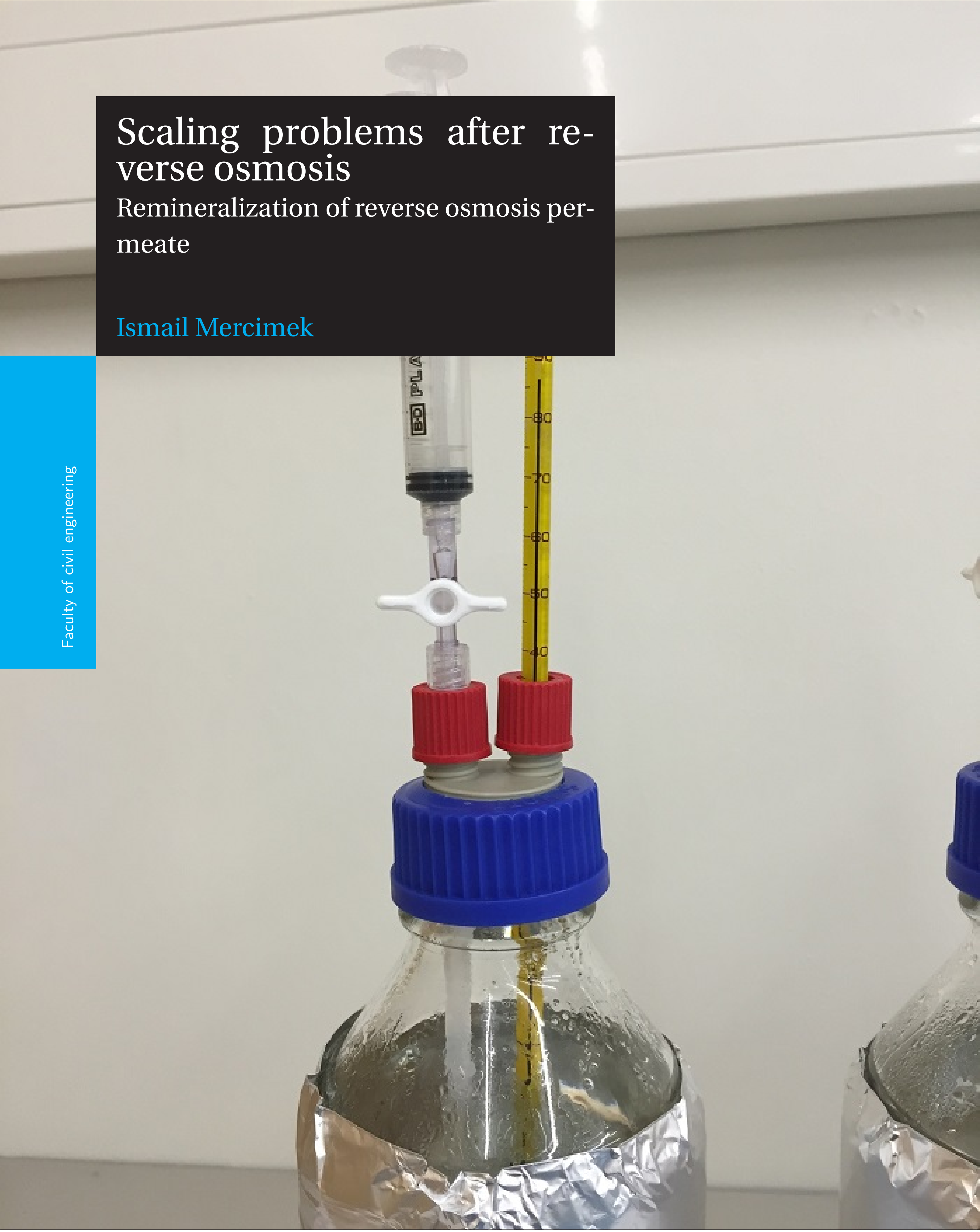

Scaling problems after reverse osmosis

Remineralization of reverse osmosis permeate

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Challenge the future

SCALING PROBLEMS AFTER REVERSE OSMOSIS

REMINERALIZATION OF REVERSE OSMOSIS PERMEATE

by

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Student number 4182804

in partial fulfillment of the requirements for the degree of

Bachelor of Science
in Civil Engineering

at the Delft University of Technology,

Supervisors:	Dr. ir. B. Heijman,	TU Delft
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An electronic version of this thesis is available at `http://blackboard.tudelft.nl`.

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Technology

PREFACE

This thesis is submitted in partial fulfilment of the requirements for a Bachelor's Degree in Civil engineering for the author and is the first step on an academic level in water treatment. Water is an essential building block of our lives as human beings and therefore, my choice on this subject was rather easy for me. The literature of this thesis is based on earlier studies and thus have I placed references to the articles on which assumptions and conclusions are based.

This report is about the earlier scaling process that occurs in reverse osmosis permeate and is meant as a starting point for a series of experiments in the same line. Since this thesis is written as the final thesis of the bachelor's degree in Civil Engineering, the text is primarily aimed at the teachers of the Delft University of Technology. However, I hope it will be of interest for any student or non-student interested in water treatment in general and scaling problems in particular.

I would like to thank Amir H.Haidari deeply for his time and support during this thesis. His integrity and dedication as well as his expertise on membrane operations have contributed to a positive memory in my life.

Ismail Mercimek
Delft, June 2015

CONTENTS

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INTRODUCTION

Throughout the history of mankind, reliable access to fresh water has been one of the fundamental pillars on which society is build. It is a necessary prerequisite for ensuring food security and a well-functioning system of public health. However, only a small fraction of the world's water, about 2.5 percent is available as fresh water of which only 0.6 percent is accessible for use, the rest being located at the poles[1, 2]. This water satisfied the needs of men during the millennia, however due to major environmental change and social conflicts, the shortage of portable water will be a major problem in the coming decades. The supply of fresh water is finite and precipitation can not recover these sources of water due to the growing demand of humans. Therefore, different methods are used to produce fresh water from sea and brackish water. One will find that many European countries use membrane operations and almost all the recently installed desalination plants use reverse osmosis, RO [3].

Membrane operations are processes which separate the salts from the solutions and are classified based on their driving force into four categories: Electrical forces, pressure forces, separation by concentration and heat gradients. Pressure driven membrane is generally used in drinking and waste water treatment and dates to about a 100 years ago [4]. The pressure driven membrane can be categorized based on their rejection ability into four categories: Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO)[5]. MF and UF use microporous membranes to remove particulate matter simply by sieving on the size of the particles[6]. Together with the particulate matter, turbidity and microorganisms are also removed. However, these two systems do not remove dissolved particles such as ions. RO and NF do remove these dissolved particles because of their semi-permeable membranes and diffusion controlled separation process[6]. NF removes close to all particles, except for the monovalent ions whilst RO removes even most of the monovalent particles, such as natrium (Na^+) and kalium (K^+), leaving pure water as permeate. Figure 1.1 shows which membranes exclude which particles.

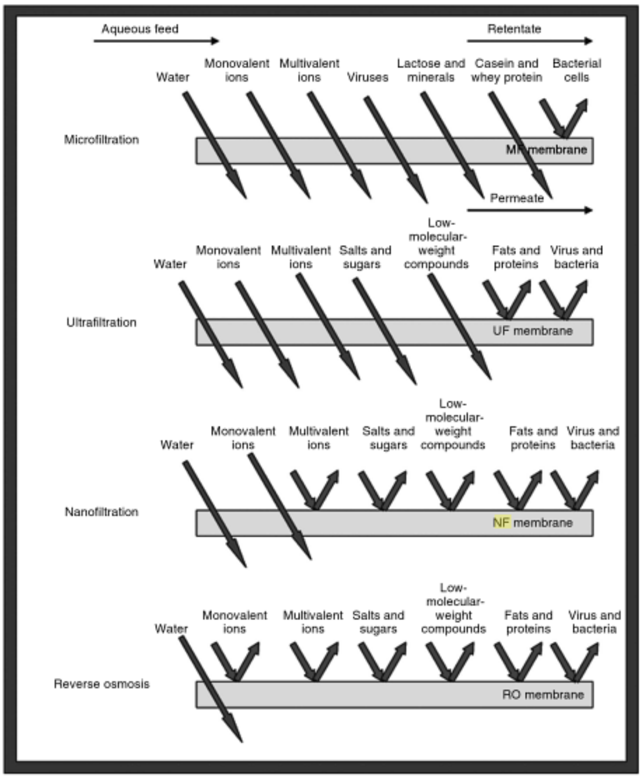


Figure 1.1: Exclusion of various compounds through different membrane processes[7]

1.1. REVERSE OSMOSIS

Osmosis occurs when two fluids are separated by a semi-permeable layer, so only water can move through the layer. The osmotic pressure is the hydro-static pressure that must be applied to the more concentrated solution to stop the net flow of water across a semipermeable membrane separating solutions of different concentrations[8]. Reverse osmosis is a pressure driven technique which by applying a difference in pressure all components except water are forced through the membrane. The process of reverse osmosis consists of a pre and post treatment respectively before and after the RO module.

1.1.1. PRE-TREATMENT

Pre-treatment is considered the key to a successful reverse osmosis process. All the organic, colloidal and biological matter are removed from the feed water before entering the RO module. This prevents the module from fouling and extends the service span[9].

1.1.2. REVERSE OSMOSIS MODULE

In this step of the treatment, the actual reverse osmosis process occurs. A flow of water Q_f with a concentration C_f enters the module after which the separation takes place. The water that is pressed through the membrane is called the permeate, Q_p, and has a concentration C_p. The water, along with the substrate, that did not pass through the membrane is exported separately and is called the concentrate with flow Q_c and a concentration C_c. The concentration in the permeate C_p is significantly less than the concentration C_f, however the percentage water that flows through the membrane is also very small. About 10 to 15 percent percent flows through the membrane and becomes the permeate, and the surplus becomes the concentrate. There is a simple mass balance for this system depicted in figure 1.3 along with equations 1.1 and 1.2:

$$Q_f = Q_c + Q_p \tag{1.1}$$

$$Q_f * C_f = Q_c * C_c + Q_p * C_p \tag{1.2}$$

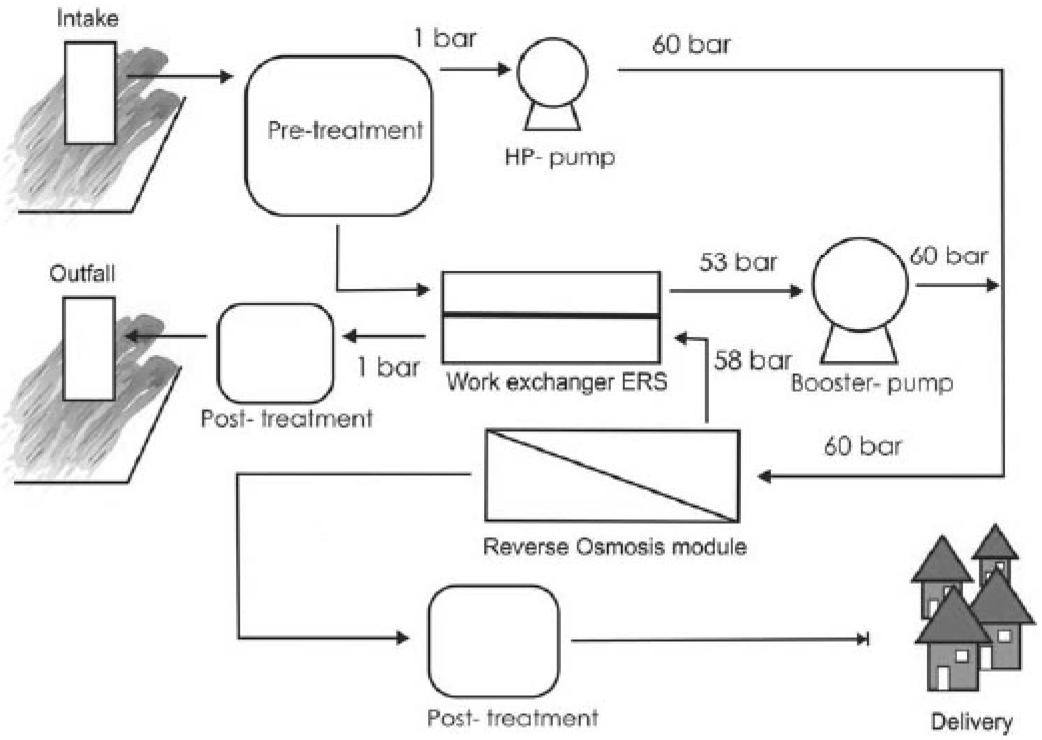


Figure 1.2: Simplified reverse osmosis scheme[3]

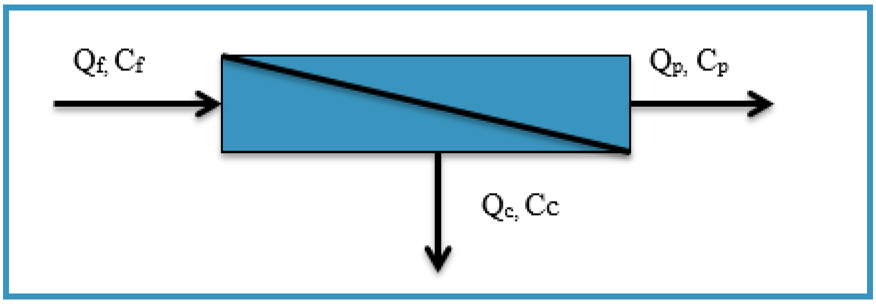


Figure 1.3: Reverse osmosis module[10]

1.1.3. POST-TREATMENT

The permeate has a very low concentration of particles and can be called pure water. However, in order to meet the requirements of standard drinking water, as is presented by the World Health organization, a remineralization process is required. To attain the requirement for drinking water, a certain amount of calcium is added. A typical value for standard drinking water in the Netherlands is 1-1.5 mmol of calcium ions[11]. This value varies for different countries and different application of the water. For instance, the requirement for marine use are not as strict as for drinking water.

Adding calcium ions prevents the corrosive working of the pure water on transportation pipes and instruments. At this point the water is completely pure, however during the remineralization process reluctantly certain bacteria's or impurities get in the permeate which have a negative effect on the transport pipelines for example bacteria growth. To prevent such situations, generally, the permeate water is passed through an UV-disinfection system after the remineralization process. The corrosive working of the water is typically expressed in the Langelier saturation index LSI[12]. This index characterizes if the water is aggressive and will have corrosive working. When the LSI index is positive the water will have a certain deposition of a calcium layer. This state is also called scaling. When the LSI index is zero, the water will either be aggressive or have scaling. Depositing a layer of calcium is not necessarily a negative quality, the layer can work as a protection for the pipelines.

Therefore a slightly positive LSI value is preferred for the permeate[13]. The LSI is defined as

$$LSI = pH - pH_s \tag{1.3}$$

1.1.4. REMINERALIZATION PROCESS

There are several remineralization processes of which the dissolution of calcium carbonate with carbondioxide in water is the most effective and widespread. In order to attain the required amount of calcium ions, the permeate water goes through a calcium carbonate column and CO_2 is added. For standard drinking water the calcium concentration should be between 1 and 1.5 mmol. The chemical reaction which occurs when the permeate passes through the column is as follows:

$$CO_2 + CaCO_3 + H_2O \rightarrow Ca(HCO_3)_2$$

CO_2 is added to attain a higher concentration of Ca^{2+} ions. Sherzad Anwari's research showed that the flow direction, up or downwards, is not relevant for the effect of the remineralization process[10].

1.2. STUDY OBJECTIVE

Water attained from a reverse osmosis treatment has shown to have an earlier scaling stage under higher temperatures than water from conventional treatment plants that has the same Ca^{2+} concentration. This study investigates why this early scaling happens. Presumed is that the the absence of materials removed by RO, such as humic acids, sodium bicarbonate and trisodium phosphate is the main cause of this early scaling. Therefore, experiments will be done with these materials added to the permeate.

2

METHODOLOGY

The study consists of a modeling part and an experimental part. The model is made in PHREEQC and is used to compare the values generated by the model and the values which are measured during the experiments. The experiments are all done in the *waterlab* at TU Delft.

2.1. MODELING WITH PHREEQC

PHREEQC is a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations[14]. In this study PHREEQC is used to compare the Ca^{2+} concentrations retrieved through a model in PHREEQC and the values obtained through measuring the electrical conductivity *EC* of the samples after they passed through the column. The *EC* is directly related to the concentration of calcium ions in the suspension. With the obtained data, a comparison is made between the values to analyze the accuracy of the model and the accuracy of the equipment. Furthermore, simple comparisons are made between *pH* values obtained through our model in PHREEQC, values received from Hatenboerwater BV and the values obtained through measuring with *pH* measuring equipment.

2.2. EXPERIMENT SETUP

Hatenboerwater BV has made a setup to investigate the scaling problems of boilers and heating machines which occur when permeate of the reverse osmosis treatment is used. As Hatenboerwater BV is a company mainly interested in the usage of RO in maritime and offshore, the setup resembles the remineralization of reverse osmosis used on small ships.

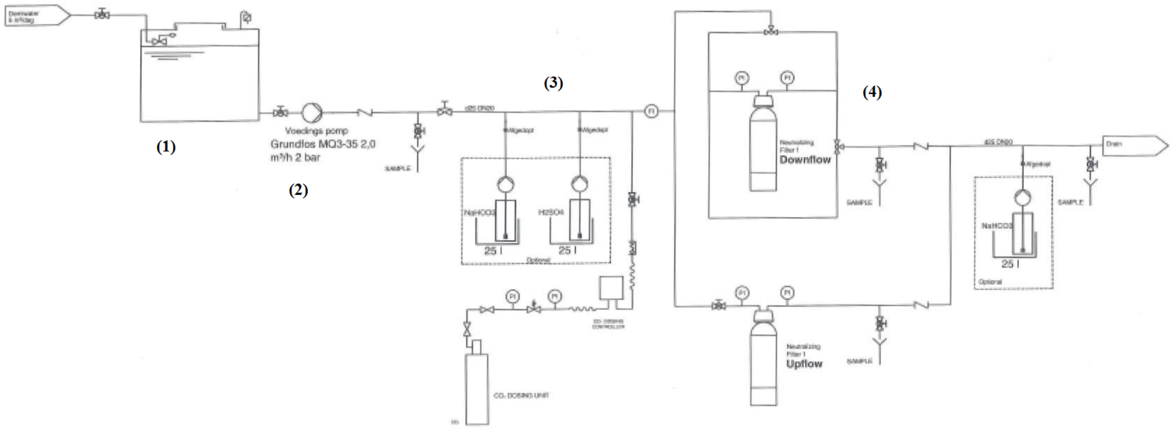


Figure 2.1: Remineralisation process at the Hatenboerwater BV complex[15]

Figure 2.1 depicts this setup. The permeate water of RO treatment enters a tank (1) which maintains the water level constant. A control valve (2), modifies the waterflow, which is an essential variable in this setup. The water is pumped into the demineralization tank (3) where additional substances, such as carbon dioxide, bicarbonate and sulfuric acid, can be added to the water. The water direction can be chosen (4) after which samples are taken. However for this research exclusively downward waterflow samples are analyzed. Hatenboerwater BV provides these samples to TU delft in bottles of 2.5 liters, along with their own measurements of the *pH*, *hardness* and the room temperature.

The bottles of 2.5 L are sampled to two glass bottles of 1 L liter, one bottle without anti scaling and the other bottle with anti scaling. Along with the sample water, sand disinfected with ethanol and dried in an oven is added to the glass bottle. The sand in the glass resembles the heating elements of a heater and is needed for acceleration of precipitation of calcium carbonate [10]. The weight of the sand before and after heating the sample is measured to determine the scaling on the sand. The water in the glass bottles is heated to 90 degrees Celsius and a magnet is constantly rotating in the bottle, to ensure that water temperature is homogeneously distributed. The sample is closed with a system as depicted in figure 2.2. The thermometer is used to measure temperature constantly and the syringe is used to take samples. The syringe is connected to the bottle via a tap, which is meant to prevent evaporation of CO_2 during the experiment.

Vial samples of the heated permeate are taken every 2.5 hours for a period of three to four days, giving a total of at least twelve measurements. Finally, these vial samples are labeled and diluted by factor ten so the *EC* can be measured with an ion chromatography machine, IC. The IC separates and measures the inorganic and organic concentrations of certain cations and anions[16]. Measuring the inorganic cations suffices to determine the CA^{2+} concentration required in this study. The IC machine separates the cations and ions due to their affinity to the ion exchanger. The eluent ions are separated in species of low conductivity and consequently the eluate can be detected with a conductivity monitor[16]. Each peak on the conductivity monitor represents a certain concentration of calcium.

The auto sampler of the IC measures a total of 56 vials at once. Three of these vials have a known calcium concentration, namely 10, 20 and 50 mg/L, and are called *standards*. These standards are used to control and calibrate the IC measurements. Furthermore, after several vial samples taken from the permeate water of Hatenboerwater BV, a *blanc* sample vial is used. These *blancs* prevent contamination of the IC meter and is used as a measure of proper working of the IC.

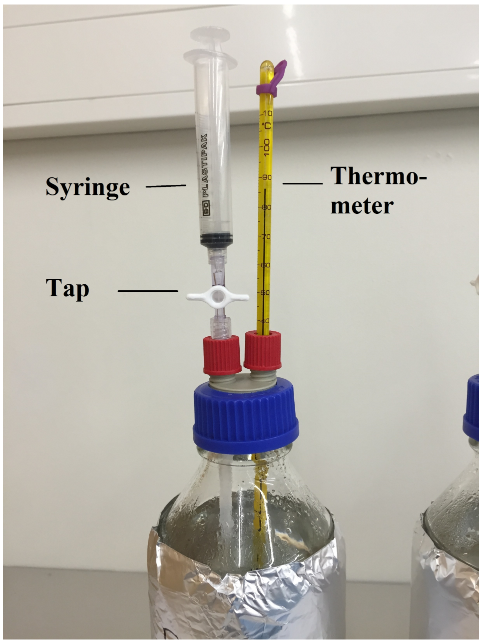


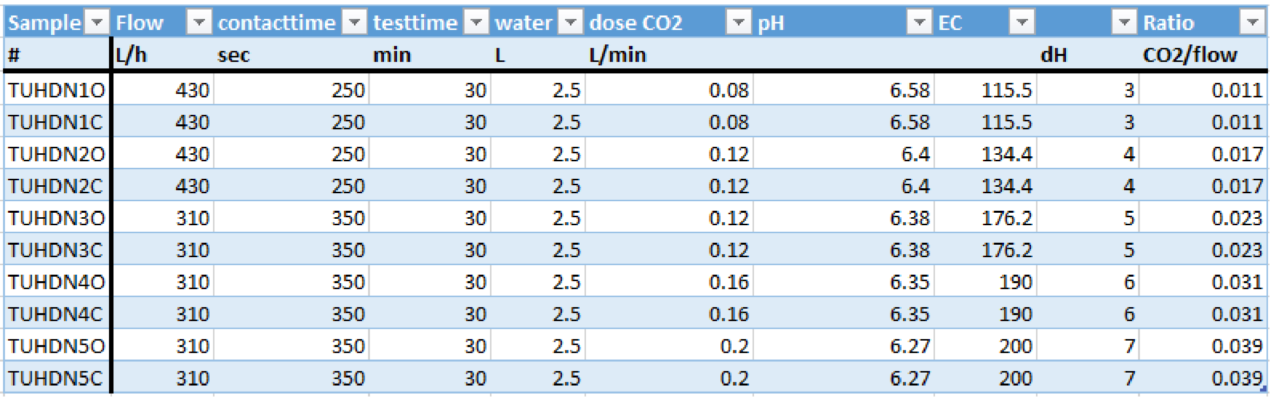
Figure 2.2: TU Delft sample glass bottle

3

RESULTS AND DISCUSSION

In this chapter, the data gained from the IC is plotted in several figures and subsequently analysed. All graphs in this chapter describe the measurements of the calcium concentration as measured with the IC during the process. The horizontal axis denotes the time in hours at which the different samples are taken. The first sample is taken at t = 0 while the sample was at room temperature, 21.8 degrees Celsius on average. All other samples are taken after attaining a constant temperatures of approximately 90 degrees Celsius. The vertical axis denotes the concentration of calcium in milligrams per litre. The graphs legends show which samples are depicted in the figure, and all samples are named separately. The continues lines represent the measurements of the samples with no anti scaling added and the dashed lines represent the samples which have 1 milligrams of trisodium phosphate (Na_3PO_4) added to the one litre samples.

The samples received from Hatenboerwater BV have varying flow rates and CO_2 dosing and therefore, the samples have a different calcium concentration. The sample data is defined in figure 3.1 for each sample separately. The 'O' and 'C' indicates whether the sample is 'open' and therefore required to be measured within a short period after making the sample, or 'closed' and hence measurable after a few weeks. Measuring the sample after a few weeks will certainly affect the measurements due to CO_2 having enough time to evaporate. There will be made no distinction between the open and closed samples except when results are exclusively discussed. When referred to sample 1, both TUHDN1O and TUHDN1C are intended.



Sample	Flow	contacttime	testtime	water	dose CO2	pH	EC		Ratio
#	L/h	sec	min	L	L/min			dH	CO2/flow
TUHDN1O	430	250	30	2.5	0.08	6.58	115.5	3	0.011
TUHDN1C	430	250	30	2.5	0.08	6.58	115.5	3	0.011
TUHDN2O	430	250	30	2.5	0.12	6.4	134.4	4	0.017
TUHDN2C	430	250	30	2.5	0.12	6.4	134.4	4	0.017
TUHDN3O	310	350	30	2.5	0.12	6.38	176.2	5	0.023
TUHDN3C	310	350	30	2.5	0.12	6.38	176.2	5	0.023
TUHDN4O	310	350	30	2.5	0.16	6.35	190	6	0.031
TUHDN4C	310	350	30	2.5	0.16	6.35	190	6	0.031
TUHDN5O	310	350	30	2.5	0.2	6.27	200	7	0.039
TUHDN5C	310	350	30	2.5	0.2	6.27	200	7	0.039

Figure 3.1: The samples obtained from Hatenboerwater BV

The flow rates of samples 1 and 2 through the calcium carbonate column at the Hatenboerwater BV complex are higher than the flow rates of samples 3 to 5 which results in a shorter retention time (contacttime). Samples 1 and 2 also have a lower dose of CO_2 and therefore, less calcium will equilibrate with CO_2 in these samples. A smaller ratio between flow rate and CO_2 dosing is used for the samples than earlier studies[10]. The CO2 dosing to flow ratio for samples 1 to 5 are respectively: 0.011, 0.017, 0.023, 0.031 and 0.039. As shown in Sherzad Anwari's study, CO_2 does have a rather large effect on the reaction with calcium. The calcium concentrations are thus low in sample 1 and increase over the different samples with the highest (initial) calcium concentration in sample number 5.

3.1. OPEN SAMPLE SET

The open sample set consists of drinking water (DW) and all the open TUHDN samples. The drinking water is taken from the tap in the *Waterlab*, which is supplied by Evides waterbedrijf, a water company in the Netherlands.

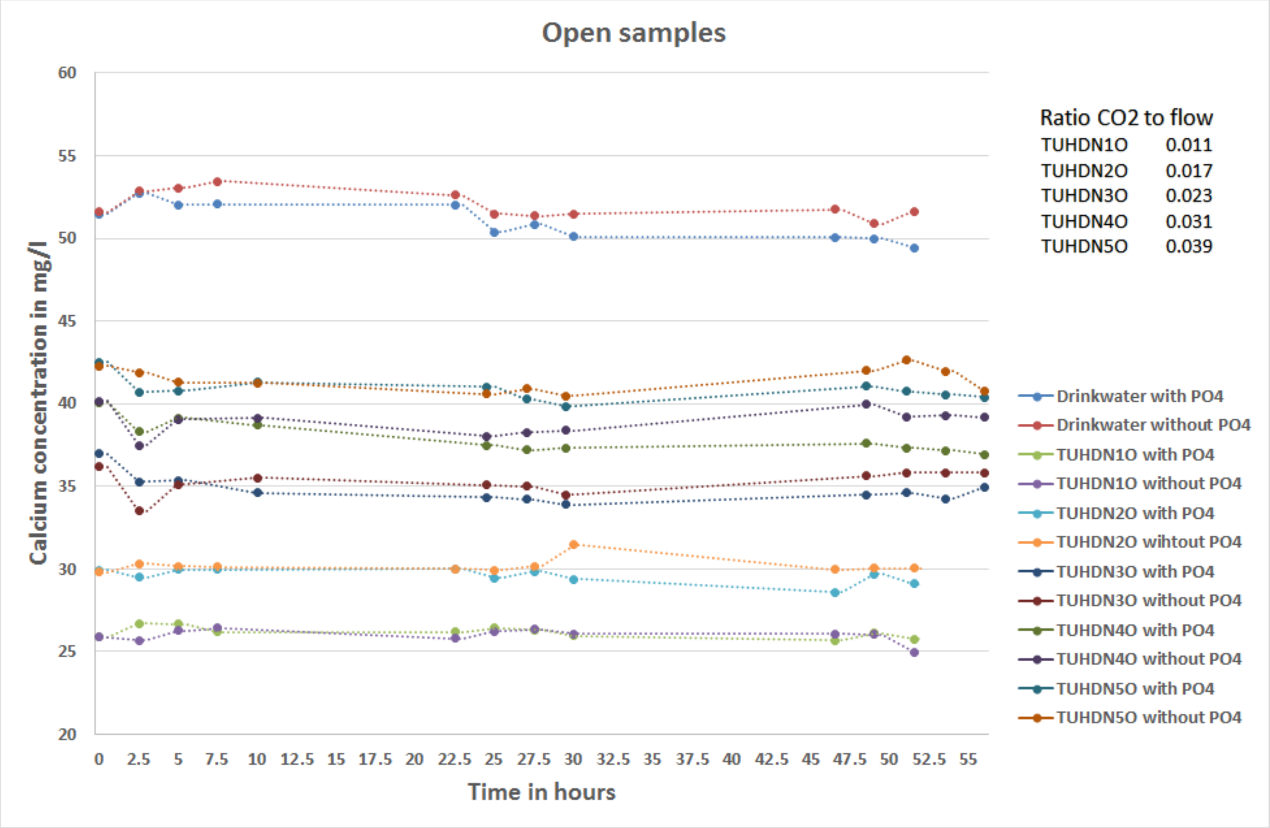


Figure 3.2: IC measurements of open samples

Figure 3.2 depicts the open sample set. The calcium concentrations of the ten Hatenboerwater samples are significantly less than the concentration in drinking water, this is due to the retention time in which the samples are made at the Hatenboerwater BV complex. As expected, drinking water has a calcium precipitation after some time of heating. After 22.5 hours one can observe a drop in both lines of the DW samples, which indicates calcium precipitation. The TUHDN1O and TUHDN2O have a lower concentration of calcium, 25 and 30 respectively, as was expected due to the shorter retention time and CO_2 dosing. Both these samples have a constant calcium concentration during the heating process and no precipitation as is observed at the DW samples takes place.

The TUHDN3O, TUHDN4O and TUHDN5O all have a different (initial) calcium concentration due to the retention time of these samples in the $CaCO_3$ column at the Hatenboerwater complex. The six samples all have a similar flow and three observations are relevant here: Firstly, the decrease of the calcium concentration in the first five hours of the heating process is remarkable. In all of the samples the calcium concentration dropped significantly in the first five hours which indicates calcium precipitation. The precipitation in sample TUHDN3O with phosphate is depicted in figure 3.3 and similar precipitation is observed in the other samples, regardless if phosphate was added or not. As observed in the first sample set, drinking water had precipitation after 22.5 hours. The early scaling property of reverse osmosis permeate is observed with this sample set. Secondly, there is no significant difference between samples with and without phosphate. Approximately the same amount of precipitation happens after the same time for samples with phosphate as for samples without phosphate. Thirdly, After 29.5 hours a sudden increase in the calcium concentration is observed, this is due to an error in the IC which caused the IC to give higher concentrations than reality. However, the course of the concentration is still of benefit for this research.

Figure 3.3: Calcium precipitation as observed in TUHDN3O with phosphate

3.2. CLOSED SAMPLE SET

Figure 3.4 depicts the second sample set which consists of two drinking water, two TUHDN1C and two TUHDN2C samples. Again, drinking water has an observable calcium precipitation, this time 29 hours after the heating was initiated. The TUHDN1C and TUHDN2C have a similar course as TUHDN1O and TUHDN2O samples, however, after 29 hours a drop in the calcium concentration is observed. The difference between the 'O' and 'C' samples is that the C samples were made the day of the measurement. The added CO_2 thus had no time to completely evaporate which aided the calcium precipitation. The samples with phosphate seem to precipitate less than the samples without phosphate, however the scaling still happens at the same time. The scaling that occurred can again be seen in the various parts of the experiment materials as depicted in the picture in figure 3.5 below.

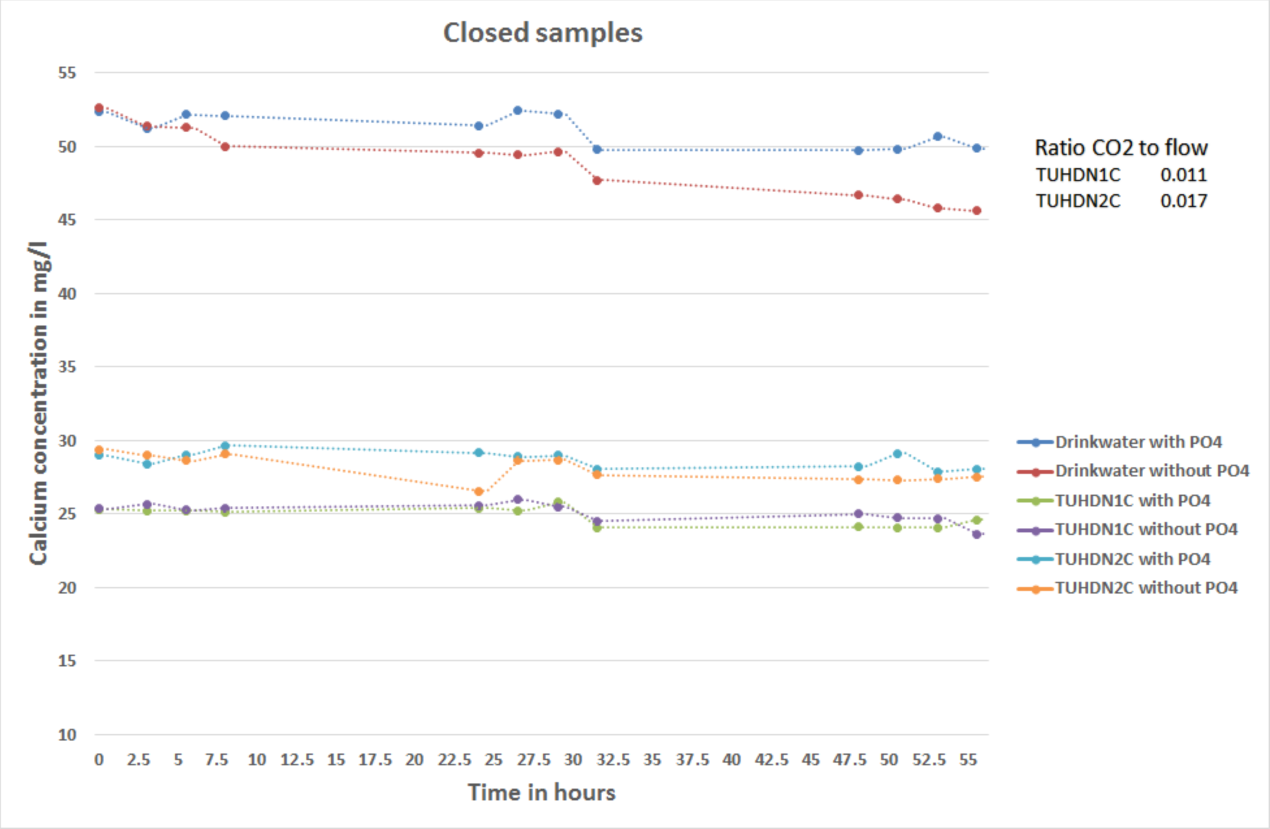


Figure 3.4: IC measurements of closed samples

Figure 3.5: Calcium precipitation as observed in TUHDN2C with phosphate

3.3. PHREEQC VALUES

The samples measured at time = 0 and the calcium concentrations gained are compared with simple models in PHREEQC. The specific conductance *SC* and the saturation index *SI* for several different known concentrations of calcium solutions are calculated with PHREEQC. These values are plotted in a graph to gain an indication of the SC and SI values at different concentrations of calcium. The plots contain calcium, carbonate, sodium and phosphate ions, the script is available in Appendix B.

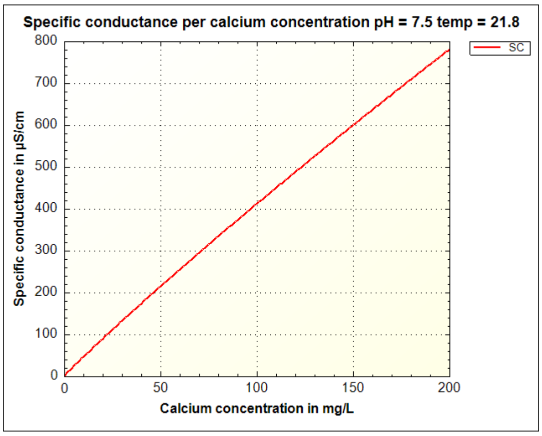


Figure 3.6: Specific conductance per calcium concentration for pH 7 and a temperature of 21.8 degrees Celsius

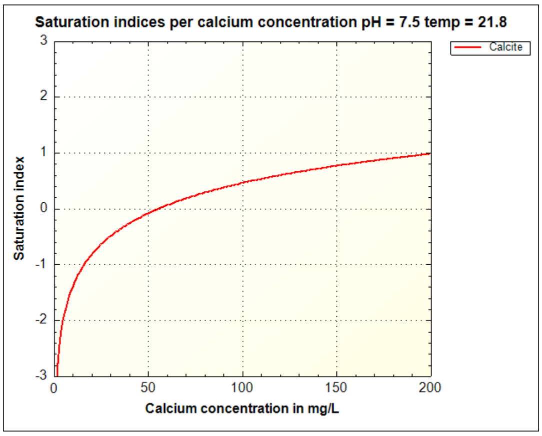


Figure 3.7: Saturation indices per calcium concentration for pH 7 and a temperature of 21.8 degrees Celsius

To compare the values obtained from PHREEQC and the measured values, a graph is made for *SI* and *SC* with the measured samples at t = 0.

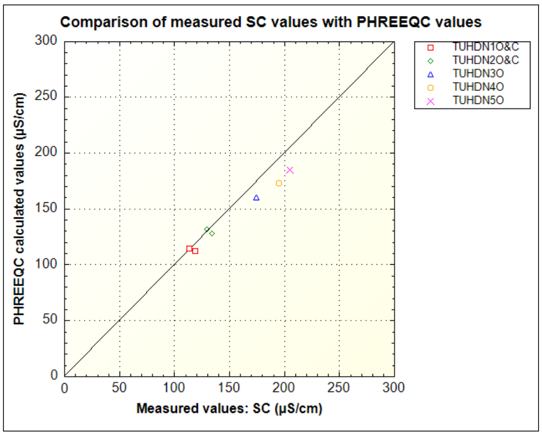


Figure 3.8: SC calculated with PHREEQC compared to measured SC values

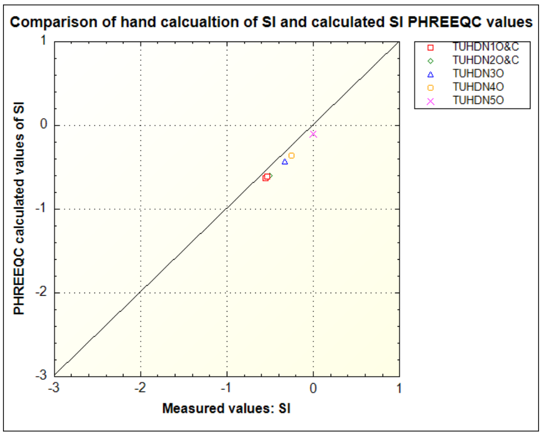


Figure 3.9: SI calculated with PHREEQC compared to measured values

As can been seen in the graph for the specific conductance (figure 3.8), the samples TUHDN1O, TUHDN1C, TUHDN2C and TUHDN2O have a close *SC* value to the theoretically calculated calcium concentrations of PHREEQC. The theoretically calculated values of TUHDN3O, TUHDN4O and TUHDN5O on the other hand, have a small difference. This is due to the fact that the CO_2 in gas form evaporates in time. The later sample set, TUHDN3O to 5O were measured later than the sample pots TUHDN1O, 1C, 2O and 2C. This caused the difference in the obtained values for the later sample sets. The graph for the saturation indices (figure 3.9) shows that the measured *SI* values are close to the calculated SI values with PHREEQC.

4

CONCLUSION

For this study, a total of 216 samples are measured on the calcium concentration dissolved in the samples. The calcium concentrations is subsequently plotted in graphs over time. During this study, the occurrence of scaling is observed, as reported in literature, earlier in Reverse osmosis permeate than in water treated with other conventional treatment processes. The effect of trisodium phosphate as an anti scaling is also measured and analysed. From the results presented in the chapter on results and discussion above, no anti scaling property can be observed in the various samples. The scaling still occurs in the RO permeate faster (in the first five hours) than in drinking water (after 22.5 hours). The scaling did not occur in the TUHDN1O and TUHDN2O samples, possibly due to the low calcium concentration in the samples. However, samples TUHDN1C and TUHDN2C do have a scaling, despite being of the same calcium concentration as samples TUHDN1O and TUHDN2O. As mentioned in the previous chapter, samples 1C and 2C were made into samplepots the same day as they were produced in the Hatenboerwater complex. Therefore, CO_2 couldn't evaporate completely and resulted in precipitation of calcium. The precipitation occurs between 29 and 31.5 hours after heating and is at about the same timing as the drinking water samples. Both drinking water and samples 1C and 2C scale at the same time. The lower calcium concentration of the samples 1C and 2C, leads to a later precipitation of calcium which happens to coincide with the scaling stage of the drinking water samples. Samples TUHDN3O, TUHDN4O and TUHDN5O all showed scaling properties in the first five hours of the heating stage, regardless of the added trisodium phosphate. Furthermore, another precipitation occurred between 24.5 and 30 hours after heating. The samples TUHDN1O and TUHDN2O have no scaling at higher temperatures in the observed time span, however, the calcium concentration of these samples do not meet the required standards of Dutch drinking water and therefore can not be used in the drinking water systems of the Netherlands. However, other countries do not have the same requirements for the calcium concentration as the Netherlands and therefore, these sample can be used as drinking water without scaling occurrence. Besides drinking water, this water can also be used in maritime and certain sea ship installations because of the lack of scaling properties in the observed timespan.

4.1. RECOMMENDATIONS

The scaling process is still observed in the samples, excluding samples TUHDN1O and TUHDN2O. Therefore, more measurements with trisodium phosphate are not necessary. Measuring the remaining samples, TUHDN3C to 5C can still be beneficial to determine the time after which the scaling occurs and completing the data set. In this study, scaling is observed in two different time regions, namely, in the first five hours after heating and between 22 and 32 hours after heating. Therefore, it is recommended to measure frequently in this time span for further study purposes. Since trisodium phosphate did not work as an anti scaling, follow up tests should be done with humic acids or sodium bicarbonate. Recommended is to quickly measure the open samples, within a day or two after the samples are made, so the CO_2 can not evaporate before doing the measurements. The measurements of the closed samples should be done after being certain that the CO_2 is evaporated. PHREEQC offers an accurate and fast way to calculate precipitation that happens in different solution compositions. Modelling more with PHREEQC will be more efficient, and less time consuming. Models for t=0 are complete and correct safe a minor difference in output data. Modeling this experiment in time will provide better insights into the scaling properties of reverse osmosis permeate.

A

APPENDIX

Action plan

As a third years student at the faculty of Civil Engineering in TU Delft, I am ought to make a Bachelors thesis which shows that I am able to do an academic research. Through this research we, as Bachelors students, will get to know the problems and difficulties of doing such a research brings along with it and in the process learn how to deal with uncertainties, contradictions and having limited knowledge. This action plan is written in order to define the goal of the project and to make a time schedule for myself and also to present my supervisors how I will execute this research.

General outlay

Throughout the history of mankind, clean drinking water has been the most important aspect of human life. Clean and safe drinking water is scarce and this scarcity is recognized as a present and future threat to human activity. Therefore, developing alternative water resources and the research to improve the already existing ones have become an increasing trend. Amongst the commonly used technologies is the membrane technology and conventional thermal separation processes. The membrane technology RO, reverse osmosis, is more often used compared to its alternatives from the conventional processes due to its lower energy consumption. The water that is produced through RO is close to pure water, however according to the Dutch law, drinking water requires a minimum amount of Calcium (and magnesium) ions to have a certain degree of hardness. Furthermore, the permeate has a corrosive effect on the pipelines of the distribution network, therefore it is needed to remineralize the permeate.

All this together still makes RO an ideal desalinizing method for European countries, due to the high cost of labor and energy in Europe. However, precipitation of calcium carbonate in heaters and washing machines occur faster when the drinking water of RO is used compared to conventional water treatment. This precipitation causes the machines to use more energy than they should. The goal of this study is to gain a better understanding why this faster precipitation happens.

Literature

My supervisor, Amir Haidari, suggested several articles on reverse osmosis. Within these articles, the authors cite extensively from other related articles, which in turn I can use for my research. Another Bachelors student at the TU Delft, Sherzad Anwari, has recently finished his bachelors thesis on the same subject The results he gained will be beneficial since my thesis is a continuation of his.

Contact

I have two supervisors to guide me through this research. The one I will be mostly in contact with for questions, meetings etc is Amir Haidari. We have a weekly appointment every Tuesday at 10:00 am the talk about my process. The other supervisor will be Bas Heijman. I can contact both through mail, telephone and face to face meetings. Research Most part of the research will be done in the “Waterlab” at the faculty of Engineering in TU Delft. This lab has all the equipment I need and I have already had an safety course through the lab led by Tonny Schuit. The results will be recorded and evaluated by me generally immediately after the tests in the lab.

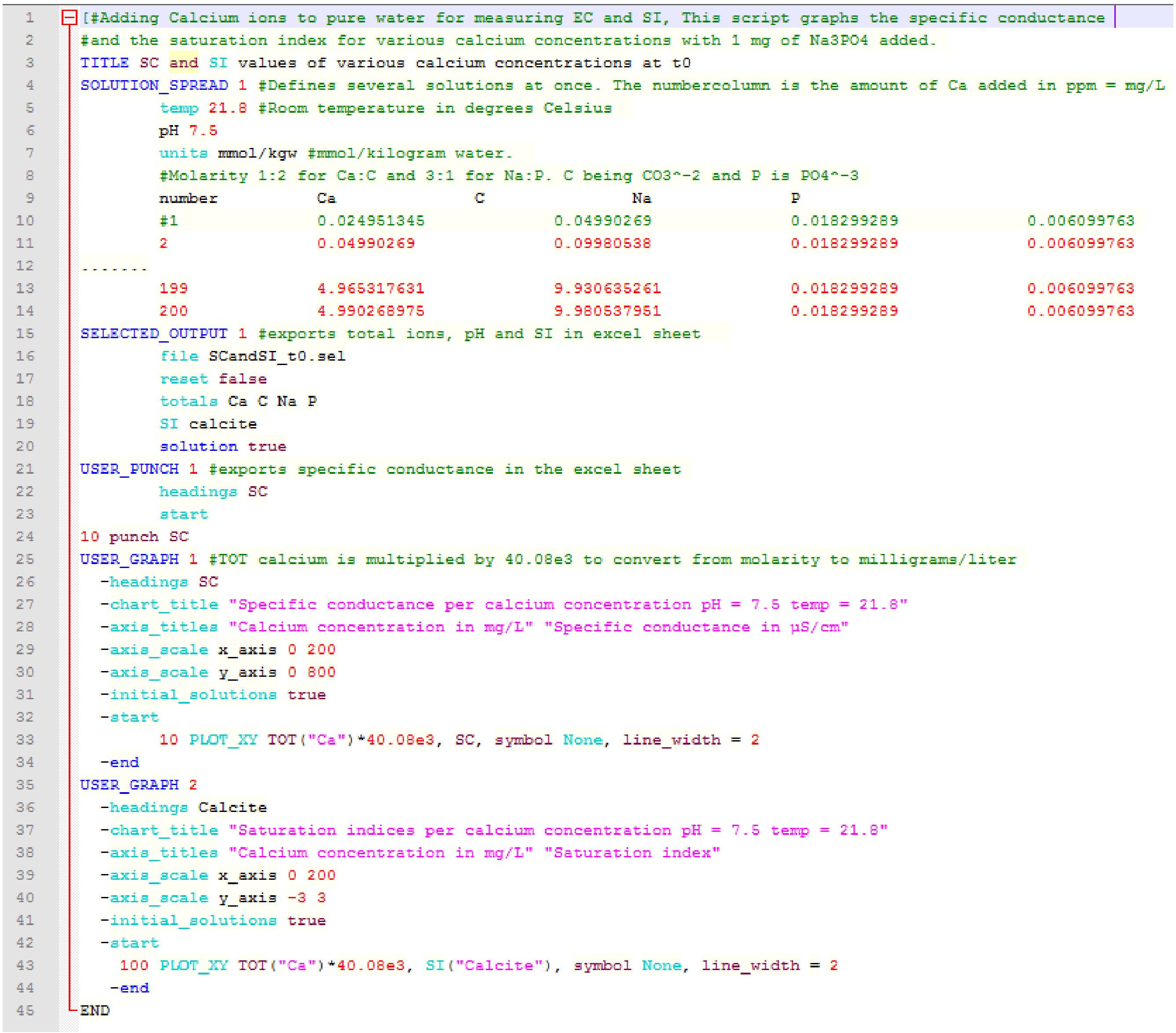
Time schedule

Week 1 – 7: Monday: Getting samples at Hatenboerwater BV and bring them to Delft. Tuesday: Preparing the samples and making measurements with EVG and thermometer. Wednesday till Friday: Warming up the samples and place them in the IC. Then take measurements every 2.5 hours. In between the measurements I can write my thesis. Week 8: Finishing the rapport and preparing the presentation.

B

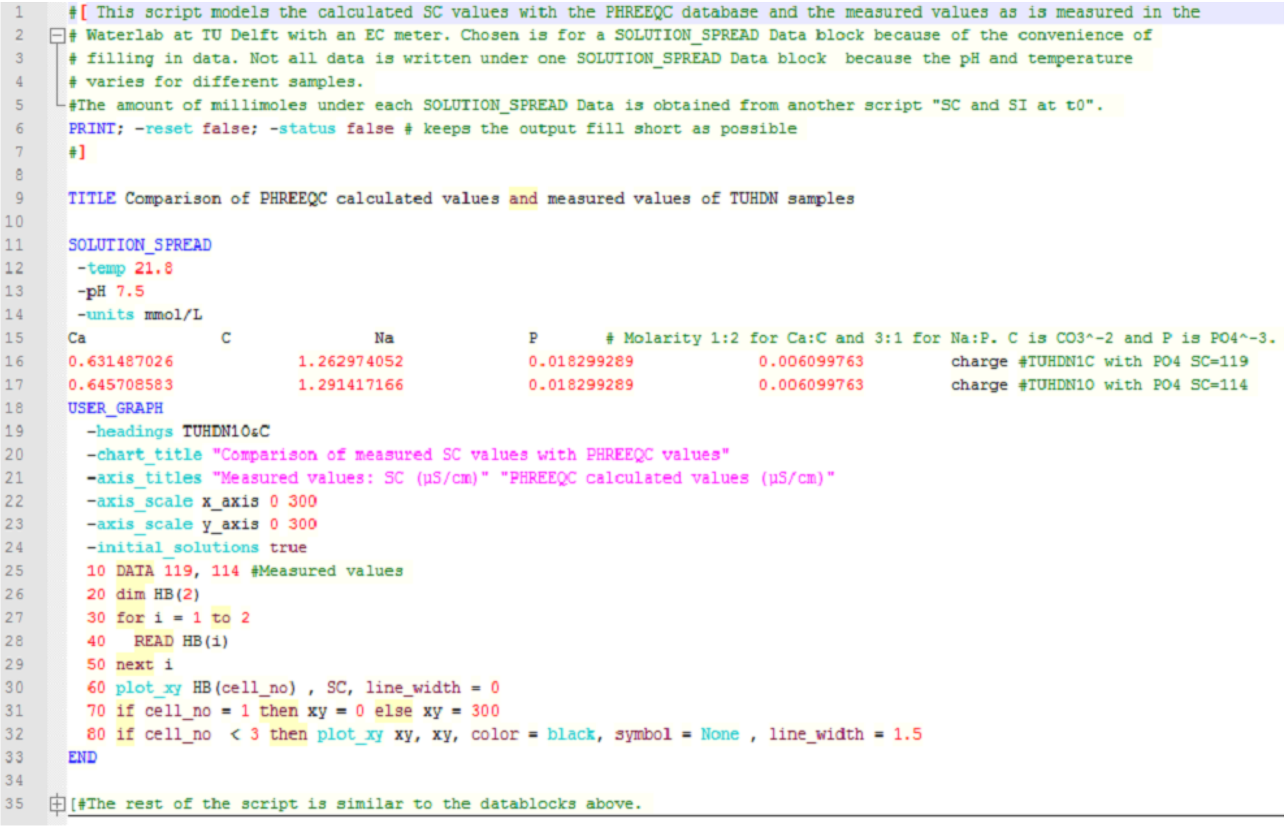
APPENDIX

B.1. SC AND SI AT T=0



```
[#Adding Calcium ions to pure water for measuring EC and SI, This script graphs the specific conductance
#and the saturation index for various calcium concentrations with 1 mg of Na3PO4 added.
TITLE SC and SI values of various calcium concentrations at t0
SOLUTION_SPREAD 1 #Defines several solutions at once. The numbercolumn is the amount of Ca added in ppm = mg/L
        temp 21.8 #Room temperature in degrees Celsius
        pH 7.5
        units mmol/kgw #mmol/kilogram water.
        #Molarity 1:2 for Ca:C and 3:1 for Na:P. C being CO3^-2 and P is PO4^-3
        number          Ca              C               Na              P
        #1              0.024951345             0.04990269              0.018299289             0.006099763
        2               0.04990269              0.09980538              0.018299289             0.006099763
.......
        199             4.965317631             9.930635261             0.018299289             0.006099763
        200             4.990268975             9.980537951             0.018299289             0.006099763
SELECTED_OUTPUT 1 #exports total ions, pH and SI in excel sheet
        file SCandSI_t0.sel
        reset false
        totals Ca C Na P
        SI calcite
        solution true
USER_PUNCH 1 #exports specific conductance in the excel sheet
        headings SC
        start
10 punch SC
USER_GRAPH 1 #TOT calcium is multiplied by 40.08e3 to convert from molarity to milligrams/liter
  -headings SC
  -chart_title "Specific conductance per calcium concentration pH = 7.5 temp = 21.8"
  -axis_titles "Calcium concentration in mg/L" "Specific conductance in µS/cm"
  -axis_scale x_axis 0 200
  -axis_scale y_axis 0 800
  -initial_solutions true
  -start
        10 PLOT_XY TOT("Ca")*40.08e3, SC, symbol None, line_width = 2
  -end
USER_GRAPH 2
  -headings Calcite
  -chart_title "Saturation indices per calcium concentration pH = 7.5 temp = 21.8"
  -axis_titles "Calcium concentration in mg/L" "Saturation index"
  -axis_scale x_axis 0 200
  -axis_scale y_axis -3 3
  -initial_solutions true
  -start
    100 PLOT_XY TOT("Ca")*40.08e3, SI("Calcite"), symbol None, line_width = 2
   -end
END
```

B.2. COMPARISON OF SC



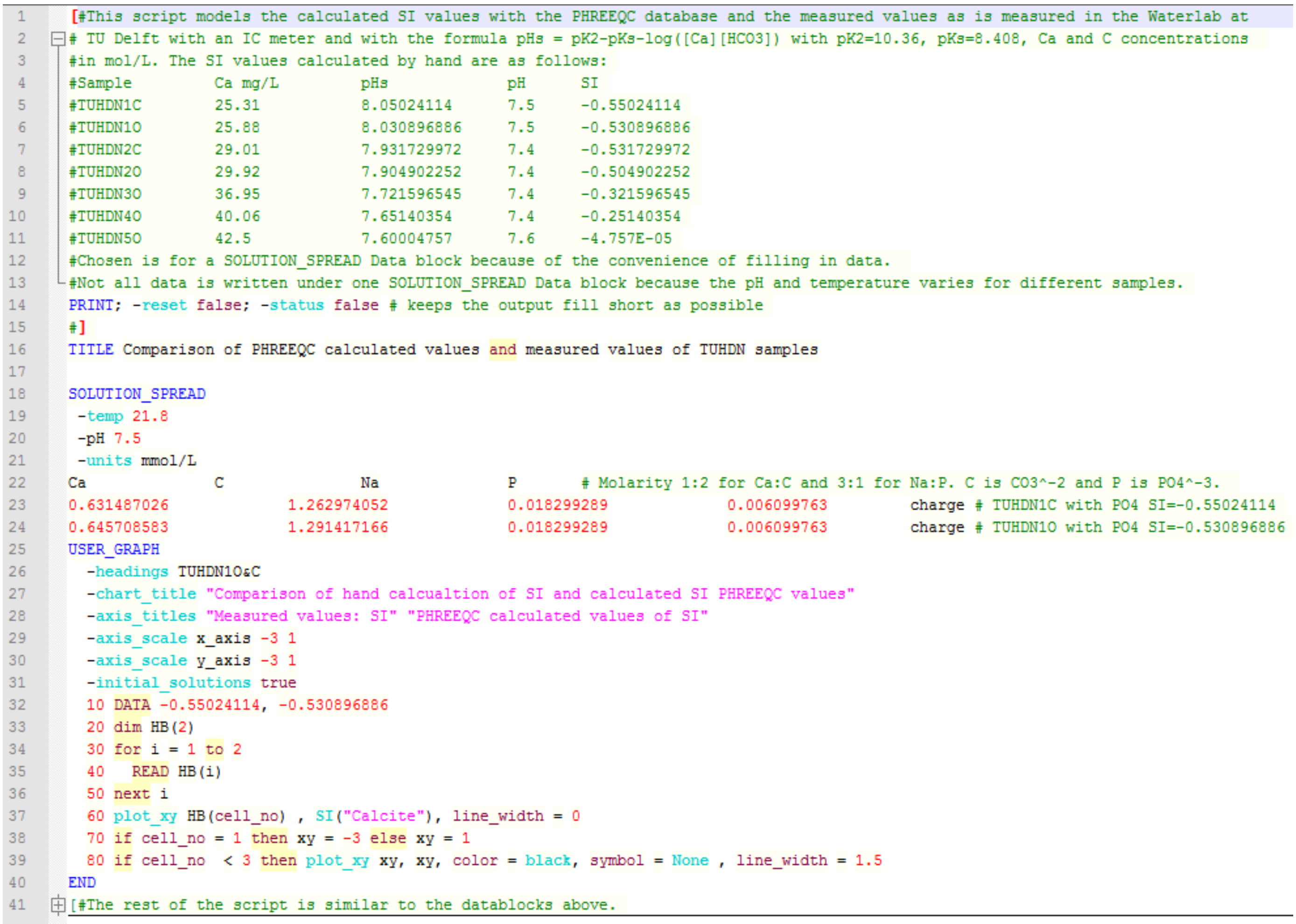
```
#[ This script models the calculated SC values with the PHREEQC database and the measured values as is measured in the
# Waterlab at TU Delft with an EC meter. Chosen is for a SOLUTION_SPREAD Data block because of the convenience of
# filling in data. Not all data is written under one SOLUTION_SPREAD Data block  because the pH and temperature
# varies for different samples.
#The amount of millimoles under each SOLUTION_SPREAD Data is obtained from another script "SC and SI at t0".
PRINT; -reset false; -status false # keeps the output fill short as possible
#]

TITLE Comparison of PHREEQC calculated values and measured values of TUHDN samples

SOLUTION_SPREAD
 -temp 21.8
 -pH 7.5
 -units mmol/L
Ca              C               Na              P       # Molarity 1:2 for Ca:C and 3:1 for Na:P. C is CO3^-2 and P is PO4^-3.
0.631487026             1.262974052             0.018299289             0.006099763          charge #TUHDN1C with PO4 SC=119
0.645708583             1.291417166             0.018299289             0.006099763          charge #TUHDN1O with PO4 SC=114
USER_GRAPH
  -headings TUHDN1O&C
  -chart_title "Comparison of measured SC values with PHREEQC values"
  -axis_titles "Measured values: SC (µS/cm)" "PHREEQC calculated values (µS/cm)"
  -axis_scale x_axis 0 300
  -axis_scale y_axis 0 300
  -initial_solutions true
  10 DATA 119, 114 #Measured values
  20 dim HB(2)
  30 for i = 1 to 2
  40   READ HB(i)
  50 next i
  60 plot_xy HB(cell_no) , SC, line_width = 0
  70 if cell_no = 1 then xy = 0 else xy = 300
  80 if cell_no  < 3 then plot_xy xy, xy, color = black, symbol = None , line_width = 1.5
END

[#The rest of the script is similar to the datablocks above.
```

B.3. COMPARISON OF SI



```
[#This script models the calculated SI values with the PHREEQC database and the measured values as is measured in the Waterlab at
# TU Delft with an IC meter and with the formula pHs = pK2-pKs-log([Ca][HCO3]) with pK2=10.36, pKs=8.408, Ca and C concentrations
#in mol/L. The SI values calculated by hand are as follows:
#Sample         Ca mg/L         pHs             pH      SI
#TUHDN1C        25.31           8.05024114      7.5     -0.55024114
#TUHDN1O        25.88           8.030896886     7.5     -0.530896886
#TUHDN2C        29.01           7.931729972     7.4     -0.531729972
#TUHDN2O        29.92           7.904902252     7.4     -0.504902252
#TUHDN3O        36.95           7.721596545     7.4     -0.321596545
#TUHDN4O        40.06           7.65140354      7.4     -0.25140354
#TUHDN5O        42.5            7.60004757      7.6     -4.757E-05
#Chosen is for a SOLUTION_SPREAD Data block because of the convenience of filling in data.
#Not all data is written under one SOLUTION_SPREAD Data block because the pH and temperature varies for different samples.
PRINT; -reset false; -status false # keeps the output fill short as possible
#]
TITLE Comparison of PHREEQC calculated values and measured values of TUHDN samples

SOLUTION_SPREAD
 -temp 21.8
 -pH 7.5
 -units mmol/L
Ca              C               Na              P       # Molarity 1:2 for Ca:C and 3:1 for Na:P. C is CO3^-2 and P is PO4^-3.
0.631487026             1.262974052             0.018299289             0.006099763         charge # TUHDN1C with PO4 SI=-0.55024114
0.645708583             1.291417166             0.018299289             0.006099763         charge # TUHDN1O with PO4 SI=-0.530896886
USER_GRAPH
  -headings TUHDN1O&C
  -chart_title "Comparison of hand calcualtion of SI and calculated SI PHREEQC values"
  -axis_titles "Measured values: SI" "PHREEQC calculated values of SI"
  -axis_scale x_axis -3 1
  -axis_scale y_axis -3 1
  -initial_solutions true
  10 DATA -0.55024114, -0.530896886
  20 dim HB(2)
  30 for i = 1 to 2
  40   READ HB(i)
  50 next i
  60 plot_xy HB(cell_no) , SI("Calcite"), line_width = 0
  70 if cell_no = 1 then xy = -3 else xy = 1
  80 if cell_no  < 3 then plot_xy xy, xy, color = black, symbol = None , line_width = 1.5
END
[#The rest of the script is similar to the datablocks above.
```

BIBLIOGRAPHY

[1] Oki and S. Kanae, *Global hydrological cycles and world water resources,* (2006), science.

[2] A. Shiklomanov, *World water resources, water in crisis,* (1993), new York, Oxford.

[3] C. Fritzmann, J. Löwenberg, T. Wintgens, and T. Melin, *State-of-the-art of reverse osmosis desalination,* Desalination **216**, 1 (2007).

[4] J. Glater, *The early history of reverse osmosis membrane development,* Desalination **117**, 297 (1998).

[5] B. Van Der Bruggen, C. Vandecasteele, T. Van Gestel, W. Doyen, and R. Leysen, *A review of pressure-driven membrane processes in wastewater treatment and drinking water production,* Environmental Progress **22**, 46 (2003).

[6] B. Alspach, *Manual of water supply practices,* (2007).

[7] A. Pabby, S. Rizvi, and A. Requena, *Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications* (Taylor & Francis, 2008).

[8] H. Lodish, A.Berk, and S. Z. et al, *Molecular cell biology,* (2000).

[9] N. P. Isaias, *Experience in reverse osmosis pretreatment,* Desalination **139**, 57 (2001).

[10] S. Anwari, *Remineralization of reverse osmosis permeate,* Bachelor thesis TU Delft (2015).

[11] F. Kožíšek, *Health significance of drinking water calcium and magnesium,* (2001).

[12] M. Lut, *Hydraulic behaviour of particles in a drinking water distribution system design and first operation of a test rig,* (2005), master thesis.

[13] P. de Moel, J. Verberk, and J. van Dijk, *Drinking water:principles and practices,* , 1558 (2006).

[14] D. Parkhurst and Appelo, *Description of input and examples for phreeqc version 3,* (2013), http://pubs.usgs.gov/tm/06/a43/ .

[15] J. A. de Ruijter, *Remineralization process in the hatenboerwater bv complex,* Hatenboerwater BV.

[16] R. M. Cassidy and S. Elchuk, *Dynamically coated columns for the separation of metal ions and anions by ion chromatography,* Analytical Chemistry **54**, 1558 (1982), http://dx.doi.org/10.1021/ac00246a023 .