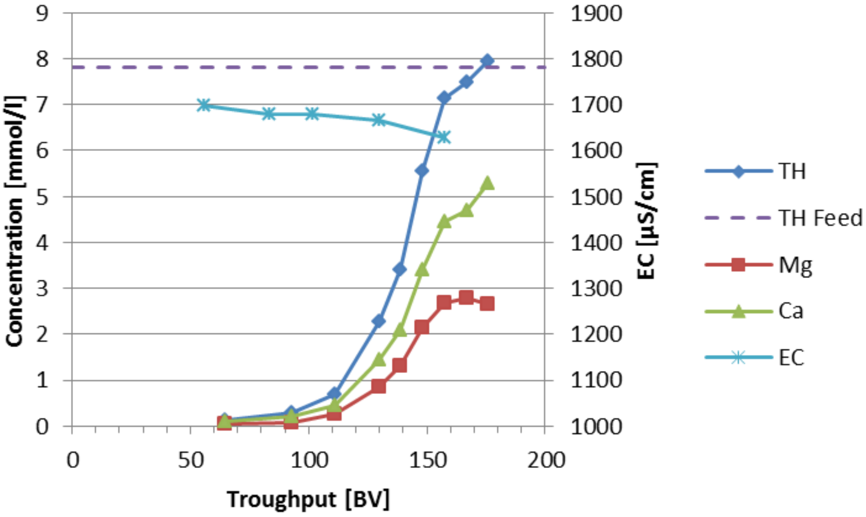


Figure 85: Breakthrough curve of column 3 at a flow of 27.77 m/h with a TH of 8 mmol/l.

In Figure 86 the elution curve for the regeneration of the resin is presented. The column is regenerated with 30 bed volumes of artificial seawater at a flow of 3.77 m/h.

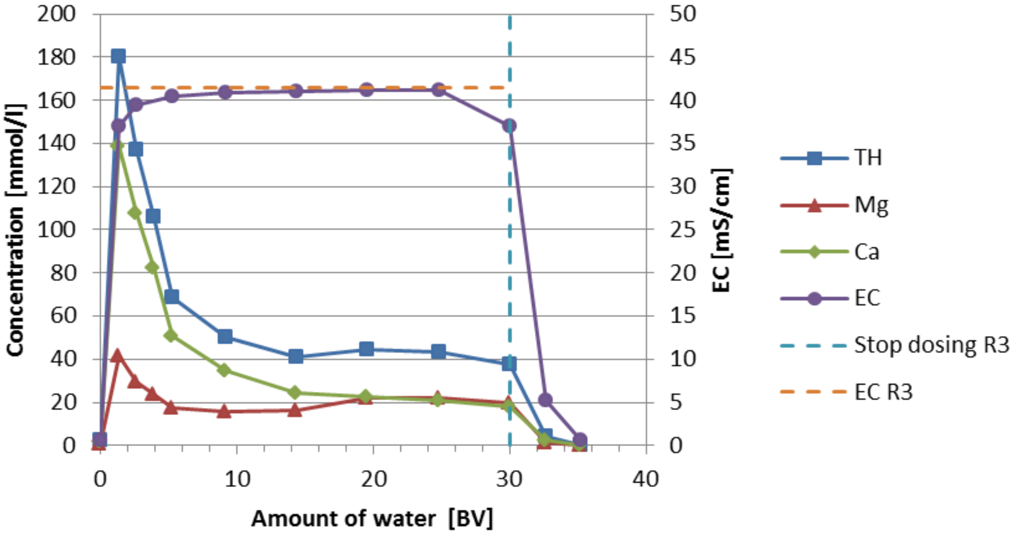


Figure 86: Elution curve of column 3 (Flow 3.91 m/h, 30 BV Artificial seawater).

The total amount of hardness that is loaded / removed from the resin is given in Table 55.

Table 55: Total amount of hardness loaded / removed from the resin of column 2.

		Total amount loaded [mmol]	**Total amount removed [mmol]**
Calculated with the trapezoid rule	TH	271.6	137.0
	Mg^{2+}	46.3	-72.6
	Ca^{2+}	225.2	209.6
Measured with a mixed sample	TH	267.6	134.1
	Mg^{2+}	45.2	-58.4
	Ca^{2+}	222.4	192.5

C.3 Regeneration experiment with RO concentrate (R_5)

C.3.1 Regenerant: RO concentrate and 1 % NaCl (R_{5-1})

The breakthrough curve of the loading of the resin is given in Figure 87.

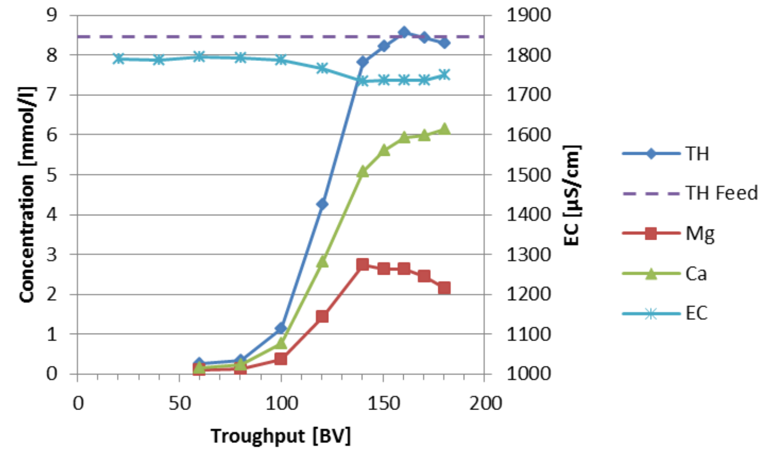


Figure 87: Breakthrough curve of column 2 at a flow of 30.09 m/h with a TH of 8 mmol/l.

In this case also only the pH and conductivity were measured during the regeneration. The result is given in the figure below. For the regeneration 33.5 bed volumes of concentrate with 1% NaCl added is used at a flow of 4.19 m/h.

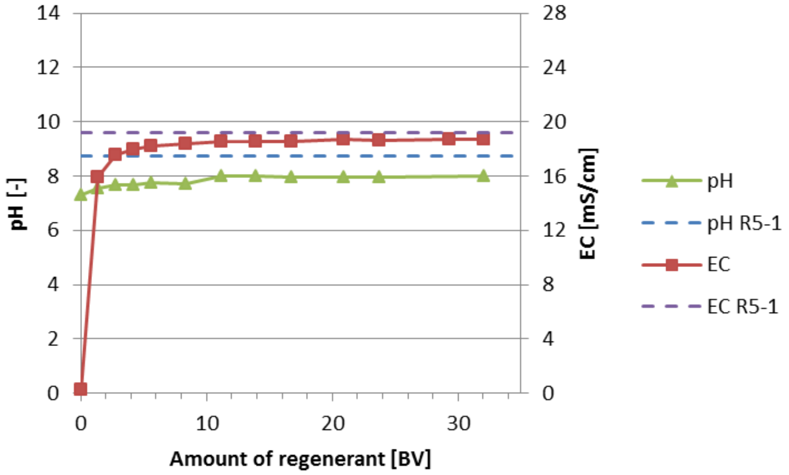


Figure 88: pH and conductivity during the regeneration with R_{5-1} (33.5 BV, flow 4.19 m/h).

The total amount loaded on the resin is still determined with the breakthrough curve and the mixed sample taken with the loading of the resin. Because no elution can be constructed the total amount that is removed from the resin is now determined with the breakthrough curve of the next loading (Figure 89) is used.

Table 56: Total amount of hardness loaded / removed from the resin of column 2.

		Total amount loaded [mmol]	**Total amount removed [mmol]**
Calculated with the trapezoid rule	TH	253.8	182.2
	Mg^{2+}	33.3	30.0
	Ca^{2+}	220.5	152.2
Measured with a mixed sample	TH	256.8	184.3
	Mg^{2+}	38.6	30.6
	Ca^{2+}	218.2	153.7

C.3.2 Regenerant: RO concentrate, 1 % NaCl and increased pH ($R_{5\text{-}3}$)

The breakthrough curve of the loading of the resin is given in Figure 89.

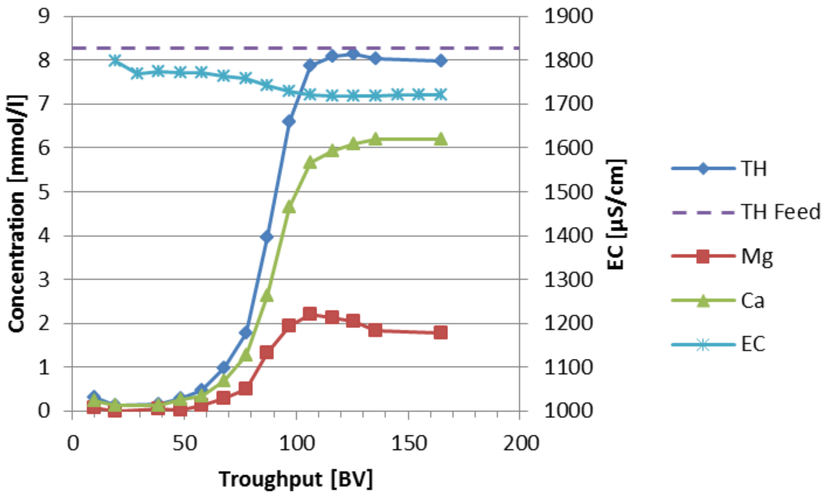


Figure 89: Breakthrough curve of column 2 at a flow of 29.05 m/h with a TH of 8 mmol/l.

Because of the possible formation of calcium and magnesium carbonate only the pH and conductivity were measured during the regeneration (with 22 bed volumes of regenerant at a flow of 4.19 m/h). The result is given in the figure below.

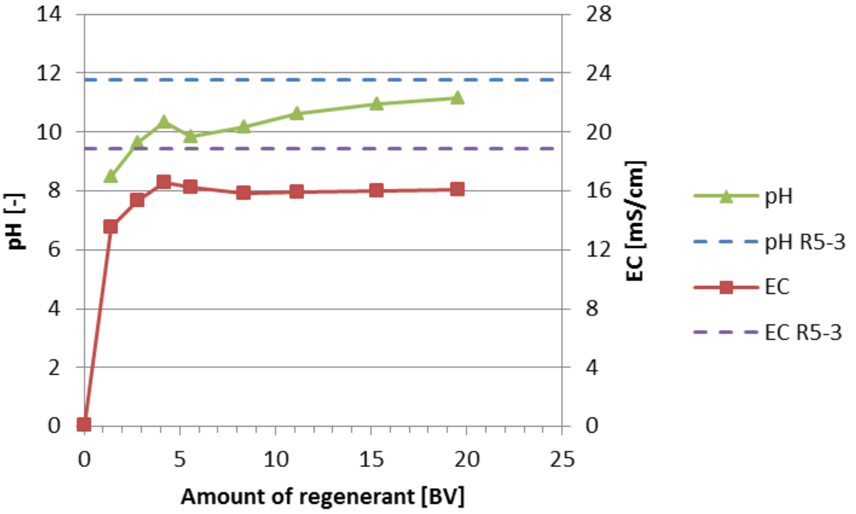


Figure 90: pH and conductivity during the regeneration with $R_{5\text{-}3}$ (21 BV, flow 4.19 m/h).

The breakthrough curve and the mixed sample are used to determine the total amount loaded on the resin. For the total amount that is removed from the resin the breakthrough curve and mixed sample of the next loading (Figure 91) is used.

Table 57: Total amount of hardness loaded / removed from the resin of column 2.

		Total amount loaded [mmol]	**Total amount removed [mmol]**
Calculated with the trapezoid rule	TH	182.2	144.8
	Mg^{2+}	30.0	16.3
	Ca^{2+}	152.2	129.1
Measured with a mixed sample	TH	184.3	143.0
	Mg^{2+}	30.6	19.4
	Ca^{2+}	153.7	123.7

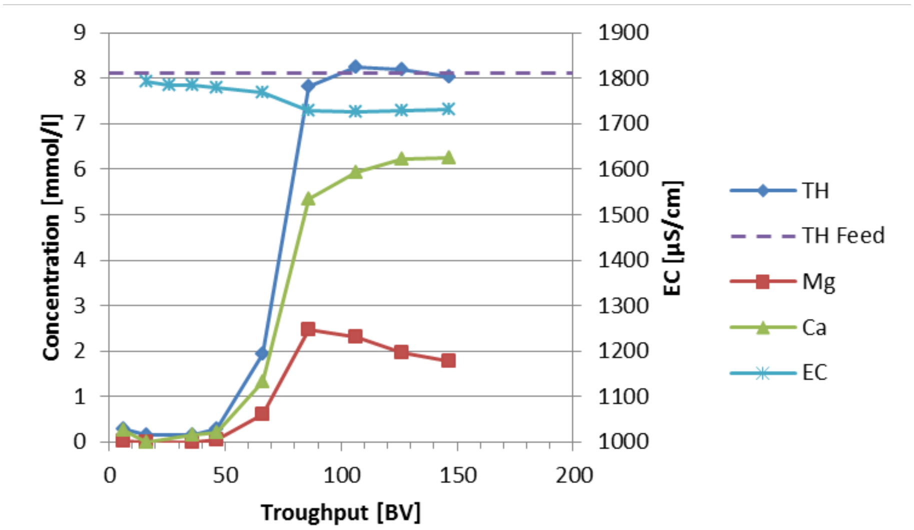


Figure 91: Breakthrough curve of column 2 after the regeneration with $R_{5\text{-}3}$ at a flow of 30.08 m/h with a TH of 8 mmol/l.

C.3.3 Regenerant: RO concentrate, 1 % NaCl and pH increased in gradient ($R_{5\text{-}6}$)

The regeneration is performed with two variants:

- Gradient pH increase from 9.14 to 11.83 (flow 4.19 m/h)
- Gradient pH increase from 10.04 to 11.92 (flow 7.07 m/h)

Gradient pH increase from 9.14 to 11.83 (flow 4.19 m/h)

The breakthrough curve of the loading of the resin is given in Figure 92.

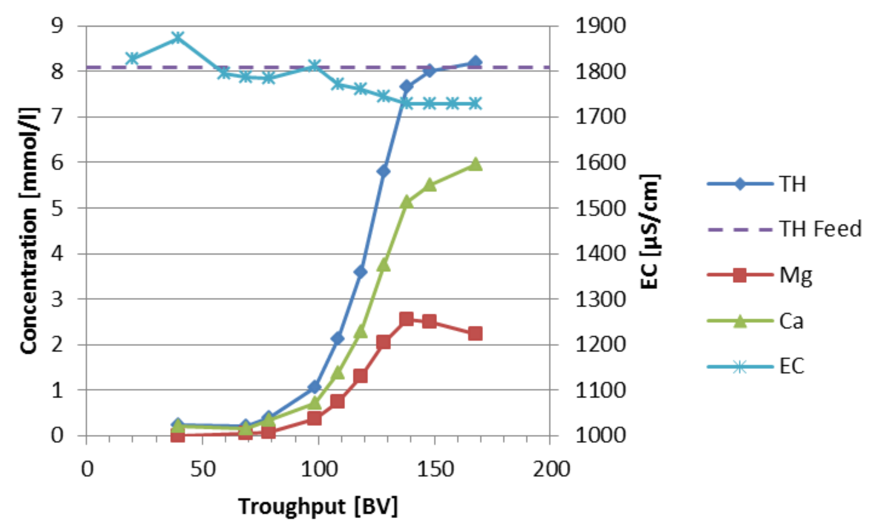


Figure 92: Breakthrough curve of column 2 at a flow of 30.08 m/h with a TH of 8 mmol/l.

Because of the possible formation of calcium and magnesium carbonate only the pH and conductivity was measured during the regeneration. The result is given in the figure below.

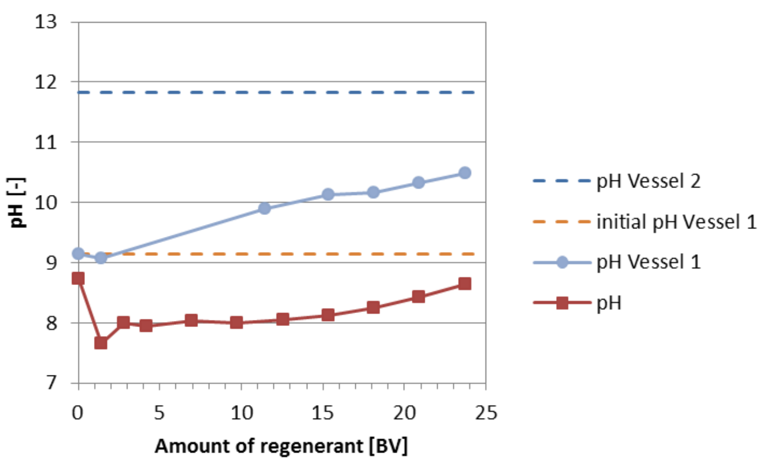


Figure 93: pH during the regeneration of the effluent and vessel 1 of the gradient mixer (flow 4.19 m/h).

In the figure the pH is given of vessel 1 of the gradient mixer and the effluent of the column. The regeneration is performed with 25 bed volumes of regenerant. At the start of the regeneration was in each vessel of the gradient mixer 22.5 bed volumes present. The regenerant in vessel 1 had a pH of 9.14 and the regenerant in vessel 2 had a pH of 11.83. To both vessel the same amount of sodium was added, 1% NaCl.

The breakthrough curve and the mixed sample are used to determine the total amount loaded on the resin. For the total amount that is removed from the resin the breakthrough curve and mixed sample of the next loading is used. That breakthrough curve is given in Figure 94.

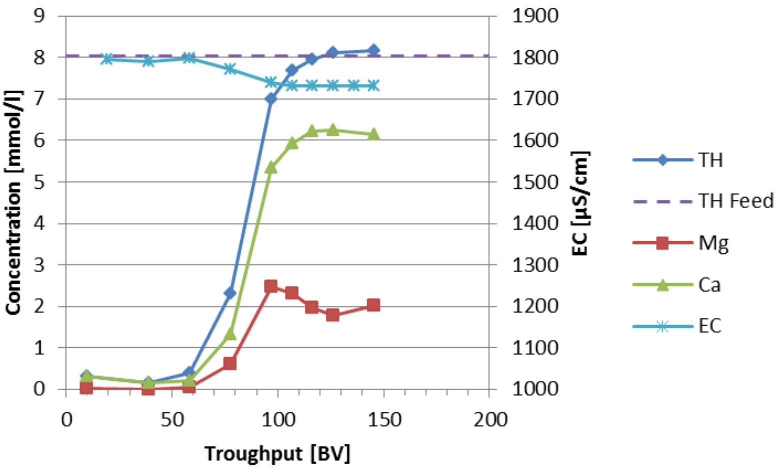


Figure 94: Breakthrough curve of the loading of column 2 after the regeneration at a flow of 29.12 m/h with a TH of 8 mmol/l.

The total amount that is loaded on and removed from the resin is presented in the table below.

Table 58: Total amount of hardness loaded / removed from the resin of column 2.

		Total amount loaded [mmol]	Total amount removed [mmol]
Calculated with the trapezoid rule	TH	238.5	166.9
	Mg^{2+}	33.1	23.0
	Ca^{2+}	205.4	141.4
Measured with a mixed sample	TH	237.5	162.3
	Mg^{2+}	38.0	18.5
	Ca^{2+}	199.5	143.8

Gradient pH increase from 10.04 to 11.92 (flow 7.07 m/h)

The breakthrough curve of the loading of the resin is given in Figure 95.

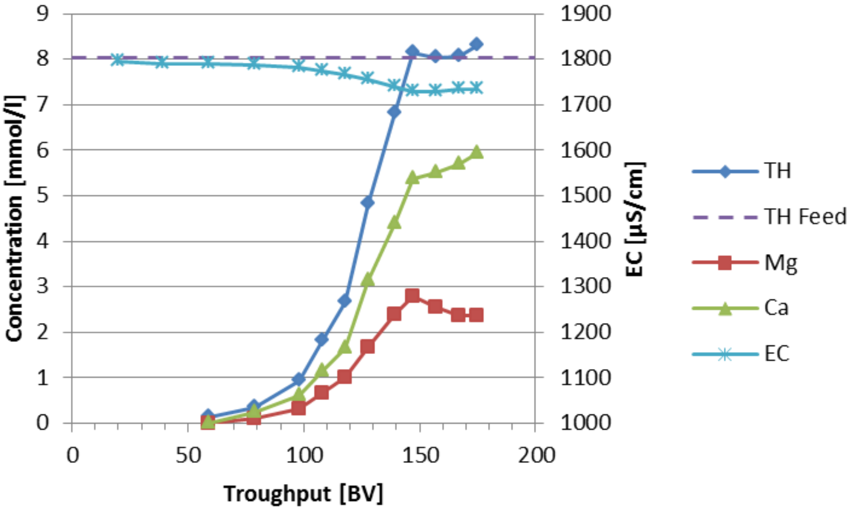


Figure 95: Breakthrough curve of column 2 at a flow of 29.44 m/h with a TH of 8 mmol/l.

With this regeneration also a gradient mixer is used. In the figure below the pH development of the regenerant in the first vessel is presented.

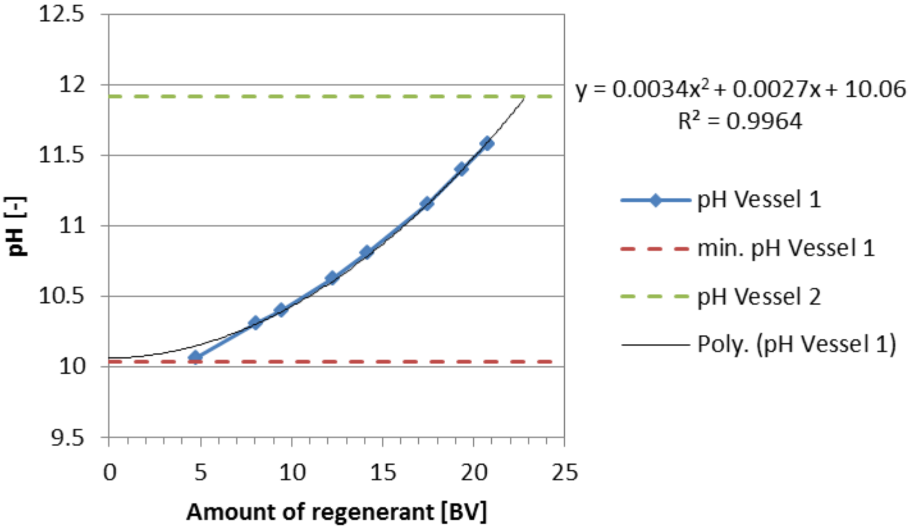


Figure 96: pH increase in vessel 1 of the gradient mixer.

The regeneration is performed with 21 bed volumes of regenerant. At the start of the regeneration was in each vessel of the gradient mixer 20.5 bed volumes present. The regenerant in vessel 1 had a pH of 10.04 and the regenerant in vessel 2 had a pH of 11.92. To both vessel the same amount of sodium was added, 1% NaCl.
Because of the possible formation of calcium and magnesium carbonate only the pH and conductivity is measured during the regeneration. The result is given in the figure below.

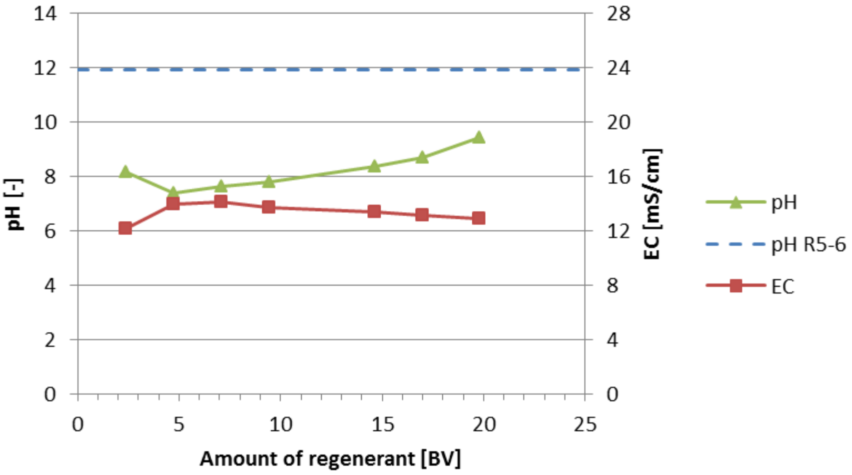


Figure 97: pH and conductivity during the regeneration (21 BV, flow 7.07 m/h).

The total amount loaded on the resin is calculated with the breakthrough curve and the mixed sample from the loading of the resin. For the total amount that is removed from the resin the breakthrough curve and mixed sample of the next loading is used. That breakthrough curve is given in Figure 98.

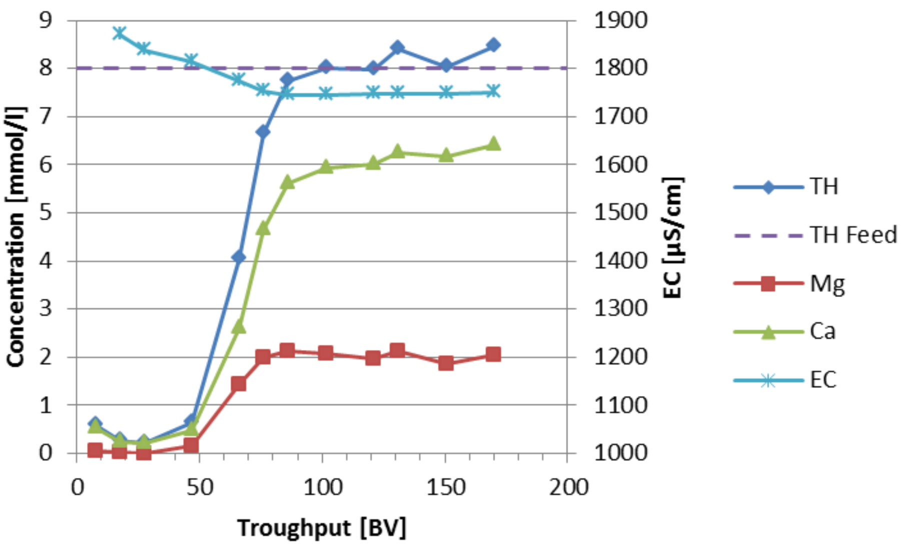


Figure 98: Breakthrough curve of the loading of column 2 after the regeneration at a flow of 29.7 m/h with a TH of 8 mmol/l.

The total amount that is loaded on and removed from the resin is presented in the table below.

Table 59: Total amount of hardness loaded / removed from the resin of column 2.

		Total amount loaded [mmol]	**Total amount removed [mmol]**
Calculated with the trapezoid rule	TH	245.7	126.3
	Mg^{2+}	36.1	12.9
	Ca^{2+}	209.9	113.4
Measured with a mixed sample	TH	243.7	126.5
	Mg^{2+}	35.1	10.9
	Ca^{2+}	208.6	115.5

C.3.4 Regenerant: RO concentrate and $CaCO_3$ (R_{5-2})

The breakthrough curve of the loading of the resin is given in the figure below.

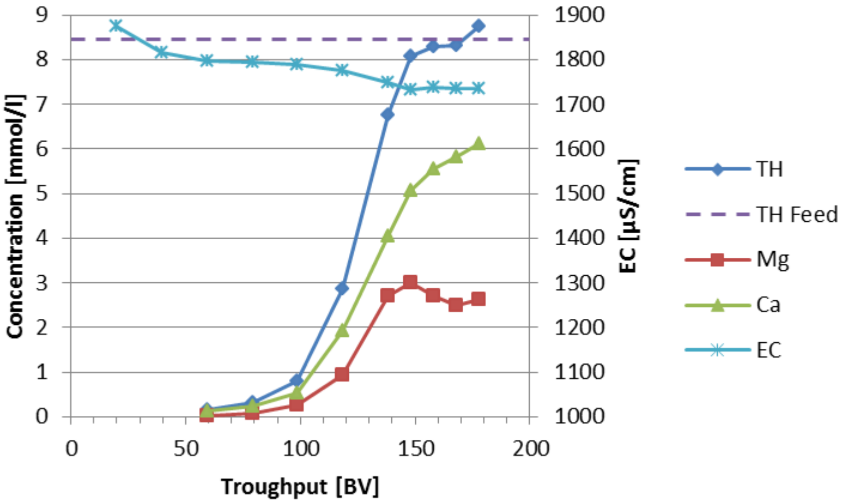


Figure 99: Breakthrough curve of column 3 at a flow of 29.64 m/h with a TH of 8 mmol/l.

Because of the addition of calcium carbonate and the formation of calcium and magnesium carbonate only the pH and conductivity was measured during the regeneration. The result is given in the figure below.

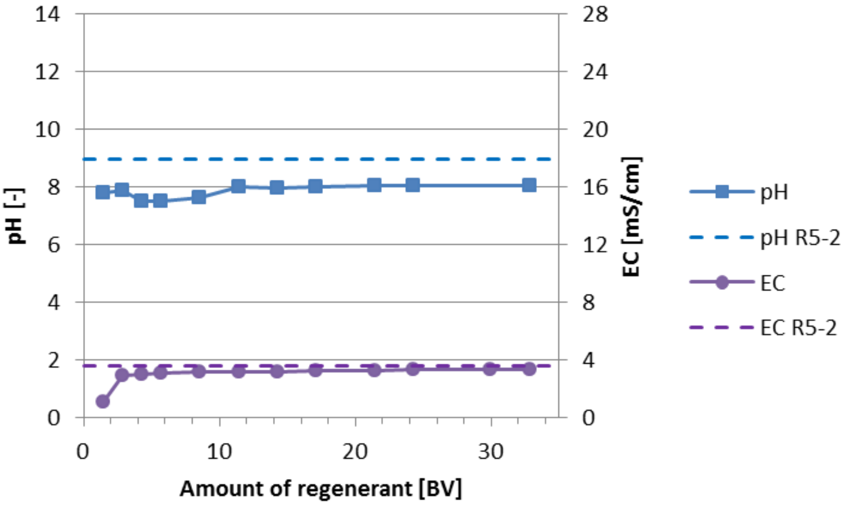


Figure 100: pH and conductivity during the regeneration (33.4 BV, flow 4.28 m/h).

The breakthrough curve and the mixed sample are used to determine the total amount loaded on the resin. For the total amount that is removed from the resin the breakthrough curve and mixed sample of the next loading (Figure 101) is used.

Table 60: Total amount of hardness loaded / removed from the resin of column 3.

		Total amount loaded [mmol]	**Total amount removed [mmol]**
Calculated with the trapezoid rule	TH	264.0	65.4
	Mg^{2+}	34.5	8.7
	Ca^{2+}	229.5	56.7
Measured with a mixed sample	TH	263.8	66.5
	Mg^{2+}	37.1	12.4
	Ca^{2+}	226.7	54.2

C.3.5 Regenerant: RO concentrate, $CaCO_3$ and increased pH (R_{5-4})

The breakthrough curve of the loading of the resin is given in the figure below.

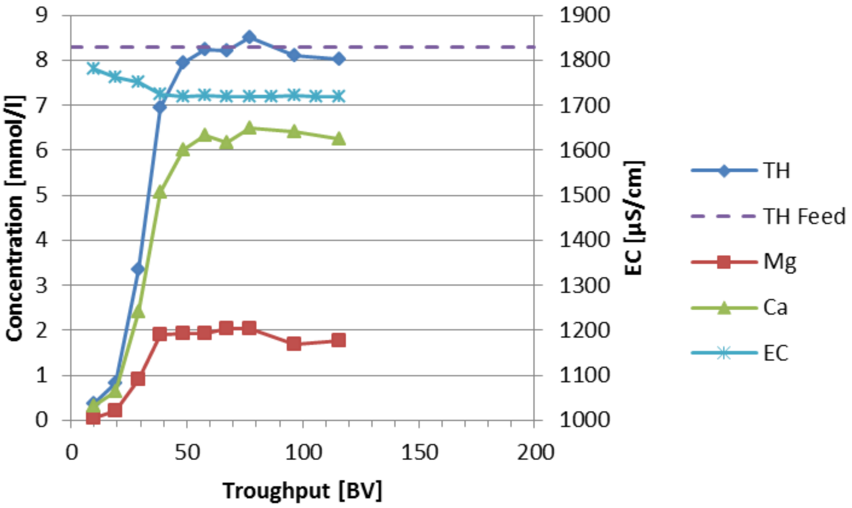


Figure 101: Breakthrough curve of column 3 at a flow of 28.93 m/h with a TH of 8 mmol/l.

Because of the addition of calcium carbonate and the formation of calcium and magnesium carbonate only the pH and conductivity was measured during the regeneration. The result is given in the figure below.

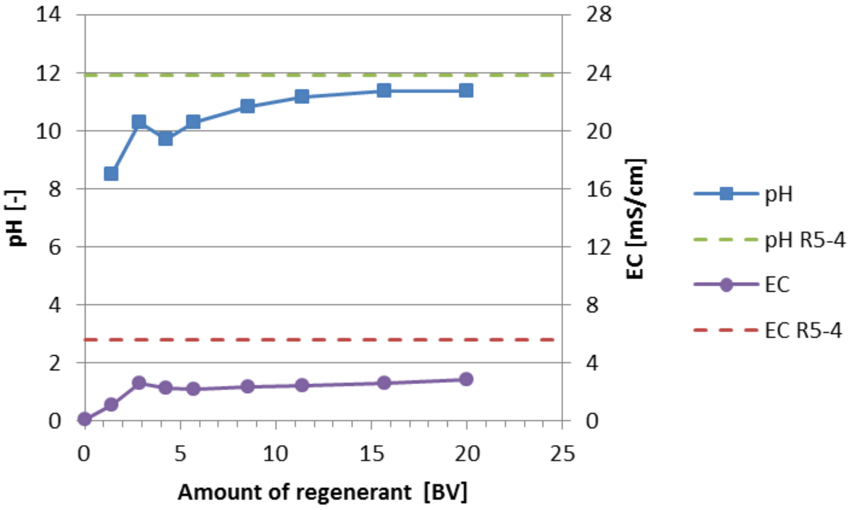


Figure 102: pH and conductivity during the regeneration (20.8 BV, 4.28 m/h).

The breakthrough curve and the mixed sample are used to determine the total amount loaded on the resin. For the total amount that is removed from the resin the breakthrough curve and mixed sample of the next loading (Figure 103) is used.

Table 61: Total amount of hardness loaded / removed from the resin of column 3.

		Total amount loaded [mmol]	**Total amount removed [mmol]**
Calculated with the trapezoid rule	TH	65.4	77.1
	Mg^{2+}	8.7	4.5
	Ca^{2+}	56.7	72.6
Measured with a mixed sample	TH	66.5	77.0
	Mg^{2+}	12.4	7.3
	Ca^{2+}	54.2	69.6

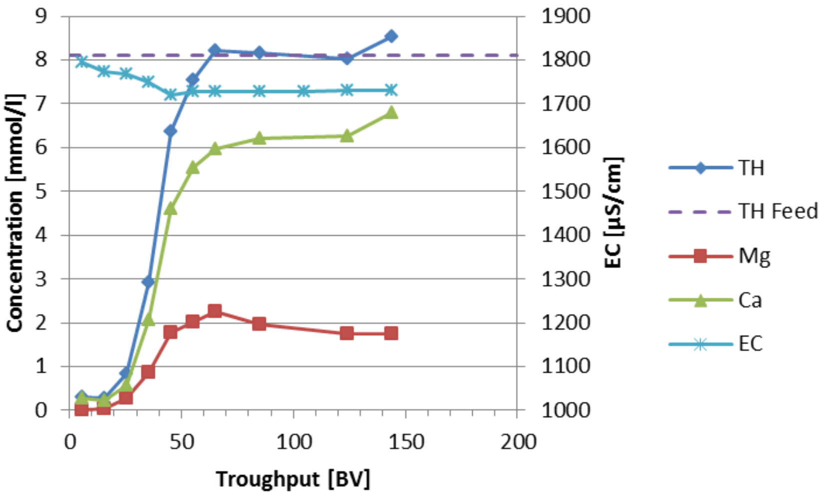


Figure 103: Breakthrough curve of the loading of column 3 after the regeneration at a flow of 29.60 m/h with a TH of 8 mmol/l.

C.3.6 Regenerant: RO concentrate and 10 % NaCl ($R_{5\text{-}5}$)

The breakthrough curve of the loading of the resin is presented in the figure below.

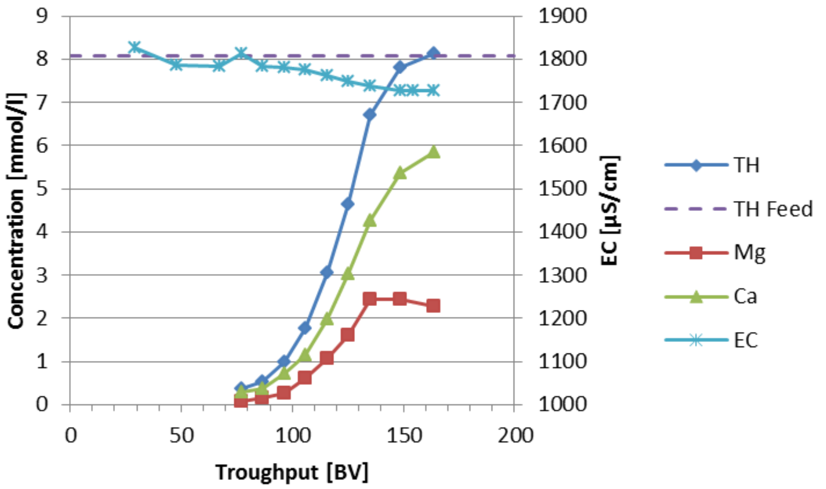


Figure 104: Breakthrough curve of column 3 at a flow of 28.92 m/h with a TH of 8 mmol/l.

Because still possibility exists of the formation of calcium and magnesium carbonate only the pH and conductivity was measured during the regeneration (Figure 105).

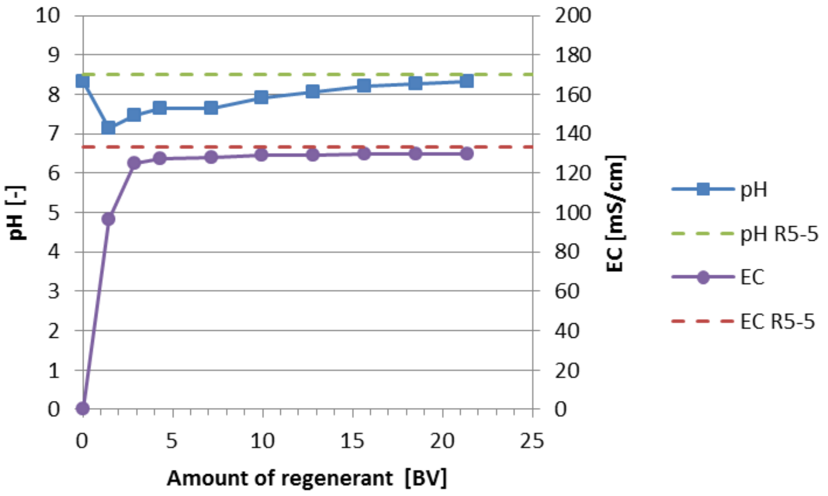


Figure 105: pH and conductivity during the regeneration (24.5 BV, flow 4.28 m/h).

For the regeneration 24.5 bed volumes of concentrate with 10% NaCl is used at a flow of 4.28 m/h. The total amount loaded on / removed from the resin is calculated with the breakthrough and mixed sample of the loading of the resin before (Figure 104) and after (Figure 106) the regeneration. The results are given in Table 62.

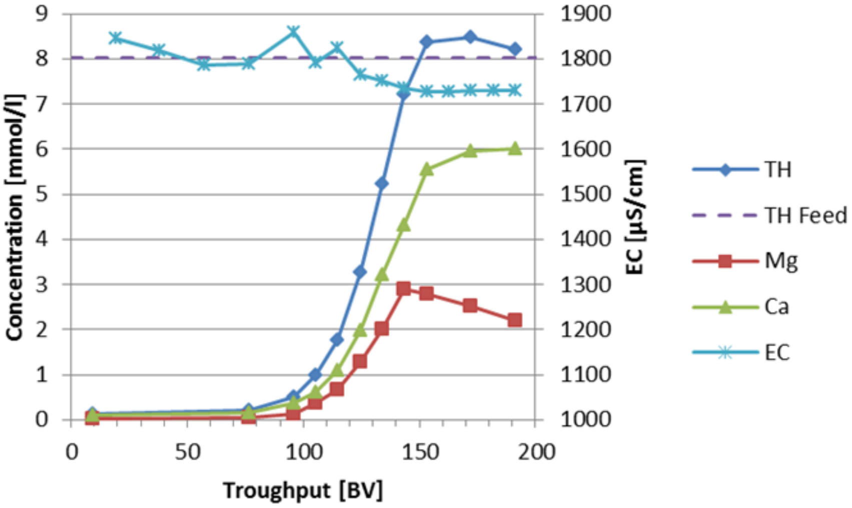


Figure 106: Breakthrough curve of column 3 at a flow of 28.71 m/h with a TH of 8 mmol/l.

Table 62: Total amount of hardness loaded / removed from the resin of column 3.

		Total amount loaded [mmol]	Total amount removed [mmol]
Calculated with the trapezoid rule	TH	245.2	248.9
	Mg^{2+}	35.2	29.2
	Ca^{2+}	210.0	219.6
Measured with a mixed sample	TH	239.6	248.4
	Mg^{2+}	38.0	30.2
	Ca^{2+}	201.7	218.2

To determine how the equilibrium is developing 6 sequential runs were performed. One run exists out of loading with tap water with added hardness to a level of 8 mmol/l and a regeneration with 10 bed volumes of RO concentrate with 10% NaCl. The breakthrough curves of the 6 runs are given in to. The regeneration is performed at a flow of 3.77 m/h.

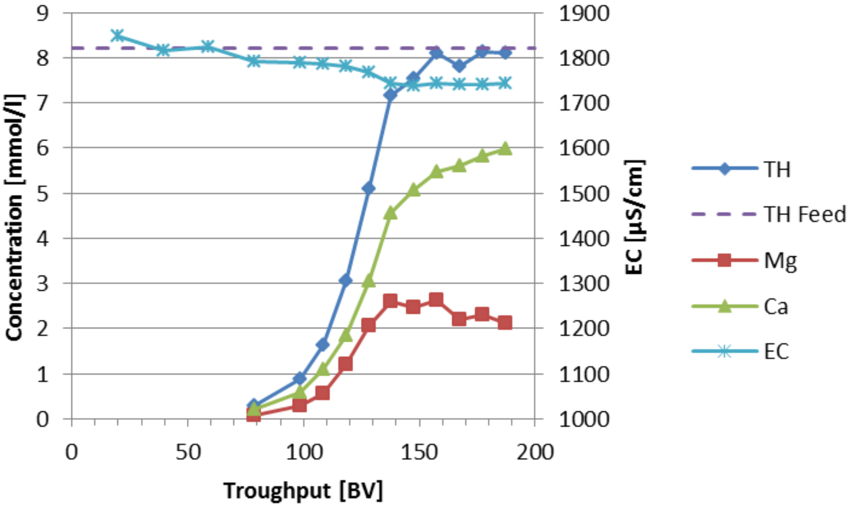


Figure 107: Breakthrough curve of run 1 at a flow of 29.55 m/h with a TH of 8 mmol/l.

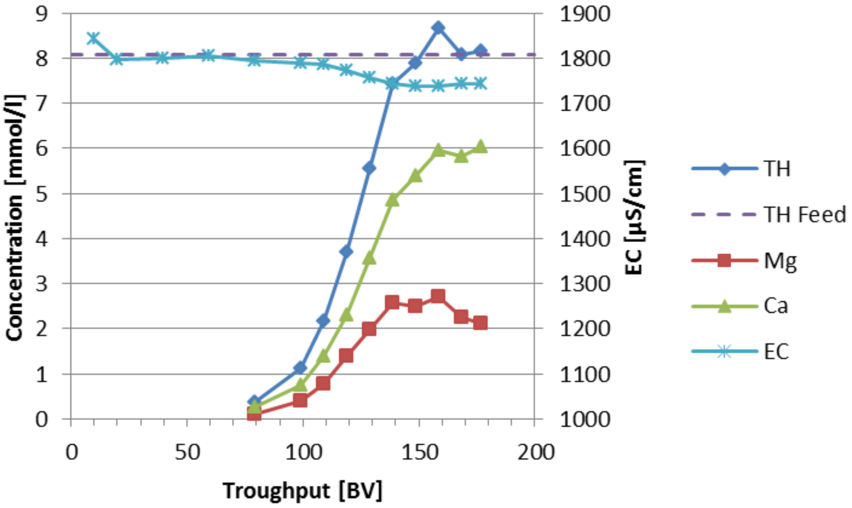


Figure 108: Breakthrough curve of run 2 at a flow of 29.77 m/h with a TH of 8 mmol/l.

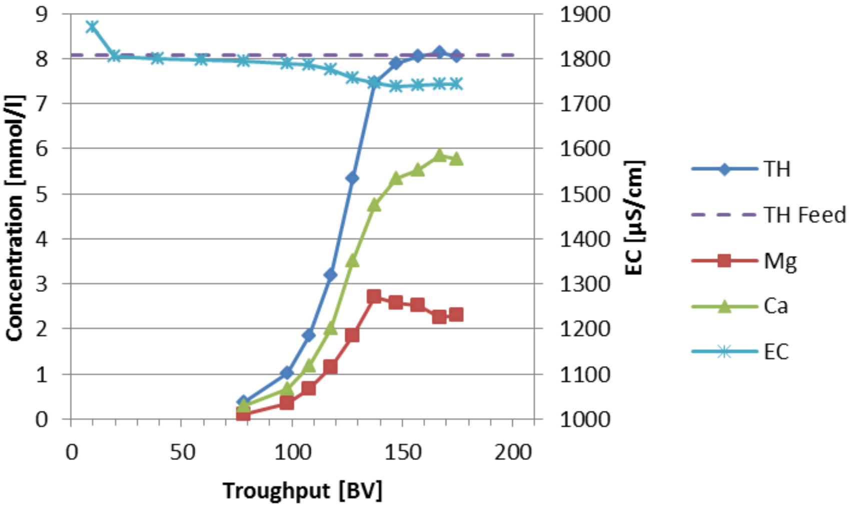


Figure 109: Breakthrough curve of run 3 at a flow of 29.44 m/h with a TH of 8 mmol/l.

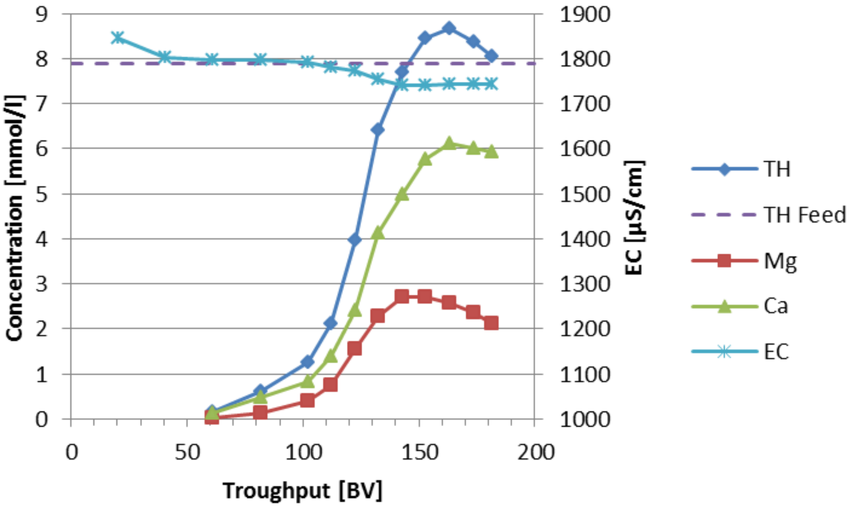


Figure 110: Breakthrough curve of run 4 at a flow of 30.61 m/h with a TH of 8 mmol/l.

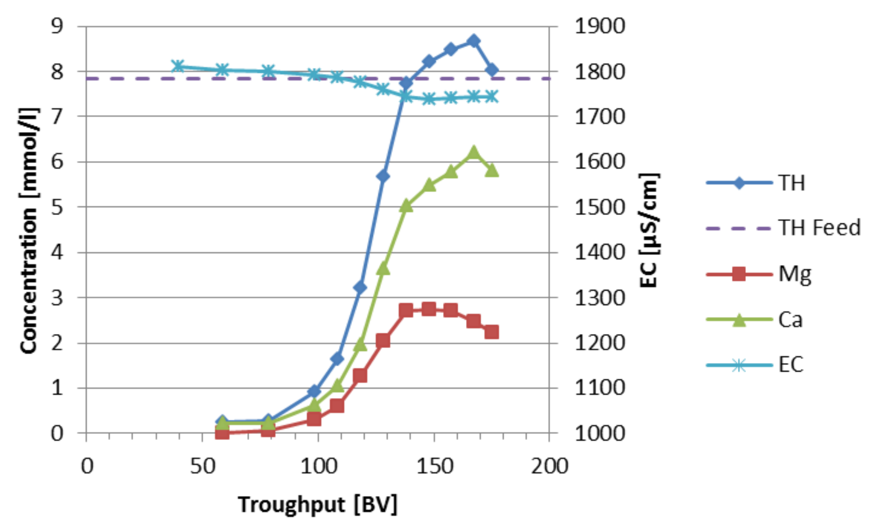


Figure 111: Breakthrough curve of run 5 at a flow of 29.57 m/h with a TH of 8 mmol/l.

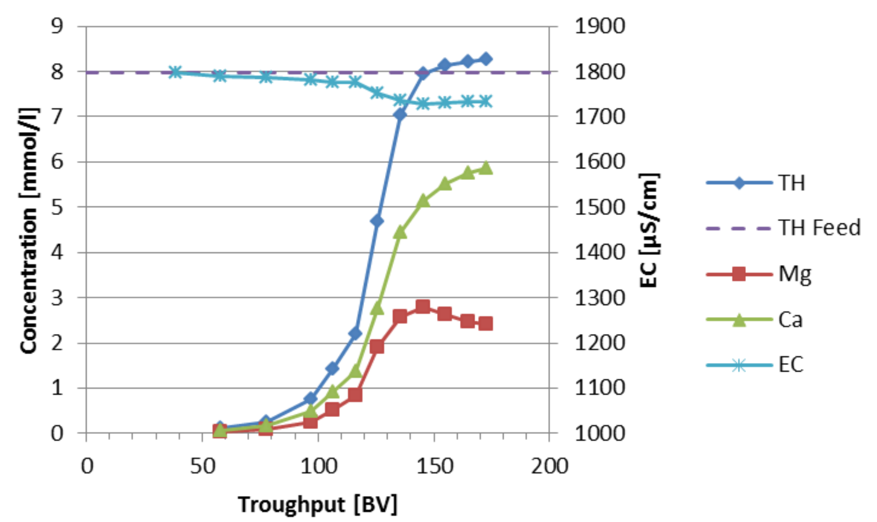


Figure 112: Breakthrough curve of run 6 at a flow of 29.05 m/h with a TH of 8 mmol/l.

The breakthrough curves are used with the trapezoid rule to determine the total amount that is loaded on the resin. Also the mixed samples are used to calculate the total amount that is loaded on the resin. The results of both determinations are given in the table below for the 6 sequential runs.

Table 63: Total amount loaded on the resin with the 6 loadings.

		Total amount loaded for each run					
		1 [mmol]	**2 [mmol]**	**3 [mmol]**	**4 [mmol]**	**5 [mmol]**	**6 [mmol]**
Trapezoid rule	TH	254.7	241.9	243.8	230.9	229.1	225.3
	Mg^{2+}	36.0	30.9	31.8	29.5	32.0	30.4
	Ca^{2+}	218.7	211.0	212.0	201.3	197.1	195.9
Mixed sample	TH	250.5	240.4	234.1	222.9	231.2	238.2
	Mg^{2+}	41.9	30.5	29.5	27.6	34.3	35.9
	Ca^{2+}	208.6	210.0	204.6	195.3	196.9	202.3

The results of the 6 runs to determine the capacity of the resin after the regeneration with different amounts of regenerant is given in the table below. The regeneration is performed at a flow velocity of 3.77 m/h, the loading at 29.7 m/h.

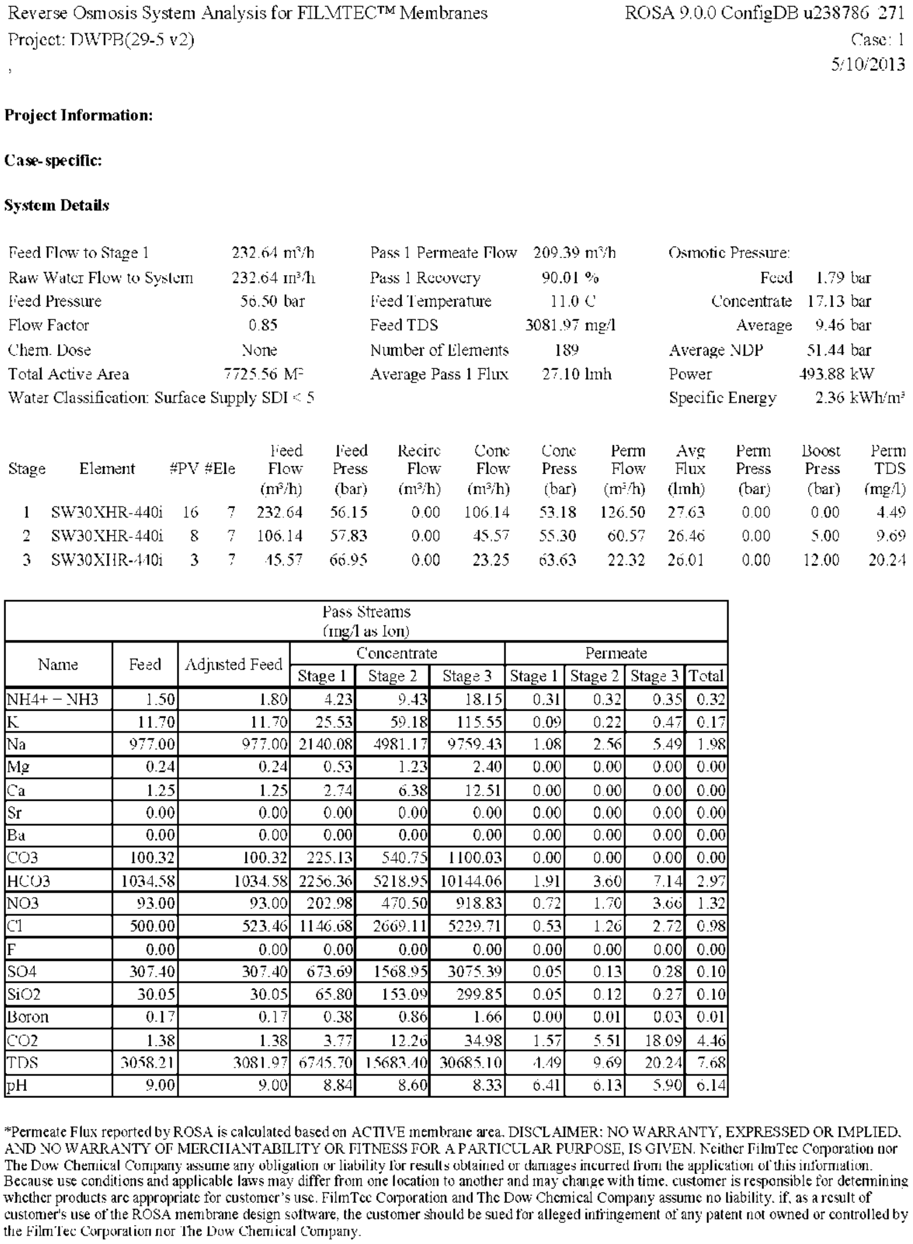
Table 64: Total amount loaded on the resin after the regeneration with different BV of R_{5-5}.

			Run					
			1	**2**	**3**	**4**	**5**	**6**
Amount of regenerant R_{5-5}		[BV]	10	8	6	4	2	1
Total amount loaded	TH	[mmol]	233.4	227.1	220.6	210.9	161.3	110.4
	Mg^{2+}	[mmol]	31.6	27.4	33.4	32.9	22.9	14.0
	Ca^{2+}	[mmol]	201.8	199.7	187.1	178.0	138.4	96.4

With these runs only a mixed sample is taken during the loading of the resin. The total amount loaded on the resin is calculated with the data form the analyses of the mixed samples.

D Results of the simulation with ROSA

D.1 Production of regenerant with RO concentrate from unit 1



Reverse Osmosis System Analysis for FILMTEC™ Membranes
Project: DWPB(29-5 v2)
,

ROSA 9.0.0 ConfigDB u238786_271
Case: 1
5/10/2013

Project Information:

Case-specific:

System Details

Feed Flow to Stage 1	232.64 m^3/h	Pass 1 Permeate Flow	209.39 m^3/h	Osmotic Pressure:	
Raw Water Flow to System	232.64 m^3/h	Pass 1 Recovery	90.01 %	Feed	1.79 bar
Feed Pressure	56.50 bar	Feed Temperature	11.0 C	Concentrate	17.13 bar
Flow Factor	0.85	Feed TDS	3081.97 mg/l	Average	9.46 bar
Chem. Dose	None	Number of Elements	189	Average NDP	51.44 bar
Total Active Area	7725.56 M^2	Average Pass 1 Flux	27.10 lmh	Power	493.88 kW
Water Classification: Surface Supply SDI < 5				Specific Energy	2.36 kWh/m^3

Stage	Element	#PV	#Ele	Feed Flow (m^3/h)	Feed Press (bar)	Recirc Flow (m^3/h)	Conc Flow (m^3/h)	Conc Press (bar)	Perm Flow (m^3/h)	Avg Flux (lmh)	Perm Press (bar)	Boost Press (bar)	Perm TDS (mg/l)
1	SW30XHR-440i	16	7	232.64	56.15	0.00	106.14	53.18	126.50	27.63	0.00	0.00	4.49
2	SW30XHR-440i	8	7	106.14	57.83	0.00	45.57	55.30	60.57	26.46	0.00	5.00	9.69
3	SW30XHR-440i	3	7	45.57	66.95	0.00	23.25	63.63	22.32	26.01	0.00	12.00	20.24

Pass Streams
(mg/l as Ion)

Name	Feed	Adjusted Feed	Concentrate			Permeate			
			Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3	Total
NH4+ − NH3	1.50	1.80	4.23	9.43	18.15	0.31	0.32	0.35	0.32
K	11.70	11.70	25.53	59.18	115.55	0.09	0.22	0.47	0.17
Na	977.00	977.00	2140.08	4981.17	9759.43	1.08	2.56	5.49	1.98
Mg	0.24	0.24	0.53	1.23	2.40	0.00	0.00	0.00	0.00
Ca	1.25	1.25	2.74	6.38	12.51	0.00	0.00	0.00	0.00
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO3	100.32	100.32	225.13	540.75	1100.03	0.00	0.00	0.00	0.00
HCO3	1034.58	1034.58	2256.36	5218.95	10144.06	1.91	3.60	7.14	2.97
NO3	93.00	93.00	202.98	470.50	918.83	0.72	1.70	3.66	1.32
Cl	500.00	523.46	1146.68	2669.11	5229.71	0.53	1.26	2.72	0.98
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO4	307.40	307.40	673.69	1568.95	3075.39	0.05	0.13	0.28	0.10
SiO2	30.05	30.05	65.80	153.09	299.85	0.05	0.12	0.27	0.10
Boron	0.17	0.17	0.38	0.86	1.66	0.00	0.01	0.03	0.01
CO2	1.38	1.38	3.77	12.26	34.98	1.57	5.51	18.09	4.46
TDS	3058.21	3081.97	6745.70	15683.40	30685.10	4.49	9.69	20.24	7.68
pH	9.00	9.00	8.84	8.60	8.33	6.41	6.13	5.90	6.14

*Permeate Flux reported by ROSA is calculated based on ACTIVE membrane area.

Design Warnings

-None-

Solubility Warnings

Langelier Saturation Index > 0
Stiff & Davis Stability Index > 0
SiO2 (% Saturation) > 100%
Antiscalants may be required. Consult your antiscalant manufacturer for dosing and maximum allowable system recovery.

Stage Details

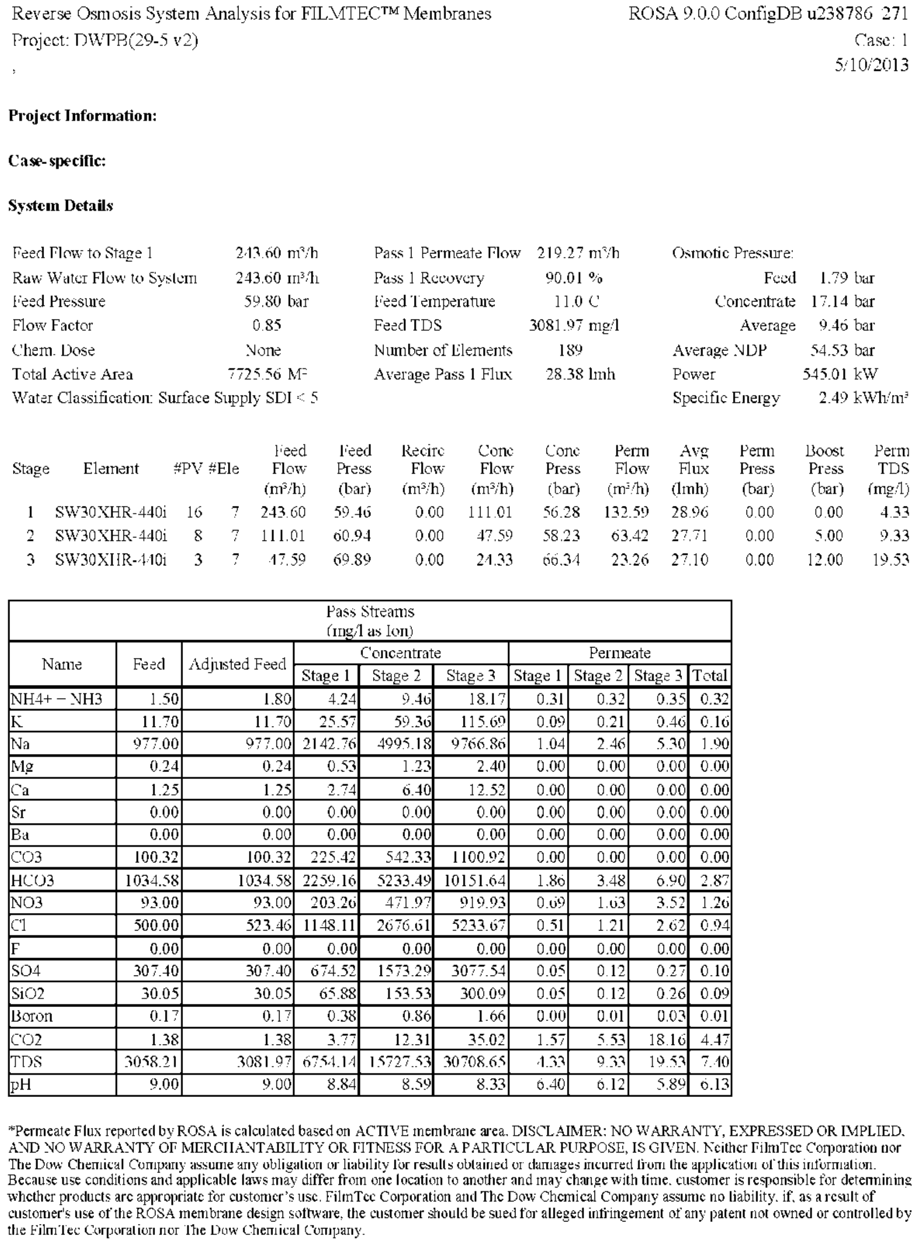
Stage 1 Element	Recovery	Perm Flow (m^3/h)	Perm TDS (mg/l)	Feed Flow (m^3/h)	Feed TDS (mg/l)	Feed Press (bar)
1	0.08	1.17	3.27	14.54	3081.97	56.15
2	0.09	1.16	3.55	13.37	3351.81	55.53
3	0.09	1.14	3.88	12.21	3669.14	54.98
4	0.10	1.13	4.29	11.07	4047.79	54.49
5	0.11	1.12	4.80	9.94	4507.39	54.08
6	0.12	1.10	5.46	8.82	5076.71	53.72
7	0.14	1.08	6.34	7.72	5799.61	53.42
Stage 2 Element	**Recovery**	**Perm Flow (m^3/h)**	**Perm TDS (mg/l)**	**Feed Flow (m^3/h)**	**Feed TDS (mg/l)**	**Feed Press (bar)**
1	0.09	1.15	6.41	13.27	6745.70	57.83
2	0.09	1.13	7.13	12.12	7386.00	57.29
3	0.10	1.11	8.02	10.98	8146.15	56.81
4	0.11	1.09	9.13	9.87	9061.60	56.39
5	0.12	1.06	10.56	8.78	10182.50	56.04
6	0.13	1.03	12.46	7.72	11580.06	55.74
7	0.15	0.99	15.08	6.69	13360.93	55.50
Stage 3 Element	**Recovery**	**Perm Flow (m^3/h)**	**Perm TDS (mg/l)**	**Feed Flow (m^3/h)**	**Feed TDS (mg/l)**	**Feed Press (bar)**
1	0.08	1.17	13.79	15.19	15683.40	66.95
2	0.08	1.14	15.36	14.02	16985.72	66.28
3	0.09	1.11	17.23	12.89	18481.24	65.68
4	0.09	1.07	19.52	11.78	20210.58	65.15
5	0.10	1.03	22.32	10.71	22224.08	64.68
6	0.10	0.99	25.85	9.68	24586.16	64.28
7	0.11	0.94	30.34	8.69	27375.11	63.93

Scaling Calculations

	Raw Water	Adjusted Feed	Concentrate
pH	9.00	9.00	8.33
Langelier Saturation Index	0.14	0.14	1.42
Stiff & Davis Stability Index	0.25	0.25	0.64
Ionic Strength (Molal)	0.05	0.05	0.50
TDS (mg/l)	3058.21	3081.97	30685.10
HCO3	1034.58	1034.58	10144.06
CO2	1.38	1.38	34.96
CO3	100.32	100.32	1100.03
CaSO4 (% Saturation)	0.05	0.05	0.93
BaSO4 (% Saturation)	0.00	0.00	0.00
SrSO4 (% Saturation)	0.00	0.00	0.00
CaF2 (% Saturation)	0.00	0.00	0.00
SiO2 (% Saturation)	15.49	15.49	231.00
Mg(OH)2 (% Saturation)	0.01	0.01	0.00

To balance: 23.46 mg/l Cl added to feed.

D.2 Production of regenerant with RO concentrate from unit 2



Reverse Osmosis System Analysis for FILMTEC™ Membranes — ROSA 9.0.0 ConfigDB u238786_271
Project: DWPB(29-5 v2) — Case: 1
, — 5/10/2013

Project Information:

Case-specific:

System Details

Feed Flow to Stage 1	243.60 m³/h	Pass 1 Permeate Flow	219.27 m³/h	Osmotic Pressure:	
Raw Water Flow to System	243.60 m³/h	Pass 1 Recovery	90.01 %	Feed	1.79 bar
Feed Pressure	59.80 bar	Feed Temperature	11.0 C	Concentrate	17.14 bar
Flow Factor	0.85	Feed TDS	3081.97 mg/l	Average	9.46 bar
Chem. Dose	None	Number of Elements	189	Average NDP	54.53 bar
Total Active Area	7725.56 M²	Average Pass 1 Flux	28.38 lmh	Power	545.01 kW
Water Classification: Surface Supply SDI < 5				Specific Energy	2.49 kWh/m³

Stage	Element	#PV	#Ele	Feed Flow (m³/h)	Feed Press (bar)	Recirc Flow (m³/h)	Conc Flow (m³/h)	Conc Press (bar)	Perm Flow (m³/h)	Avg Flux (lmh)	Perm Press (bar)	Boost Press (bar)	Perm TDS (mg/l)
1	SW30XHR-440i	16	7	243.60	59.46	0.00	111.01	56.28	132.59	28.96	0.00	0.00	4.33
2	SW30XHR-440i	8	7	111.01	60.94	0.00	47.59	58.23	63.42	27.71	0.00	5.00	9.33
3	SW30XHR-440i	3	7	47.59	69.89	0.00	24.33	66.34	23.26	27.10	0.00	12.00	19.53

Pass Streams
(mg/l as Ion)

Name	Feed	Adjusted Feed	Concentrate			Permeate			
			Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3	Total
NH4+ − NH3	1.50	1.80	4.24	9.46	18.17	0.31	0.32	0.35	0.32
K	11.70	11.70	25.57	59.36	115.69	0.09	0.21	0.46	0.16
Na	977.00	977.00	2142.76	4995.18	9766.86	1.04	2.46	5.30	1.90
Mg	0.24	0.24	0.53	1.23	2.40	0.00	0.00	0.00	0.00
Ca	1.25	1.25	2.74	6.40	12.52	0.00	0.00	0.00	0.00
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO3	100.32	100.32	225.42	542.33	1100.92	0.00	0.00	0.00	0.00
HCO3	1034.58	1034.58	2259.16	5233.49	10151.64	1.86	3.48	6.90	2.87
NO3	93.00	93.00	203.26	471.97	919.93	0.69	1.63	3.52	1.26
Cl	500.00	523.46	1148.11	2676.61	5233.67	0.51	1.21	2.62	0.94
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO4	307.40	307.40	674.52	1573.29	3077.54	0.05	0.12	0.27	0.10
SiO2	30.05	30.05	65.88	153.53	300.09	0.05	0.12	0.26	0.09
Boron	0.17	0.17	0.38	0.86	1.66	0.00	0.01	0.03	0.01
CO2	1.38	1.38	3.77	12.31	35.02	1.57	5.53	18.16	4.47
TDS	3058.21	3081.97	6754.14	15727.53	30708.65	4.33	9.33	19.53	7.40
pH	9.00	9.00	8.84	8.59	8.33	6.40	6.12	5.89	6.13

*Permeate Flux reported by ROSA is calculated based on ACTIVE membrane area. DISCLAIMER: NO WARRANTY, EXPRESSED OR IMPLIED, AND NO WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE, IS GIVEN. Neither FilmTec Corporation nor The Dow Chemical Company assume any obligation or liability for results obtained or damages incurred from the application of this information. Because use conditions and applicable laws may differ from one location to another and may change with time, customer is responsible for determining whether products are appropriate for customer's use. FilmTec Corporation and The Dow Chemical Company assume no liability, if, as a result of customer's use of the ROSA membrane design software, the customer should be sued for alleged infringement of any patent not owned or controlled by the FilmTec Corporation nor The Dow Chemical Company.

Design Warnings

-None-

Solubility Warnings

Langelier Saturation Index > 0
Stiff & Davis Stability Index > 0
SiO2 (% Saturation) > 100%
Antiscalants may be required. Consult your antiscalant manufacturer for dosing and maximum allowable system recovery.

Stage Details

Stage 1 Element	Recovery	Perm Flow (m^3/h)	Perm TDS (mg/l)	Feed Flow (m^3/h)	Feed TDS (mg/l)	Feed Press (bar)
1	0.08	1.23	3.17	15.23	3081.97	59.46
2	0.09	1.21	3.43	14.00	3351.76	58.79
3	0.09	1.20	3.74	12.78	3669.14	58.20
4	0.10	1.18	4.13	11.59	4048.00	57.68
5	0.11	1.17	4.62	10.40	4508.13	57.24
6	0.13	1.16	5.25	9.23	5078.58	56.86
7	0.14	1.14	6.10	8.08	5803.67	56.54

Stage 2 Element	Recovery	Perm Flow (m^3/h)	Perm TDS (mg/l)	Feed Flow (m^3/h)	Feed TDS (mg/l)	Feed Press (bar)
1	0.09	1.20	6.19	13.88	6754.14	60.94
2	0.09	1.18	6.88	12.67	7394.58	60.35
3	0.10	1.16	7.72	11.49	8155.22	59.84
4	0.11	1.14	8.79	10.33	9071.79	59.40
5	0.12	1.11	10.16	9.19	10194.45	59.02
6	0.13	1.08	11.98	8.07	11596.60	58.71
7	0.15	1.04	14.49	6.99	13386.62	58.44

Stage 3 Element	Recovery	Perm Flow (m^3/h)	Perm TDS (mg/l)	Feed Flow (m^3/h)	Feed TDS (mg/l)	Feed Press (bar)
1	0.08	1.21	13.36	15.86	15727.53	69.89
2	0.08	1.18	14.86	14.65	17025.65	69.17
3	0.09	1.15	16.65	13.47	18515.91	68.53
4	0.09	1.11	18.83	12.32	20239.85	67.97
5	0.10	1.08	21.51	11.20	22247.90	67.47
6	0.10	1.03	24.86	10.13	24605.54	67.04
7	0.11	0.98	29.13	9.09	27393.10	66.67

Scaling Calculations

	Raw Water	Adjusted Feed	Concentrate
pH	9.00	9.00	8.33
Langelier Saturation Index	0.14	0.14	1.42
Stiff & Davis Stability Index	0.25	0.25	0.64
Ionic Strength (Molal)	0.05	0.05	0.50
TDS (mg/l)	3058.21	3081.97	30708.65
HCO3	1034.58	1034.58	10151.64
CO2	1.38	1.38	35.01
CO3	100.32	100.32	1100.92
CaSO4 (% Saturation)	0.05	0.05	0.93
BaSO4 (% Saturation)	0.00	0.00	0.00
SrSO4 (% Saturation)	0.00	0.00	0.00
CaF2 (% Saturation)	0.00	0.00	0.00
SiO2 (% Saturation)	15.49	15.49	231.23
Mg(OH)2 (% Saturation)	0.01	0.01	0.00

To balance: 23.46 mg/l Cl added to feed.

Delft University of Technology
Faculty of Civil Engineering and Geosciences
Department of Water Management
Section of Sanitary Engineering
Stevinweg 1
2628 CN Delft

www.sanitaryengineering.tudelft.nl