Pilot research and modelling of remineralisation of low temperature desalinated water by calcite filtration

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Last but not least, I would like to thank my dear family and friends for the love, care, and support in difficult times.

S. Ghanbari
Delft, January 2018
Abstract
To prepare for future challenges, such as possible upcoming organic micro pollutants in the source water, including traces of medicines, pesticides, and industrial by-products, it is expected that the conventional treatment does not ensure a reliable quality of drinking water. As a result, during the past few years, Oasen started to research a new treatment concept based on 100% reverse osmosis (RO) membrane filtration to provide an excellent barrier for organic micro pollutants. However, the water produced by the RO membranes, called permeate, is corrosive, bitter in taste and does not comply with the drinking water regulation standards in the Netherlands. Therefore, a certain degree of remineralisation is crucial to solve these problems and improve the water quality. A commonly used remineralisation process is to filter the desalinated water through a calcite contactor, providing the appropriate amount of bicarbonate and calcium in the water. In order to properly design and operate the calcite filters as well as to predict the final water quality, it is essential to understand the processes that occur in the filter.

The aim of this study was to find the best kinetic calcite dissolution model in order to understand the calcite grains dissolution behavior inside the filter and subsequently to adequately design and operate the calcite filter. Therefore, extensive pilot research was conducted to investigate the effect of various parameters on calcite dissolution such as the calcite grain size, velocity and carbon dioxide concentration. On top of that, the dissolution was modelled based on a successful empirical expression given by Yamauchi et al. (1987). However, it was found that the effect of the flow rate on the diffusion boundary layer around the calcite grains has not been taken into account in the study carried out by Yamauchi et al. (1987). Therefore, the effect of velocity on the calcite dissolution coefficient was investigated at five different velocity, i.e., 5, 10, 15, 20, 30 m/h. From there, a function was developed to describe the correlation between flow rate and the dissolution rate coefficient. In order to calculate the equilibrium concentration, the chemical reactions were simulated using PhreeqPython (Phreeq built in Python).

The main difference of this study compare to previous investigations was the low temperature of the water (12 °C vs 22-40 °C) and the smaller grain size of the calcite (0.5-1.2 mm vs 1-2 and 2-3mm) which was tested. Besides that a high range of CO₂ dosing (1.45- 9.5 mmol/l) was tested. As expected from theory, the dissolution rates was strongly affected by the varied parameters. It is concluded that the smaller grain size of 0.5-1.2 mm reduced the required empty bed contact time (EBCT) to 15 min where operating the filter with the larger grain size of 1-2mm needs a minimum EBCT of 25 min to reach calcite equilibrium. The CO₂ dosing is recommended to be less than 3 mmol/l, since the CO₂ efficiency will drop under the 60% at higher CO₂ concentrations.

Eventually, the optimal design will be introduced for the remineralisation process at Oasen treatment plant De Hooge Boom located in Kamerik. For this purpose various operational scenarios were compared on capital and operational cost. The overall cost including, both Capital expenses (CAPEX) and Operational expenses OPEX, was estimated between € 0.048 and 0.064 per m³ for different scenario’s where 71% consists of investment cost. The total treatment cost of this design is 0.057 €/m³ and the investment cost was found to be € 1.351.000 which is 32% less than price estimated by previous study done by Oasen.
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Delft University of Technology, Delft
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List of abbreviations

- **CAPEX**: Capital expenses
- **EBCT**: Empty Bed Contact Time
- **EC**: Electric conductivity
- **MFC**: Mass Flow Controller
- **MSFE**: Multi-Stage Flash Evaporator
- **OMP**: Organic micro pollutants
- **OPEX**: Operating expenses
- **PWP**: Plummer-Wigley-Parkhurst
- **RO**: Reverse Osmosis
- **TDS**: Total Dissolved Solids

Nomenclature

- $k_1, k_2, k_3$: reaction constant
- $K$: (calcite) dissolution rate constant
- $dM$: mass transfer
- $dC$: concentration change
- $A/V$: surface over volume ratio
- $d$: particle diameter
- $ε$: porosity
- $φ$: form factor
- $R$: Overall dissolution rate (moles/cm$^2$.s)
- $r_1, r_2, r_3$: reaction rate of equation I, II, and III
- $κ_1, κ_2, κ_3$: rate constant for reaction 1, 2 and 3
- $κ_4$: rate constant for the backward reaction
- $α_1, α_2, α_3$: ions the activities
- $C_e$: concentration at equilibrium (mmol/l)
- $C_i$: concentration at each bed height (mmol/l)
- $C_0$: concentration at start (mmol/l)
- $Z_i$: bed height (mm)
- $U_i$: superficial velocity (mm/s)
- $Φ$: Ya coefficient (dissolution rate constant including the form factor)
- $Ca_0$: initial calcium concentration (molar)
- $S$: the concentration of dissolved calcium carbonate
- $S'$: the concentration of dissolved calcium carbonate at equilibrium
- $K_w$: the activity-coefficient-corrected ion product for water
- $DIC_0$: Initial dissolved inorganic-carbon concentration (molar)
- $C_c$: the influent concentrations of cations excluding calcium and hydrogen
- $C_a$: the influent concentrations of anions excluding DIC species and hydroxide
- $α_1$ & $α_2$: the ionization fractions for the deprotonation of carbonic acid and are
- $N_d$: axial dispersion number, dimensionless ($N_d = \frac{F \cdot ε}{(U_i \cdot L)}$)
- $F$: dispersion coefficient
- $Z$: dimensionless axial distance ($z=z/L$)
- $r$: reaction rate expression
- $a$: $\frac{ε(1−ε_L)}{β_p \varphi}$
- $k_l$: Liquid film mass transfer
- $k_c$: Surface reaction
- $k_r$: Residual layer mass transfer
- $MR$: modified Reynolds
- $SC$: Schmidt number
- $ν$: kinematic viscosity
- $D$: calcium-ion diffusivity
1 Introduction

1.1 General background

Oasen is a drinking water company located in the province South Holland of the Netherlands, and provides reliable and fresh water for 750,000 people and 7200 companies in this region, using riverbank infiltration as its main water source. The water quality of the wells, recharged by bank filtration from the river Lek, are susceptible to pollution. This pollution consist of, among others, organic micro pollutants (OMP) such as traces of pharmaceuticals and pesticides, which could be a serious threat for drinking water treatment in the future. Furthermore, it is expected that on the long term, due to the effect of climate change, source water will increase in salinity. The current conventional treatment, consisting of tower aeration, rapid sand filtration, pellet softening and granular activated carbon followed by a UV disinfection is limited to remove OMP and chloride and therefore is not seen as a long term, robust solution (Van Der Laan et al., 2016). Consequently, in past years Oasen started to research a new treatment concept based on 100% reverse osmosis (RO) membrane filtration, to be prepared for possible future OMP and increasing chloride concentrations in the water source.

The product water from the RO step, called permeate, is aggressive, has a low pH, is bitter in taste and does not comply with the drinking water regulation standards in the Netherlands. Moreover, carrying such aggressive water through water supply systems without an appropriate treatment, will create the possible deterioration in the piping system (Yamauchi et al., 1987; Letterman et al.1987). In order to prevent the corrosion in the transport system and provide healthy water to consumers a remineralisation step is therefore essential. For this purpose various types of remineralisation techniques have been proposed. Table 1 gives an overview of the results from the pilot study done by Oasen during 2014-2016. The aim was to find the optimal remineralisation technology to use as post-treatment of RO permeate at treatment plant De Hooge Boom in Kamerik. Based on several studies, calcite filtration was found to be the best remineralisation technique, since it is inexpensive, easy and safe to operate and maintain, and does not require continuous feed of chemicals compared to the other techniques (Benjamin et.al 1992; Letterman, 1995; Shemer et al., 2015; Van Der Laan et al., 2016).
Table 1. Results of pilot study conducted by Oasen Water Company on remineralisation techniques (Van Der Laan et al., 2016)

<table>
<thead>
<tr>
<th>Source</th>
<th>Calcium carbonate</th>
<th>Calcium Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Granular</td>
<td>Micronised</td>
</tr>
<tr>
<td>Grain size</td>
<td>0.5 - 1.2mm</td>
<td>3 µm</td>
</tr>
<tr>
<td>Technology</td>
<td>Filter</td>
<td>Dosing</td>
</tr>
<tr>
<td>Partial/Full treatment</td>
<td>100%</td>
<td>25%</td>
</tr>
<tr>
<td>Required additives (CIP = Cleaning</td>
<td>-</td>
<td>CO₂</td>
</tr>
<tr>
<td>In Race: CEB = Chemically Enhanced Backwash)</td>
<td>-</td>
<td>CEB</td>
</tr>
<tr>
<td>Turbidity, SI, pH</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Growth potential</td>
<td>11%</td>
<td>8%</td>
</tr>
<tr>
<td>Contact time</td>
<td>min</td>
<td>15-20</td>
</tr>
<tr>
<td>CO₂ efficiency</td>
<td>%</td>
<td>85%</td>
</tr>
<tr>
<td>CO₂ use</td>
<td>mmol/L</td>
<td>10</td>
</tr>
<tr>
<td>Energy use</td>
<td>kWh/m²</td>
<td>0.06</td>
</tr>
</tbody>
</table>

In the calcite filtration step, the desalinated water, if required acidified with CO₂, is fed to the filter filled by calcite particles. This results in increasing calcium and bicarbonate concentration in the water due to the following reaction (Yamauchi et al. 1987):

\[
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^{-}
\]

The effectiveness and costs of this process are strongly dependent on the parameters such as bed height, temperature, contact time and inlet CO₂ concentration which affect the dissolution of calcium carbonate (Shemer et al., 2012). In order to understand and predict the calcite dissolution rate as a function of design parameters, the knowledge of the kinetics and equilibrium of the processes is required. For this purpose, Oasen aims to develop a model for design and optimization of the calcite filtration as one of the main steps in its treatment processes.

Several theoretical and practical models (e.g. Erga & Terjesen 1956; Plummer et al., 1979; Yamauchi et al. 1987 and Letterman et al. 1991) have been developed to describe the kinetics.
of the calcite dissolution. Hasson et al. (2006) evaluated various published kinetics expressions in literature to determine the most reliable dissolution kinetics model. It was concluded that the model given by Yamauchi et al. 1987 was the most accurate model to describe the kinetics of calcite dissolution. This is also confirmed by extensive experimental data obtained from a study conducted by Shemer et al., (2012) on this subject. Besides published models, there are also more complex computer models based on a multilayer concept such as one proposed in the MSc study conducted by Bang (2012) and the recent work by Zweere (2016).

1.2 Problem definition

Although an extensive literature has been published in the field of calcite dissolution kinetics, the study conducted by Hasson & Bendrihem (2006) has shown that a theoretical models such as Plummer et al., (1978,1979) are not applicable to simulate the calcite dissolution rate in practice as they overestimate the dissolution rate. This is because, Plummer et al. (1979) determined the calcite dissolution rate under turbulent flow conditions and using the large specific surface area which reduce the rate limited effects of mass transport and surface reactions rate on the calcite dissolution (Bang, 2012). On the other hand, the presented empirical models are generally tested at high temperature water and larger grain size range. This is because the previous studies mainly were carried out in Middle East countries where the temperature is higher compare to the Netherlands temperature or they used other techniques such as multi-stage flash evaporator (MSFE) to desalinate the water, which increases the water temperature. Oasen works with a relatively low groundwater temperature of 12 to 14 degrees Celsius. In addition, it is questionable whether the accuracy of more multi-layer models such as one given by Bang (2012) or Zweere (2016) is significantly better than the more simple models with one layer to describe the kinetics of the dissolution of calcium carbonate.

Furthermore, the calcite dissolution kinetics play a key role in the efficient design, operation and maintenance of a calcite filter. Lack of a reliable kinetics model may not only result in incorrectly designed calcite filters, but also in the improper maintenance of the filter.

As a conclusion, despite all previous work done by various authors on kinetics and equilibrium of calcite dissolution, the accuracy of available models still needs to be improved at low temperature for the application of Oasen. Hereby a simpler model would be preferred over a complex multilayer model, questioning whether an increase in complexity may result in a higher uncertainty. A proper model is important as the effectiveness and costs of the process are dependent on the design parameters of the calcite filter, such as flow rate, acid type and concentration, bed height, bed porosity, temperature and grain size.
1.3 Research questions

The objective of this research is to develop a kinetics model as a function of the design parameters to simulate the dissolution kinetics of calcite in practice. The model could be used to optimize on the design and operating conditions as well as to predict product water quality regarding calcium and bicarbonate concentration.

For this purpose, two main research questions are defined:

1. What is the most reliable calcite dissolution kinetics model among the available models?

To answer this question, first the following sub-questions should be answered:

- What are the design parameters that have an influence on this model?
- How might the calcium and bicarbonate concentration be affected by these parameters?
- How can the model be validated and calibrated using pilot trials?
- Is the one-layer model accurate enough compared to the multilayer model in which filters will be divided into several layers and the effluent water quality of each layer is used as influent water quality of its bottom layer?

2. How could the design and operational conditions be optimized using the dissolution model?

With this question the following sub-questions could be answered:

- What is the effect of the calcite dissolution rate on the bed height?
- What are the optimal design parameters, such as empty bed contact time (EBCT), filtrate velocity and required bed height?
- What is the refilling frequency of the filter to keep the design EBCT and consequently effluent water quality of filter constant?

1.4 Boundary conditions

Table 2 illustrates the targets for the water quality, which should be achieved based on the drinking water regulations and internal standards of Oasen. It should be noted that there are several parameters that determine the final water quality but they are beyond the scope of this research. These include the saturation index (SI) and pH values that will be further adjusted by the final aeration step. The turbidity of and presence of particles in the effluent water, that could be affected by the filtration velocity and backwash regime, are not taken into account here too, because a model to predict the occurrence of particles in the final water quality is beyond the scope of this research.
1.5 Research approach

To answer the above research questions, various experiment have been carried out in the period from May to August 2017. The pilot research aimed to examine the calcite dissolution at low temperature using two different calcite grain sizes and various changes in operational conditions such as filtration velocity and inlet CO\textsubscript{2} concentration. Based on measured data obtained from pilot research, the empirical model given by Yamauchi (1987) has been modified in order to better capture the calcite dissolution kinetics at low temperature for various calcite grain sizes. Subsequently, the developed kinetics model would be applied to translate the results of the pilot study into a full-scale application based on a kinetics model and cost efficiency analyses. Finally, the model will be used to optimize the design of the calcite filter at De Hooge Boom and analyse the various operational scenario's.

Table 2. Drinking water quality targets

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Oasen standard (mmol/L)</th>
<th>Dutch legal standard (mmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Hardness</td>
<td>1</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>HCO\textsubscript{3}</td>
<td>2</td>
<td>&gt; 0.99</td>
</tr>
<tr>
<td>pH</td>
<td>7.8 &lt; pH &lt; 8.3</td>
<td>7.5 &lt; pH &lt; 9.5</td>
</tr>
<tr>
<td>SI (Calcite)</td>
<td>-0.2 &lt; SI &lt; 0.4</td>
<td>SI &gt; -0.2</td>
</tr>
<tr>
<td>Turbidity</td>
<td>≤ 0.15 NTU</td>
<td>≤ 1 NTU</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.625</td>
<td>?</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.375</td>
<td>?</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>&gt; 2 mg/L</td>
<td>&gt; 2 mg/L</td>
</tr>
</tbody>
</table>
2 Literature review

2.1 Introduction

Since the permeate water from the RO process is free from minerals, has a low buffering capacity and a low pH, a certain degree of remineralisation is essential in order to prevent the corrosion in the transport system as well as to mitigate corrosion by-products such as copper and consequently to provide healthy water to a consumer (Shemer, Hasson, Semiat, et al., 2013). There are several remineralisation processes, however, the calcite filter is the most cost efficient and widespread method for remineralisation (Hasson & Bendrihem, 2006; Ruggieri et al., 2008; Shemer et al., 2013; Van Der Laan et al., 2016).

2.2 Theory of calcite filtration

In the remineralisation process, the permeate water, if necessary acidified by carbon dioxide, flows through a packed bed of calcite when the system is closed to the atmosphere. The chemical reactions, which occur when the permeate passes through the column, are as follows: (Lehmann et al., 2013)

Calcium carbonate acid equilibrium at 10 °C:

\[
\begin{align*}
\text{CaCO}_3 & \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} & K_s = [\text{Ca}^{2+}][\text{CO}_3^{2-}] & = 4.4 \times 10^{-9} \quad \text{pk}_s = -8.36 \quad (2.1) \\
\text{CO}_2 + \text{H}_2\text{O} & \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+ & K_1 = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{CO}_2]} & = 3.44 \times 10^{-7} \quad \text{pk}_1 = -6.46 \quad (2.2) \\
\text{HCO}_3^- + \text{H}_2\text{O} & \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+ & K_2 = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} & = 3.25 \times 10^{-11} \quad \text{pk}_2 = -10.49 \quad (2.3) \\
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} & \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- & K_a = \frac{[\text{HCO}_3^-]^2[\text{Ca}^{2+}]}{[\text{CO}_2]} & = 4.6 \times 10^{-5} \quad \text{pk}_a = -4.33 \quad (2.4) \\
[\text{Ca}^{2+}] & = \frac{1}{2} [\text{HCO}_3^-] & (2.5)
\end{align*}
\]

Where:
- \( K \) = reaction constant, with given temperature and ionic strength (mole/m²/s)
- \( \text{pk} = -\log(k) \)
- \([\] = stoichiometric molar concentration (mol/l)).

2.3 Reaction rate of calcite dissolution

In general the dissolution of solids in water could be expressed either based on the mass balance or based on the kinetics of dissolution. Based on the mass balance, the mass change in the solid phase is equal with mass change in the liquid phase: (Bang, 2012)

\[
dM = dC \times V
\]

Where:
- \( dM \) = mass change (mol)
\[ dC = \text{mole change per volume of the same substance (mole/m}^3) \]
\[ V = \text{volume (m}^3) \]

On the other hand, the kinetics of dissolution could be calculated as follows:

\[ \frac{dM}{dt} = K \ast A \quad (2.7) \]

Where:
\[ dt = \text{retention time (s)} \]
\[ K = \text{calcite dissolution rate constant (mole/m}^2/\text{s)} \]
\[ A = \text{surface area of calcite grains (m}^2) \]

Therefore the general dissolution rate of CaCO\(_3\) (as a solid) is given in equation 2.8:

\[ dM = K \ast A \ast dt = dC \ast V \quad (2.8) \]
\[ \frac{dC}{dt} = K \ast \left(\frac{A}{V}\right) \]

K is the calcite dissolution rate constant which involves complex mechanisms controlled by mass transport at low pH, by surface reactions at high pH and by a combination of the two at intermediate pH levels (Shemer et al., 2013).

Furthermore, as it can be seen from equation 2.8 that the surface-to-volume ratio (A/V) of the calcite particles also plays an important role in the calcite dissolution rate. This parameter for sphere or irregularly shaped grains could be calculated by equation 2.9. The porosity also influences the surface area of calcite grains in a filter bed which should be taken into account in calculating A/V.

\[ A_{\text{sphere}} = \pi d^2 \text{en} \quad V_{\text{sphere}} = \frac{\pi d^3}{6} \quad \rightarrow \quad \frac{A_{\text{sphere}}}{V_{\text{sphere}}} = \frac{6}{d} \quad (2.9) \]

For a irregular particels: \( \phi = \frac{A_{\text{sphere}}}{V_{\text{irregular}}} \rightarrow \frac{A}{V} = \frac{6}{d+\phi} \], \( \frac{A}{V} = \frac{6.\left(1-\varepsilon\right)}{d} \)

Where:
\[ d = \text{particle diameter (m)} \]
\[ \varepsilon = \text{porosity of the filter bed (-)} \]
\[ \Phi = \text{form factor} \]

### 2.4 Calcite dissolution model

In general, there are two perspectives that describe the calcite dissolution. One assumes that the dissolution process is controlled by surface reactions and neglects the diffusional mass transport processes (Erga & Terjesen, 1956; Plummer et al., 1979 and Yamauchi et al., 1987). The other perspective defines the calcite dissolution rate by assuming a mass transfer as main controlling process (Letterman et al., 1987). The purpose of this paragraph is to discuss
previous studies that have been done on calcite dissolution rate and summarizes the central features of three main studies on dissolution kinetic in absent of metal impurities in the water.

2.4.1 Plummer-Wigley-Parkhurst model
The most extensive study to describe the dissolution of calcite is given by Plummer et al., 1979 and Plummer, 1978. This model nowadays is used as standard model in modelling environments such as a PHREEQC (Parkhurst & Appelo, 1999).

Experimental setup: Dissolution of calcite in stirred system with following characteristic:
- 0.3–0.6 mm CaCO₃ powder
- Temperatures of 5–60°C
- Open-to-atmospheric-carbon-dioxide condition (in contact with constant pressure CO₂)

Method to determine dissolution rate: pH-stat far from equilibrium and drift free near to the equilibrium

Assumption: (1) The diffusional mass transfer is neglected due to the turbulent flow; (2) Describes the dissolution rates on the heterogeneous surface as a function of the surface activities of the species Ca²⁺, H⁺, HCO₃⁻ and H₂CO₃ where the A/V ratio is too large; (3) The dissolution is governed by three following chemical reaction as the main process for dissolution and precipitation of calcite:

\[
\begin{align*}
\text{CaCO}_3 + \text{H}^+ & \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \quad (I) \\
\text{CaCO}_3 + \text{H}_2\text{CO}_3 & \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (II) \\
\text{CaCO}_3 + \text{H}_2\text{O} & \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \quad (III)
\end{align*}
\]

In this model the dissolution rate defined as follow:

\[
R_{\text{pwp}} = r_I + r_{II} + r_{III} \tag{2.10}
\]

Where:
- \(R\) = Overall dissolution rate (moles/cm².s)
- \(r_I, r_{II}, r_{III}\) = reaction rate of equation I, II, and III
- \(k_1, k_2, k_3\) are forward reaction constants and are equal with: (mmol/cm²/s)
  - \(k_1 = 10^{0.198 - 444/T}\)
  - \(k_2 = 10^{2.84 - 2177/T}\)
  - \(k_3 = 10^{(-5.86 - 317/T)} \quad (T \leq 298 \text{ kelvin})\)
  - \(k_3 = 10^{(-1.1 - 1737/T)} \quad (T > 298 \text{ kelvin})\)
- \(k_4\) describes the rate of the backward reaction of I (precipitation) and is a function of both temperature and P_{CO₂}
- \(\alpha_i's\) = the ion activities (-)
2.4.2 Yamauchi et al., (1987)

According to the Yamauchi et al., (1987) the calcite dissolution rate is controlled by excess CO$_2$ concentration, i.e. the concentration of CO$_2$ above equilibrium, also called aggressive CO$_2$.

**Experimental setup:** Dissolution by flow of CO$_2$-acidified distilled water at 40°C in a 100 mm diameter column, packed with CaCO$_3$ particles with following characteristic:

- Packing length = 0.5–2.4 m
- Particle sizes = 1.4–10 mm
- [CO$_2$]$_o$ = 2.4–5 mM
- Superficial velocity = 2.5–9 mm/s
- Retention time = 55–270 s
- Closed-to-atmospheric-carbon-dioxide condition

**Method to determine dissolution rate:** Describe the dissolution rate of CaCO$_3$, the using Tillman’s curve (Figure 2).

**Assumption:** (1) The surface chemical reaction controls the dissolution reaction; (2) Diffusional mass transfer could be neglected as they are fast processes; (3) Steady state condition; (4) The aggressive CO$_2$ concentration used as a driving force; (5) The calcite dissolution has no effect on calcite particle size as the calcite will be refilled frequently with fresh calcite.

![Figure 2. Remineralisation process diagram in limestone dissolution (Yamauchi et al., 1987)](image)

$C_0$ is initial CO$_2$ concentration at the filter inlet and C is final CO$_2$ concentration at the filter outlet and $C_e$ is equilibrium CO$_2$ concentration. The equilibrium line can be calculated using the constant values derived from equations 2.1, 2.2 and 2.3.

$$[\text{CO}_2] = (K_3/K_i)^* K_s [\text{Ca}^{2+}][\text{HCO}_3^-]^2 = C_e$$  \hspace{1cm} 2.10

Furthermore, the operation path in calcite filter start from inlet to the outlet towards the equilibrium point and could be represented as follows:
\[(C_0-[\text{CO}_2])/[\text{HCO}_3^-] = \frac{1}{2}\]  

Yamauchi et al., (1987) reported that, in reality, the equilibrium could not be reached within a finite time, as it is also shown in Figure 2. This means that the calcite dissolution stopped before the equilibrium is reached (c>c_s). The difference between initial CO\(_2\) (C\(_0\)) and the CO\(_2\) concentration at the end is defined as aggressive CO\(_2\) which is driving force of dissolution rate. As a result the relation between the reaction rate and aggressive CO\(_2\) concentration could be defined as follows:

\[- \frac{dc}{dt} = k (C - C_e)\]  \[2.12\]

By integrating the equation 2.12 from \(t_0\) to \(t=t\), the equation 2.13 could be derived.

\[\frac{\ln(C - C_e)}{(C_0 - C_e)} = -kt\]  \[2.13\]

Subsequently, the reaction can be expressed with equation 2.14:

\[\frac{C - C_s}{(C_0 - C_e)} = e^{-kt}\]  \[2.14\]

Moreover, the conversion ratio of carbon dioxide could be calculated as follows:

\[\eta = \frac{(C_0 - C)}{(C_0 - C_e)}\]  \[2.15\]

From equation 2.14 and 2.15 could be concluded that:

\[1 - \eta = \frac{C - C_s}{(C_0 - C_s)} = e^{-kt}\]  \[2.16\]

Moreover \(t\) is an EBCT and could calculated and represents the ratio of empty column volume to the volumetric water flow rate and is defined as follows:

\[t = \frac{zL}{U_L}\]  \[2.17\]

Where:

\[Z_L = \text{height of the calcite filter (m)}\]
\[U_L = \text{superficial liquid velocity (m/s)}\]
\[t = \text{residence time of the water inside the filter (s)}\]

The reaction rate also depends on the specific surface area A/V which could be derived from equation 2.9.

\[R \propto \frac{\text{particle surface}}{\text{bed volume}} = \frac{A_p}{V_p} = \frac{(1-\varepsilon)}{D} = \frac{6(1-\varepsilon)}{d_4p}\]  \[2.18\]
By replacing the equations 2.17 and 2.18 in the equation 2.13 and multiplying it in the calcite dissolution rate constant, the final Yamauchi reaction can be rewritten as below:

$$\ln \frac{C - C_s}{C_0 - C_s} = -\frac{6k(1 - \varepsilon)}{D_p \varphi} \frac{z_L}{U_L} \quad 2.19$$

From now on the $\frac{6k}{\varphi}$ defined as Ya coefficient which is calcite dissolution rate including the form factor and should be experimentally found.
Letterman et al. (1987) developed a model of CaCO₃ dissolution rate which is sensitive to variables such as particle size, bed depth, flow velocity and pressure drop since these parameters affect the dissolution rate and refilling frequency.

**Experimental setup:** Dissolution by flow of HCl acidified soft water at 9°-22°C in four 150-380 mm diameter column, packed with CaCO₃ particles with following characteristic:  
- Packing length = 2.1–3.5 m  
- Particle sizes = 9.6-32 mm  
- [CO₂] and HCl acidity= 0.002–0.4 mM  
- Superficial velocity = 0.15–12 mm/s  
- Retention time = 230-3800 s  
- Closed-to-atmospheric-carbon-dioxide condition

**Method to determine dissolution rate:** Describe the dissolution rate of CaCO₃, using mass balance and modelled the process based on studies done by (Sjöberg & Rickard, 1983; Sjöberg & Rickard, 1984) in which kinetics of reaction modelled using three resistances in series: (1) Liquid film transfer; (2) Surface reaction; (3) Residual layer mass transfer.

**Assumption:**  
(1) The mass transfer and first order surface reaction control the dissolution reaction;  
(2) Steady state condition;  
(3) The calcium difference used as a driving force;  
(4) The calcite dissolution has no effect on calcite particle size.

Letterman et al., 1987 described the calcite dissolution model based on a calcium-ions transport rate from surface of calcite to bulk solution where the dissolution rate is function of calcium concentration at equilibrium. Based on a charge balance relationship under closed-to-atmospheric-carbon-dioxide condition:

\[
2(C_0 + C) + C_c + [H^+] = (DIC_0 + S)(\alpha_1 + 2 \alpha_2)] + C_a + \frac{k_w}{[H^+]} \quad 2.20
\]

Where:  
- \( S \) = the concentration of dissolved calcium carbonate  
- \( K_w \) = the activity-coefficient-corrected ion product for water  
- \( DIC_0 \) = Initial dissolved inorganic-carbon concentration (molar)  
- \( C_c \) = the influent concentrations of cations excluding calcium and hydrogen  
- \( C_a \) = the influent concentrations of anions excluding DIC species and hydroxide  
- \( \alpha_1 \) & \( \alpha_2 \) = the ionization fractions for the deprotonation of carbonic acid and are calculated using the pH, activity-coefficient-corrected ionization constants, and standard relationships used in aquatic chemistry (Colombani, 2008)

Subsequently, solubility product (\( k_{sp} \)) could be calculated as follows:

\[
(C_0 + S')(\alpha_2)(DIC_0 + S') = k_{sp} \quad 2.21
\]

Where:  
- \( S' \) = the concentration of dissolved calcium carbonate at equilibrium

The calcium concentration at any point of calcite filter (\( C_L \)) could be calculated by:
\[ C_L = C_0 + S \quad ; (S \leq S') \]  \hspace{1cm} 2.22

The calcium concentration at equilibrium condition could be calculated by:

\[ C_e = C_0 + S' \quad ; (S \geq S') \]  \hspace{1cm} 2.23

Where the \( S' \) could be calculated by solving the equation 2.20 and 2.21.

Based on a dispersion model for packed bed given by Levenspiel et al., (1972) and the reaction rate expression, Letterman et al., (1987) presents a calcite dissolution rate model given in equation 2.22.

Levenspiel et al., (1972) developed the dispersed plug flow model with the rate equation of 2.24. In this model it is assumed that there is no stagnant pockets and no gross bypassing or short-circuiting of fluid in the vessel. However, the dispersion number represents the back mixing to some extent.

\[ N_d \frac{d^2 \text{Ca}}{dZ^2} - \varepsilon \frac{d\text{Ca}}{dZ} + rt = 0 \]  \hspace{1cm} 2.24

Where:

- \( N_d \) = axial dispersion number, dimensionless \( (N_d = \frac{F*\varepsilon}{U_L*L}) \) and
- \( F \) = dispersion coefficient
- \( Z \) = dimensionless axial distance \( (z=z/L) \)
- \( r \) = reaction rate expression

And calcium carbonate dissolution rate define as follow:

\[ R = k \ a \ (C_{eq} - C) \]  \hspace{1cm} 2.25

Where:

- \( a = \frac{6(1-\varepsilon_L)}{D_p \varphi} \) and is an area of \( \text{CaCO}_3 \) per unit volume of fluid, cm\(^{-1}\)

Based on Letterman, Hadad, & Driscoll (1991), the overall dissolution rate coefficient depends on three following constants: (1) Liquid film mass transfer \( (k_L) \); (2) Surface reaction \( (k_c) \); (3) Residual layer mass transfer \( (k_l) \) and could be expressed as below:

\[ k = \left( \frac{1}{k_f} + \frac{1}{k_c} + \frac{1}{k_L} \right)^{-1} \]  \hspace{1cm} 2.26

**Liquid film mass transfer \( (k_L) \):**

A set of expressions given by Chu et al. (1953) could be used to calculate the liquid film mass transfer \( (k_L) \) given in equations

\[ k_1 = 5.7 \ U_k \ (MR)^{-0.87} \ (Sc)^{2/3} \quad 1 \leq MR \leq 30 \]  \hspace{1cm} 2.27

\[ k_1 = 1.8 \ U_k \ (MR)^{-0.44} \ (Sc)^{2/3} \quad 30 \leq MR \leq 10000 \]
MR and SC are modified Reynolds and Schmidt number respectively and defined as follows:

\[ MR = \frac{dU_s}{\nu(1-\varepsilon)} \quad , \quad Sc = \frac{\vartheta}{D} \tag{2.28} \]

Where:
\[
\nu = \text{kinematic viscosity} \\
D = \text{calcium-ion diffusivity}
\]

**The surface reaction (k_c):**
The surface reaction controlled by the surface protonation and the equation derived empirically using experiments conducted by (Sjoberg & Rickard, 1984)

\[ \log k_c = 14.2 - 1.7 pHeq \tag{2.29} \]

**Residual layer mass transfer (k_f):**
As the calcite used in this study has high purity (higher than 99%) and the filter is frequently filled with fresh calcite, it is assumed that the impurities layer does not exist. Consequently, \( k_f \) could be neglected.

Replacing equation 2.25 in equation 2.24 and solving it, the following equation is represented by Letterman et al., 1987:

\[
\frac{[Ca]_e-[Ca]_o}{[Ca]_e-[Ca]_o} = \exp\left[\frac{-6k(1-\varepsilon_L)}{D_p \varphi} \cdot \frac{z_L}{U_L} + \left(\frac{6k(1-\varepsilon_L)}{D_p \varphi} \cdot \frac{z_L}{U_L}\right)^2 N_d\right] \tag{2.30}
\]

Where \( N_d \) calculated using expression given by Levenspiel et al., (1972) for \( N_d < 0.01 \).

\[ N_d = 2\left(\frac{D}{L}\right) \tag{2.31} \]

However since the dispersion term \( N_d \) is small (<0.01), equation 2.30 could be simplified to the Yamauchi equation given in 2.19. This is because, in equation 2.30, the term \( \frac{6k(1-\varepsilon_L)}{D_p \varphi} \cdot \frac{z_L}{U_L} \) is often around 10 to 20 so that the second term is about 1 to 4 and can be neglected. This makes the Letterman equation identical to Yamauchi equation which neglects dispersion (Shemer et al., 2015).

2.4.4 Conclusion
As demonstrated above, there are disparities in the experimental set-ups, the methods utilized for measuring the dissolution rate and the models applied for correlating the dissolution rate data. A critical study carried out by Hasson & Bendrihem (2006) showed that the calcite kinetics expression given by Plummer et al. (1979) and Plummer (1978) overestimates the dissolution rate by factor of 3-4 at high CO\(_2\) concentration and 1.5-2 at low CO\(_2\) level. This is also confirmed by the recent study done by (Bang, 2012). Yamauchi et al. 1987 and Letterman et al., 1991 are both suitable empirical model to be improved in this study since both of them investigate the calcite dissolution kinetics throughout the packed bed of calcite.

The main difference between Letterman model and Yamauchi model is the driving force which controls the dissolution process. Letterman (1991) defined the mass transfer as the
process controller while Yamauchi (1987) considers the surface chemical reactions as a process controller and uses CO₂ as a driving force while they derived the same equation. However, Letterman (1991) considers the dispersion effect on calcite dissolution while the Yamauchi (1987) assumed the ideal plug flow inside the filter.

Later on, Shemer (2015) shows that the magnitude of the dispersion coefficient is insignificant and rewrites the Yamauchi equation based on a material balance as it is given in equation 2.32. This made the Yamauchi expression identical to the Letterman (1987) equation without the dispersion modification.

\[
\ln \frac{[Ca]_e - [Ca]_l}{[Ca]_e - [Ca]_o} = \ln \frac{[HCO_3]_e - [HCO_3]_l}{[HCO_3]_e - [HCO_3]_o} = \ln \frac{[CO_2]_l - [CO_2]_e}{[CO_2]_o - [CO_2]_e} = -k \frac{(1 - \varepsilon)}{d \cdot \varphi} \cdot \frac{z_L}{U_L}
\]  

2.32

Therefore the equation of Yamauchi is further used as starting point to consolidate the reliability of Yamauchi model and subsequently to investigate the effect of operational such as velocity, CO₂ concentration and specific calcite grain on calcite dissolution rate.

2.5 Parameters affecting calcite dissolution rate

Several studies investigated the effect of various chemical and physical parameters on the calcite dissolution. In the following paragraph the effect of each parameter on the kinetics of calcite dissolution is investigated based on available literature.

2.5.1 Water composition

Several studies confirmed the influence of substances such as magnesium, organic matter (Morse 1974a, 1974b; Berner and Morse, 1974) and copper (Erga & Terjesen, 1956) in the influent water on the calcite dissolution rate. However, the focus of this study is on remineralisation of high quality water from a RO membrane. Therefore the influence of inhibitors such as metallic impurities on the dissolution of calcium carbonate is beyond the scope of this study.

The initial water carbon dioxide concentration is an important parameter to the determine calcite dissolution. The amount of CO₂ dosage is associated with initial pH value. However, as shown in the Tillman curve in Figure 2, by increasing the buffer capacity the amount of aggressive CO₂ decreased, resulting in a decrease in the calcite dissolution rate.

2.5.2 Calcite characteristics

A study conducted by Ruggieri et al. (2008) showed that the calcite dissolution rate is influenced by the reaction surface area of calcite grains as well as the impurities that they contain. This could be explained by the general rate formula for CaCO₃ dissolution given in equation 2.8. As it can be seen from this equation a higher specific surface area (A/V) accelerates the calcite dissolution rate. In general, A/V is affected by the calcite grain size as well as the sphericity of a calcite particle. Several articles showed that, the larger calcite particle has a slower dissolution rate due to its smaller specific surface area (Yamauchi et al., 1987; Letterman et al., 1991; Shemer et al., 2013). Moreover, the sphericity of a particle is equal to the specific surface area of a sphere divided by the surface area of the particle when their volumes kept same. The shape factor could be estimated using the known factors for various shapes given in Table 3. As it can be seen irregular grain size provides larger surface area than the spherical shape ones.
Table 3. Shape factor for various shapes and their ratio compared to standard sphere shape (calculated using volume and surface formula of each shape when volume were same in all shapes)

<table>
<thead>
<tr>
<th>Units</th>
<th>Form</th>
<th>V(mm3)</th>
<th>a(mm)</th>
<th>A(mm²)</th>
<th>A/V(mm)</th>
<th>Compare to spherical (A/V /A/Vₚ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Spherical</td>
<td>0.52</td>
<td>1.0</td>
<td>3.14</td>
<td>6</td>
<td>1.00</td>
</tr>
<tr>
<td>a, b = a/3 h =2a</td>
<td>Rectangle</td>
<td>0.52</td>
<td>0.9</td>
<td>5.11</td>
<td>10</td>
<td>0.62</td>
</tr>
<tr>
<td>a</td>
<td>Square</td>
<td>0.52</td>
<td>0.8</td>
<td>3.90</td>
<td>7</td>
<td>0.81</td>
</tr>
<tr>
<td>a, h = 2a</td>
<td>Tetrahedron</td>
<td>0.52</td>
<td>1.6</td>
<td>4.68</td>
<td>9</td>
<td>0.67</td>
</tr>
<tr>
<td>a, a=h</td>
<td>Cone</td>
<td>0.52</td>
<td>1.3</td>
<td>5.17</td>
<td>10</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average</td>
</tr>
</tbody>
</table>

Calcite impurities has also an effect on the kinetics of calcite dissolution as impurities in the calcite provides a thin residue coating which leached from the calcite surface matrix (Letterman et al., 1991). The regulation defines by Dutch drinking water law, that calcium carbonate should comply with NEN-EN 1018:2006. Based on this regulation, the purity of calcite use for calcite filter should be higher than 98%. At these high purities the effect of the porous layer formed by insoluble impurities in the calcite matrix on mass transfer to and from the calcite surface are considered to be negligible.

2.5.3 Empty Bed Contact Time (EBCT)

The empty bed contact time (EBCT), represents the ratio of the filter volume to flow rate and it could be calculated from equation 2.33:

\[ \text{EBCT} = \frac{\text{(Volume of the filter)}}{\text{(Flow rate)}} = \frac{\pi D^2}{4} \times \frac{Z_L}{U_L} = \frac{Z_L}{U_L} \quad 2.33 \]

The EBCT could be varied either by adjusting the flow over the filter or by sampling over the calcite height. From a process control point of view, it is advantageous that the reaction approaches the equilibrium before water leaves the filter. This is because if the EBCT shifts slightly due to production variation or maintenance, the effect on effluent quality stays minimal (Van Der Laan et al., 2016). In general, according to (Voutchkov, 2013), the EBCT should range from 10 to 30 min. This is also confirmed by recent study by Evides drinking water company (Van Opijnen et al, 2017).

2.5.4 Velocity

The hydrodynamic condition is also one of the variables affecting the calcite dissolution process. Increasing the flow rate tends to minimize the thickness of the boundary layer around the grain, influencing film diffusion, due to elevating Reynolds numbers which enhance the flux of mass between the solid surface and bulk solution, i.e. increasing reaction rate (Lehmann et al., 2013). Figure 3 shows the dissolution rate (illustrated by slope of figure) increased by elevating the flow velocity from 10m/h to 20 m/h. (Lehmann et al., 2013).
Figure 3. Average [Ca2+] in the calcite reactor as a function of retention time for the six case studies: 10, 20 and 30 m/h flow rates (□, Δ and X, respectively) and grey and black signs for 2 different acid dosage of 490 or 721 mg H2SO4/L. (Lehmann et al., 2013)

The modified Reynolds number is inversely proportional with the kinematic viscosity and porosity of the filter bed and proportional with the filtration rate and grain diameter (Letterman et al., 1991)

$$MRe = \frac{d \ast U_L}{\theta(1 - \varepsilon)}$$

2. 34

Where: 
Re = Reynolds number [-]

Calculating the Reynolds number for both grains size shows that the velocity effect is more visible by grain size range 1 - 2 mm as it has larger diameter.

Figure 4. The relation between the velocity and the Reynolds number with porosity of 49% and mean diameter of 0.81 and 1.5 mm and kinematic viscosity at 12 °C.
However, it should be noted that the design EBCT (required EBCT to reach equilibrium) is inversely related to the filtration rate. Therefore, a higher filtration velocity requires a higher calcite bed height to maintain the design EBCT constant.

In conclusion, the reaction rate will be increased by:

- Decreasing the influent pH, increasing the CO$_2$ concentration
- Decreasing the particle size
- Decreasing the sphericity of a particle
- Increasing the velocity
- Increasing EBCT
3 Materials and methods

3.1 Introduction

To investigate the kinetics of calcite dissolution, the pilot research was conducted. In general the research period is divided into three following periods:

- In the period from 08-05 till 25-06 both columns were filled with grain size 0.5-1.2 mm which from now on referred as run 1.
- In the period from 29-06 till 24-07 both columns were filled with grain size 1-2 mm which from now on referred as run 2.
- In the period from 24-07 till 20-08 one column was filled with grain size 0.5-1.2 mm, while the other column was refilled with fresh calcite grain range between 1-2 mm, from now on referred as run 3.

Table 4 lists an overview of the experiments which were conducted and their objective. The details of each experiment will be explained in Part 3.4

Table 4. List of experiments and aims of experiments

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Aim of experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size test</td>
<td>Investigate the effect of calcite grain size on dissolution rate and subsequently required EBCT</td>
</tr>
<tr>
<td>Velocity test</td>
<td>Investigate the effect of velocity on calcite dissolution rate</td>
</tr>
<tr>
<td>CO₂ test</td>
<td>Investigate the effect of extra CO₂ on the calcite dissolution rate/ Required EBCT/ The ratio of the bypass</td>
</tr>
<tr>
<td>EBCT test</td>
<td>Find the required EBCT to reach the equilibrium</td>
</tr>
<tr>
<td>Run time test</td>
<td>Investigate the effect of filter runtime on calcite dissolution rate/ required EBCT</td>
</tr>
</tbody>
</table>

The pilot installation was used to investigate the influence of various parameters on calcite dissolution rate as well as to verify the reliability of the Yamauchi model (Yamauchi et al., 1987), and possibly improve the model. Finally the model was used as a tool to answer research questions regarding water quality and calcite filter operation. In order to limit manual calculations and to increase the accuracy of calculations the modelling environment PhreeqPython\(^1\) was used to simulate the chemical reactions and calculate the equilibrium values. PhreeqPython made it possible to organize all steps in one simulating environment.

3.2 Pilot installation

To answer the research questions a pilot research was carried out in which the results in terms of water quality could be extrapolated to a practical scale. This pilot installation was placed at the production site of “De Hooge Boom” in Kamerik and used ground water, extracted by an existing water treatment plant. The calcite filter Preceded by the RO filters and ion exchanger.

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\(^1\) PhreeqPython is an extension of the Phreeqc chemical calculation engine (Parkhurst & Appelo, 1999) written in Python and is (partly) derived from the (PhreeqPy) extension for IPhreeqc (Mike Müller).
3.2.1 Pilot set-up

Figure 5 shows the process scheme of the pilot set-up. A storage tank was applied as an intermediate buffer in front of the calcite filters. Subsequently, the feed water was pumped and went from the top of the column through each set of filters. The pilot line consists of closed columns filled with granular calcium carbonate (CaCO₃) in two different sizes, followed by a degasification tower with integrated backwash buffer for the contactors. Furthermore, the column itself has a CO₂ injection line controlled by a mass flow controller (MFC). The water quality was continuously measured at different places. Figure 6 shows the pilot plant.

Figure 5. The main water flow scheme of the pilot installation located the production site of “De Hooge Boom” in Kamerik
Both pilot lines shared an influent pump but the flow rate was individually adjustable for each contactor and controlled with automatic control valves. Therefore the contact time was adjustable regardless of the calcite bed height in each contactor. The air supply for the degasification tower and the CO\textsubscript{2} dosage were also both adjustable using the so-called Automatic Settings Program (ASP) in which up to 20 different settings could be programmed.

The other relevant aspects of the contactors were:

- To inspect the contents of the contactors, columns were fitted with sight glasses divided along the height of the contactor.
- The bed height was monitored continuously during the second run using ultrasonic interface sensor while during the first run it is measured with tape measure though the sight glasses.
- Both columns were filled through the top sight glass.
- To prevent CO\textsubscript{2} accumulation, a sensor and vent valve at the top of the contactors were mounted. When a certain amount of CO\textsubscript{2} had accumulated the vent valve opened automatically.
- 20 sampling points were embedded in the column: one just after the CO\textsubscript{2} dosage in the influent line and 19 divided along the height of the column.
- There were six sample points where the calcite along the filter could be taken out.
- Table 5 lists some of the design and operational characteristics of the pilot installation.

Further details about the pilot installation can be found in Appendix V.

| Table 5: Design and operational characteristics of pilot calcite filter at Kamerik |
|---|---|
| Inner diameter | 318 mm |
| Filtration rate | 2.6-28.7 m/h* |
| Flow orientation | Downward |
| Sampling point | Started from 250cm above the filter with distance of 12.5cm between each sampling point |

*The maximum velocity can only be reached when one column is used.
3.2.2 Sensors

As it is depicted in Figure 5, different kinds of sensors were installed to continuously measure the water quality parameters before and after remineralisation as well as after degasification. There were two sets of analysers consisting of similar sensors for each column that measured turbidity, electrical conductivity, and pH levels. Moreover, there were two online CO₂ meters: the first one just after filter 1 while the second one measured permeate flow CO₂ concentration at the beginning of the experiments, but afterwards it was replaced to the flow of filter 1. Furthermore, the process was monitored and controlled by several online sensors that measured operational parameters such as flow, pressure, and temperature. The details of various sensors such as accuracy and detection limits are given in the appendix V-A. In addition, the following details are given:

- The reliability of the data from the water quality sensors were verified a number of times by handheld meters and lab measurements;
- From the second run of the experiment, the automatic bed height meter was installed to record the bed height each minute, where the bed height was estimated by watching through the sight glass for run one;
- Online pH and turbidity meters were calibrated prior to each experiment;
- Data from the various online sensors were collected every second and recorded in an online PI database;
- The calcite dissolution path along the packed bed was tracked by testing the composition of water extracted from 20 sampling points located along the length of the two columns. Each sample was analysed to determine its pH, carbon dioxide, bicarbonate, and calcium contents.

3.2.3 Calcite product

Two different sizes of calcium carbonate were used to investigate the effect of the grain size on calcite dissolution. In our experiments the Juraperle calcium carbonate from the Aqua-techniek company in two different grain size classes of 0.5-1.2 mm and 1-2 mm and a purity of 99.1% was used. The characteristics of these kind of grains are given in appendix V-B.

![Filter bed material, namely: Juraperle 0.5-1.2 mm, Juraperle 1.0-2.0 mm](image-url)
Figure 8 depicts the irregular shape of calcite grain, as well as size variation between two tested grains.

![Image of calcite grains](image)

**Figure 8.** The microscope photo of Juraperle 0.5-1.2 mm at the right side and Juraperle 1-2 mm at the left side with magnification of 4 times

### 3.2.4 Sieving analyses

In order to find the particle size distribution and subsequently the representative calcite diameter size, calcite samples of both grain size classes were analysed using sieve analyses executed by the Vitens laboratory. Subsequently the median diameter (D50) is chosen as a representative diameter in future calculations (Bear, 1988)

Particle size affects the calcite dissolution rate. The result from the sieving analyses are depicted in Figure 9, as the cumulative distribution curve. Based on the results, the median diameter (D50) of 0.81 mm and 1.5 mm were chosen as the representative diameter for particle range between 0.5-1.2mm and 1-2mm respectively.

![Graphs showing particle distribution](image)

**Figure 9.** The Cumulative distribution curve for grain size range between 0.5-1.2mm at the left side and 1-2mm at the right side derived from sieving analyses of 2 samples per each grain size.
3.2.5 Bed porosity

By definition, the bed porosity is equal to the ratio of the void space ($v_p$) to the total enclosed volume of the bed ($v_t$). The following steps were taken to calculate each volume and subsequently to obtain the porosity:

- The calcite filters were filled with nine bags of calcite weighing 25 kg. Given the known calcite density by the supplier (2.7 g/cm$^3$), the calcite volume was calculated with equation 3.1.

$$v_s = \frac{\text{No. of bags to fill the filter} \times \text{weight of each bag}}{\text{Calcite density}}$$  \hspace{1cm} 3.1

- Using calcite height in the column and the area of the column, the total volume of bed were calculated.

$$v_t = H_{\text{calcite}} \times A_{\text{column}}$$  \hspace{1cm} 3.2

- As $v_t$ is the sum of the pores and solid volumes, having $v_t$ and $v_s$, the pore volume ($v_p$) was calculated.

- Finally, by replacing $v_t$ and $v_p$ into the porosity equation, $\varepsilon = v_p / v_t$, the porosity was calculated for each grain size range separately.

The measured porosity for the column that contained the calcite particles ranged between 0.5-1.2mm was 0.5, whereas the porosity of the calcite particles ranged between 1-2 mm was 0.49. Although several studies have illustrated that the porosity of a packed bed is higher near the wall (Vortmeyer & Schuster, 1983) the wall effect was negligible by a column-to-particle diameter ratio higher than 10. (Delgado, 2006; Letterman et al., 1991).

3.2.6 Feed water

During the experimental period, there were 15 wells from which the feed water of treatment plant De Hooge Boom was extracted. This water was also used as feed water in the pilot plant. However, based on water demand during a day the number of in-use wells could also change. The various combinations of these wells formed four different wells configurations. Table 6 shows these well configurations and the number of operating wells during each experiment day. It should be noted that increasing the number of wells could either reduce or increase the CO$_2$ concentration since the extra wells could have lower or higher CO$_2$ concentrations, respectively. To find the water quality of each well combination, the water quality in four consecutive days was sampled and analysed by the Vitens Laboratory, as well as continuously monitored by quality sensors at the pilot plant.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Date</th>
<th>NO. in use wells</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10-5-2017</td>
<td>6-8</td>
</tr>
<tr>
<td></td>
<td>15-5-2017</td>
<td>7-9</td>
</tr>
<tr>
<td></td>
<td>23-5-2017</td>
<td>7-9</td>
</tr>
<tr>
<td></td>
<td>29-5-2017</td>
<td>8-10</td>
</tr>
</tbody>
</table>
As is shown in Figure 5, the feed water to the calcite pilot filters is the permeate water produced by the RO membrane installation that had a post treatment of ion exchange to remove the remaining ammonium. Several water analyses were carried out to identify the permeate water quality. For this purpose, in four consecutive days from 17-20 July four water samples were taken and water composition was analysed at the lab.

Table 7 lists the average cation and anion composition from water analyses carried out during 17-20 July 2017. As expected, the permeate water contained only a low concentration of sodium and chloride. However, due to the low EC and alkalinity capacity as well as fluctuating in CO$_2$ concentration, it was challenging to measure the pH and carbon dioxide in the permeate water. Therefore the reliability of pH and carbon dioxide measurement was further investigated throughout various experiments as it is described in chapter 4.

<table>
<thead>
<tr>
<th>Feed water characteristic</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium</td>
<td>mg/L NH$_4$</td>
<td>0.0</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Mg/l</td>
<td>0.0</td>
</tr>
<tr>
<td>Calcium</td>
<td>mg/L Ca</td>
<td>0.0</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg/L Cl</td>
<td>1.3-2</td>
</tr>
<tr>
<td>Iron</td>
<td>mg/L Fe</td>
<td>0.0</td>
</tr>
<tr>
<td>Magnesium</td>
<td>mg/L Mg</td>
<td>0.0</td>
</tr>
<tr>
<td>Manganese</td>
<td>mg/L Mn</td>
<td>0.0</td>
</tr>
<tr>
<td>Potassium</td>
<td>mg/L K</td>
<td>0.0</td>
</tr>
<tr>
<td>Nitrate</td>
<td>mg/L NO$_3$</td>
<td>0.0</td>
</tr>
<tr>
<td>Sodium</td>
<td>mg/L Na</td>
<td>3.5-4</td>
</tr>
<tr>
<td>Sulphate</td>
<td>mg/L SO$_4$</td>
<td>0.15</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>mg/L HCO$_3$</td>
<td>7.9-12</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>&gt; 5.5</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>mg/L CO$_2$</td>
<td>?</td>
</tr>
<tr>
<td>Methane</td>
<td>mg/L CH$_4$</td>
<td>1.3 - 2.5</td>
</tr>
<tr>
<td>O$_2$</td>
<td>mg/L O$_2$</td>
<td>0.0</td>
</tr>
<tr>
<td>CO$_3$</td>
<td>mg/L CO$_3$</td>
<td>0.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>12±2</td>
</tr>
</tbody>
</table>

Table 7. The average Water quality characteristics from four samples taken between 17-20 July.
A change in the concentration of ions will alter the conductivity value. As a result, to confirm the stability of permeate water quality regarding to the ions content, the electrical conductivity (EC) of permeate water was continuously monitored during a longer period of time than the lab analyses, using the EC sensor at the pilot plant. Figure 10 shows the constant value of EC which confirmed the stability of permeate water regarding its ion content.

![Graph showing EC in permeate water](image)

Figure 10. The EC of permeate water between 10-30 July

3.3 Sensors validation

3.3.1 Reliability of CO\textsubscript{2} and pH sensors at pilot plant

As described in chapter 0, the calcite dissolution rate is strongly affected by the CO\textsubscript{2} concentration in the feed water. Therefore, it is crucial to measure the CO\textsubscript{2} concentration in the feed water with high accuracy. However, as it is illustrated in Figure 11, the permeate water contained a certain amount of carbon dioxide that fluctuated from day to day as well as within each day due to the various well configurations. This made it difficult to measure the exact concentration of carbon dioxide concentration in the feed water of filter.

![Graph showing CO\textsubscript{2} consumption](image)

Figure 11. CO\textsubscript{2} consumption measured by CO\textsubscript{2} sensor in the pilot plant during 4 consecutive days from 17 to 20 July
To measure the carbon dioxide in a reliable way, CO$_2$ was captured in a form of carbonate in which it could not escape. Figure 12 shows the distribution of CO$_2$ species at different pH level. Based on this relation in order to convert all the carbon dioxide to the carbonate the pH of solution should be increased to above 12. For this purpose, sodium hydroxide was applied in the sample bottle before sampling and subsequently the CO$_2$ concentration was calculated using p and m alkalinity measured by the laboratory. This concentration took as a reference CO$_2$ concentration to determine the accuracy percentage of other methods. The further description of this method is given in appendix I.

Moreover, the CO$_2$ were either measured directly using CO$_2$ meter at pilot plant or calculated based on pH, alkalinity, EC and temperature of each sample using NPR 6538, NEN 6533 article.

![Figure 12. Distribution of CO2 species at different pH level simulated in PhreeqPython (Appendix VIII-F)](image)

Figure 13 depicts the error percentage of each method from reference CO$_2$ concentration described above. This error was calculated based on equation 3.3:

$$\text{Error CO}_2 \text{ method} = \frac{\text{CO}_2 \text{ measured or calculated}}{\text{CO}_2 \text{ measured based on p and m alkalinity}} - 1 \quad 3.3$$

The result confirmed the reliability of CO$_2$ meter at the pilot plant while the CO$_2$ calculated based on pH measured at pilot plant showed a considerable overestimation in CO$_2$ concentration. Moreover, the CO$_2$ calculated based on pH determined by the laboratory seemed to be more accurate at low pH values, while it also overestimated the CO$_2$ at lower concentrations. This could be explained by the error in pH measurement.

There are several reasons which cause an error in pH measurement (McDermand, 2017):

- Low electrical conductivity and buffering capacity of the RO permeate which made the pH value unstable;
- Inappropriate of/and irregular calibration of pH meter;
- The CO$_2$ release during sampling or analyses;
- The CO$_2$ absorption from the air into the sample;
- The temperature variation affecting the hydrogen mobility;
- The CO$_2$ absorption in the water which creating carbonic acid and cause pH drop in the time that between sampling and analyses;
- The fluctuating in CO$_2$ concentration reduce the accuracy of pH meter and increase the calibration interval.
Figure 13. Comparing calculated CO₂ concentration based on p and m alkalinity (reference value) with CO₂ measured or calculated from pH

In conclusion, the CO₂ meter was used to estimate the CO₂ concentration in further calculations as it has the less error percentage. The error percentage of this method found to be 9% at high CO₂ percentage. This could be because of device accuracy given by sensor characteristic (appendix V-A). However, as there was no CO₂ measurements at the pilot plant during the first run, the CO₂ concentration calculated by laboratory based on pH, bicarbonate and EC from lab were used as start points in this runs.

3.3.2 The relation between electrical conductivity (EC) and calcium/bicarbonate concentrations

As the permeate water has an constant EC value increases in EC values could be explained by changes in calcium and bicarbonate concentrations. Therefore, to find the relation between EC and these two ions, the results from the EC measured at the pilot plant is plotted against calcium as well as bicarbonate levels that were measured by the laboratory. Figure 14 illustrates a linear correlation between EC and calcium as well as EC and bicarbonate respectively. Fitting data using Python result in the following equations:

\[
\begin{align*}
\text{Ca} \ (\text{mmol/l}) &= 0.005506 \times \text{EC} (\mu \text{s/cm}) - 0.1357 \\
\text{HCO}_3 \ (\text{mmol/l}) &= 0.01081 \times \text{EC} (\mu \text{s/cm}) - 0.1127
\end{align*}
\]

Figure 14. Plotting EC vs calcium at the left side and plotting EC vs bicarbonate at right side with \( R^2 = 0.9991 \)
To check the reliability of relation derived above, several samples over both filters, one with grain size of 0.5-1.2 mm and filter two with grain size of 1-2 mm, were taken on a random day. Figure 15 and Figure 16 illustrate both filters data versus predicted data using the EC relation. As can be seen from these two graphs, the predicted data closely match the measured data for both filters. Moreover, the error calculated for both filters, except for the sample with calcium concentration below 0.4 mmol/l, is around 1%.

![Figure 15](image1.png)

*Figure 15. Predicted calcium and bicarbonate based on EC are shown in red lines, and blue points are measured data in the filter with a grain size of 0.5-1.2 mm and a velocity of 5 m/h and error bar shows the 5% error from the actual data.*

![Figure 16](image2.png)

*Figure 16. Predicted calcium and bicarbonate based on pilot-EC meter and measured data in the filter with a grain size of 1-2 mm and velocity of 5 m/h and error bar shows the 5% error from the actual data.*

As it can be seen from Figure 15 and Figure 16, the predicted data felt between 5% of actual data which confirms the reliability of these two relations. However, when the calcium concentration is too low, the error could become more that 5% due to the low pH values as the EC will be affected by pH values. This relation was further investigated in the details using a PhreeqPython simulation in appendix III. This relation will be used to calculate the calcium and bicarbonate concentration in run two for extra CO₂ dosage experiment.

Another important factor affecting the EC is temperature. A higher temperature implies a lower viscosity which results in increasing the mobility of ions and consequently the EC (Baron and Ashton, 2005). Furthermore, the temperature coefficient is dependent on the type of solution and it is expressed as a percentage of EC increase, when temperature increase by 1 °C (Baron and Ashton, 2005). The RO permeate water composition is almost constant while the water temperature changes between 12-14 °C. Therefore, to extract the effect of temperature variations on EC, the temperature compensation of 2 % was applied to the EC sensor, which converted the EC at any temperature to EC at a reference temperature of 25 °C.
3.3.3 Tracer test on the calcite filter

The dispersion of a fluid in the filter may cause less contact time and consequently less calcium dissolution. However, the effect of axial dispersion expected to be negligible since several studies have been shown the minor dispersion when the ratio of column diameter to length were small (Klinkenberg et al., 1953, Miller et al., 2004; Delgado, 2006). In order to confirm the effect of longitudinal dispersion on calcite dissolution and exclude its possible effect from the dissolution rate the tracer test were conducted. The following steps were followed for tracer test:

- Filter 1 and 2 were filled with grain size range 1-2mm and 0.5-1.2 mm, respectively.
- Both filters were operated at same velocity of 5 m/h.
- Two sample points in the filter were chosen and their EC continuously were measured. To exclude the effect of possible mix flow in the water above the filters, sample point just below the calcite layer were chosen (see Figure 17) and its EC were compared with EC of effluent water.
- The sodium chloride brine was used as a tracer and was pumped through the filter from sampling point behind the filter by impulse injection i.e. the pomp was on for 2 minutes.
- Since the EC is also influenced by the dissolution of calcium and bicarbonate, it is crucial to apply a high concentration of salt to provide a noticeable peak.

![Figure 17. The filter drawing filled with the calcite and sample point EC was measured](image)
Figure 18 and Figure 19 depict the results from filter 1 and filter 2 respectively. By removing the phase difference between the curves in each figure and removing the extra EC which was provided due to the calcite dissolution both curves almost overlapped in both filters which shows that the effect of dispersion was negligible in both filters. The slight difference between the EC values in filter filled with calcite grain size 1-2mm could be explained by equation 2.31 given by Levenspiel et al., (1972) for $N_D < 0.01$. Based on this relation bigger diameter result in greater dispersion.

![Graphs showing EC values for filter 1 and filter 2.](image)

*Figure 18. The left side figure shows the original values of EC measured for filter one with grain size of 1-2mm and right side figure is the same figure where the extra EC from calcite dissolution excluded and the time phase between two samples is removed.*

![Graphs showing EC values for filter 1 and filter 2.](image)

*Figure 19. The left side figure shows the original values of EC measured for filter one with grain size of 0.5-1.2mm and right side figure is the same figure where the extra EC from calcite dissolution excluded and the time phase between two samples is removed.*

### 3.3.4 Ca vs HCO$_3$

To investigate the stoichiometric ratio between calcium and bicarbonate (1:2), the result from measured bicarbonate plotted against the calculated bicarbonate concentration based on a calcium concentration. As it can be seen from the Figure 20, the experimental data confirmed the 1:2 ratio between calcium and bicarbonate. This result could be used to calculate the bicarbonate based on calcium concentration.
Figure 20. The measured and calculated bicarbonate concentration at various height over the filter with grain size 0.5-1.2 and error bars shows the 2% deviation from measured data.
3.4 Overview of experiments

Several parameters affect the calcite dissolution rate. Various experiments were conducted to measure pertinent physical characteristics of the packed-bed contactors and to investigate their effect on calcite dissolution rate at low temperature.

3.4.1 Velocity

In order to study the influence of the incoming flow rate, two sets of velocity tests were conducted. For this purpose, both reactors/columns were fully packed with calcite granules with a diameter of 0.5-1.2 mm for set 1 and 1-2 mm for set 2. Each set of experiments consisted of six different velocities (i.e. 5, 10, 15, 16.5 m/h and later 20 and 30 m/h at a different day). During each test, both filters were run under the same condition to create duplicate data. Samples were collected from 13 sampling ports that were positioned over the height of the column, starting from the top of the column and moving downwards, in order to avoid interference in flow rate during sampling. Each sample was analysed to determine its bicarbonate and calcium concentration.

3.4.2 EBCT

The aim of EBCT experiment was finding the EBCT at which the equilibrium was reached. This experience was repeated three weeks later to investigate the effect of calcite-filter runtime. The EBCT is a function of bed height and flow rate. In the velocity test during each experiment the velocity was kept constant and the EBCT was calculated by changing the bed height while in this experiment EBCT varied by changing the flow rate and it could be calculated using \( \text{EBCT} = \frac{V}{Q} \).

For this purpose, the EBCT range between 10-40 minutes, corresponding to flow velocity of 3.0-12.0 m/h, were tested. The experiment was conducted at a constant temperature of 12°C and the bed height of 2 m and the filters were operated for each given flow condition for 3 hours.

3.4.3 Carbon dioxide dosage

The effect of inlet carbon dioxide concentration on dissolution rate was examined at following conditions:

- Both filters were filled with calcite grain size of 0.5-1.2 mm and 1-2 mm in first run and second run respectively.
- To confirm the reliability of the results, both filters were operated under the same conditions for an hour before samples were taken.
- During both runs the temperature was constant at 12 ± 2°C.
- During the first run, nine samples were taken over the height of each column per carbon dioxide concentration test, while in the second run from all 16 sampling points along the filters samples were taken.
- The calcium, carbon dioxide and bicarbonate content were measured in the lab at the first run; however, since the reliability of electrical conductivity relation with calcium and bicarbonate concentration was shown by previous experiments, this relation was used to estimate the calcium and bicarbonate concentration in the second run.
- The EBCT varied by changing the bed height at a constant filtration velocity of 3.8 m/h.
• The bed heights were measured with a measuring tape through the sight glass in first run and with bed height sensor during second run.

• The carbon dioxide efficiency is calculated as follows:

\[
\text{CO}_2 \text{ efficiency \% } = \frac{\text{Ca}_{\text{in}} - \text{Ca}_{\text{out}}}{\text{CO}_2 \text{ initial} + \text{CO}_2 \text{ dosing}}
\]

Where \( \text{Ca}_{\text{in}}, \text{Ca}_{\text{out}} \) are initial and effluent calcium concentration respectively.

• The initial \( \text{CO}_2 \) concentration measured by the \( \text{CO}_2 \) sensor at the pilot plant with the correction of 9\% is used as inlet \( \text{CO}_2 \) concentration.

• The \( \text{CO}_2 \) concentration of samples at other bed heights were calculated by the laboratory based on bicarbonate, calcium, EC, pH and temperature of each sample using NPR 6538, NEN 6533 article.

• During each run, an additional \( \text{CO}_2 \) concentration (i.e., 2, 4, 6, and 8 mmol/l) was injected into the inlet flow using a mass flow controller (MFC).

### 3.5 Used software

To prevent the complicated and time consuming chemical calculations to find the equilibriums, reactions were simulated in the chemical simulation environment of PhreeqPython (Heinsbroek, 2017). PhreeqPython is an object oriented wrapper around the VIPhreeqc extension of the Phreeqc chemical modelling environment (Parkhurst & Appelo, 1999), written in Python. PhreeqPython uses the STIMELA database and is partly derived from the PhreeqPy extension for IPhreeqc ((Müller et al., 2011). Moreover, Stimela is a modelling environment for standardized mathematical models of drinking water treatment processes developed specifically by Omnisys and Delft University of Technology as part of the Stimela modelling environment (Van der Helm & Rietveld, 2002). Moreover, the modified Yamauchi model (chapter 5) is also implemented in PhreeqPython to calculate the kinetic of dissolution reaction. The main advantage of PhreeqPython over the Phreeqc (Parkhurst & Appelo, 1999) is the combination of Phreeqc and Python in one software. This made it possible to gather the chemical reaction results from Phreeqc and dissolution rate from modified Yamauchi model in one place and simulate the final water quality in Python in the form of graphs or tables. In other words, the user need only to add initial water quality and operational parameters of calcite filter such as velocity, grain size, porosity and bed height in the excel sheet and run the model in PhreeqPython where all calculations will be done at the background and the output will be final water quality regarding calcium and bicarbonate concentration.
4 Results of pilot plant experiments

In this chapter the results of the performed tests are presented and the influence of each parameter is further investigated through sensitivity analyses in chapter 7.

4.1 Velocity tests

The results of velocity variation are depicted in Figure 21. In order to make the data comparable it was crucial to keep the other operating parameters constant. However, the CO\(_2\) concentration fluctuated during the experiments as well as between the velocity tests due to the wells’ configurations which also affected the calcite dissolution. To rule out this effect, the calcium concentration was divided by the corresponding calcium saturation concentration for each sample calculated in PhreeqPython.

In all velocity tests, most of the calcite dissolution took place in the first half meter of the reactor where a high concentration of carbon dioxide was present. It was found that after five minutes empty bed contact time in the filter, the concentration of dissolved calcite reached the 62-72% of the maximum potential mass that could be dissolved (calcium concentration at equilibrium) in the filter with small grain sizes, where this value was between 32-52% for the larger grain sizes when the CO\(_2\) concentration was below 1.5mmol/l.

As it is shown in Figure 21 the dissolution rate slowed down considerably, when water reached approximately the last third of the reactor volume. Furthermore, comparing the calcium concentration in the last section of reactors it is evident that an increase in velocity caused a reduction in calcium concentration as it results in less EBCT.

![Figure 21. Measured [Ca\(^{2+}\)] concentration divided by equilibrium concentration of calcium calculated by PhreeqPython as a function of bed height for the five tested velocities of 5, 10, 15, 20 and 30 m/h flow rates and the CO\(_2\) concentration less than 1.5mmol/l.](image)

Figure 21 and Figure 23 show the results of velocity tests corresponding to run one (grain size 0.5-1.2 mm) and run two (grain size of 1-2mm), respectively, where the EBCT was calculated based on the position of each sample over the bed height.

Calcite dissolution rate represented by the slope (R= dCa/dt) in Figure 22 and Figure 23. To depict the variation between slopes more clearly, each figure is zoomed into the first 10 minutes of the reaction which is shown at the right side. Comparing the experimental results from both grain size, it is evident that, the bigger grain size was more sensitive to the velocity variation than the smaller one, indicating diffusion limitation at lower velocities. The effect of flow rate on calcite dissolution will be further investigated in the model.
Figure 22. Measured [Ca²⁺] concentration divided by equilibrium concentration of calcium calculated by PhreeqPython as a function of retention time for the five tested velocity: of 5, 10, 15, 20 and 30 m/h flow rates where the CO₂ concentration was less than 1.5mmol/l.

Moreover from Figure 22 and Figure 23 could be concluded that, the dissolution rate in the calcite filter with grain size range 0.5-1.2 was clearly higher than the other one. This could be explained based on a equations 2.8 and 2.9 since the smaller grain has a higher specific surface area (A/V) which results in a higher dissolution rate. Moreover, as a result of the faster reaction velocity, the smaller calcite size reaches the equilibrium quicker than the bigger grain size which makes it more efficient to use.

Furthermore, the EC of the effluent water was monitored in seven consecutive days while filter one and two were filled with the 1-2mm and 0.5-1.2mm grain size respectively and both filter were operated at the same conditions. The result confirmed the effect of grain size on calcite dissolution rate as higher EC represents the calcium concentrations. However, from the appeared that, the effect of grain size is more significate at the higher inlet CO₂ concentration.
Figure 24. Effluent EC converted to the reference temperature of 25°C measured at the pilot plant in 7 consecutive days. Filter 1 and 2 contain grain size range 1-2 mm and 0.5-1.2 mm, respectively.
4.2 EBCT effect

As it is mentioned in section 3.4.2, in this experiment the bed height was kept the same and this time the EBCT was varied by changing the flow rate and effluent water quality were compared. Moreover, the experiments were repeated after around three weeks to investigate the effect of the filter run time on calcite dissolution. The result were depicted in Figure 25. The main observations are:

- The grain size of 1-2mm approached the equilibrium after 25 minutes when the CO₂ concentration was low, however it is slightly increased when the CO₂ concentration rose. However, the grain size 0.5-1.2 needed only around 15 min to reach the equilibrium at high CO₂ concentrations as it is depicted by yellow line.
- The performance of filters does not change noticeably after the three weeks of run period.
- Both grain size met the target calcium concentration of 0.625 mmol/l in all tested EBCT.

![Graph showing calcium concentration over EBCT for two grain sizes](image)

**Figure 25.** The calcium concentration at various EBCT at the beginning of the running period with CO₂ concentration of 2 and 1.45 mmol/l and after 3 weeks with a CO₂ concentration of 1.3 and 1.7 mmol/l.

4.3 Carbon dioxide concentration effect

The carbon dioxide concentration is expected to have a noticeable effect on calcite dissolution based on a reaction equation. This could be seen from Figure 25 where the CO₂ concentration changed between 1.3-2 mmol/l. As mentioned in section 3.4.3 to investigate the effect of initial CO₂ concentration, the various CO₂ concentrations were dosed to the water before entering the calcite filter. The influent contained various amount of CO₂. However: reported here is the total CO₂ content (influent + dose). The results of this experiments are given below.

An overview of the calcite dissolution with a grain size of 0.5-1.2 mm and 1-2mm are depicted in Figure 26. The main observations are:

- There is a clear connection between the amount of CO₂ dosage and the calcium production. However, the increase in calcium concentration over the time, slowed down as the calcium concentration approaching the equilibrium concentration. This equilibrium value depends on the initial CO₂ concentration which was applied before the filter.
• When the CO₂ concentration increased, the required EBCT also elevated.

• The maximum efficiency for the grain size 0.5-1.2 was around 81% while the grain size 1-2mm cannot reach the efficiency higher than 74% within the given EBCT.

• The slope of the graphs represents the calcite dissolution rate (R= dCa/dt). As in can be seen from Figure 26, by increasing the carbon dioxide concentration, the calcite dissolution rate also elevated noticeably, especially during the first 10 minutes.

• Additional CO₂ dosage accelerated the calcite dissolution, however, it resulted in a CO₂ efficiency drop as in is shown in Figure 27 and subsequently more effort is required to correct the pH value after the filter due to the high concentration of unreacted CO₂ concentration.

As it is depicted in Figure 27, by increasing the CO₂ dosage, the maximum CO₂ efficiency decreases. Furthermore, the CO₂ efficiency for the grain size 1-2 is less than grain size range between 0.5-1.2 mm at same operation condition such as EBCT. This is reasonable as there is less reaction surface area available by this grain size.

Figure 28 shows the CO₂ efficiency at various EBCT for different inlet CO₂ concentrations. As it can be seen, by reducing the EBCT below the 15 minutes, the CO₂ efficiency drops below 80%. This is because at shorter EBCT, part of aggressive CO₂ leaves the filter unreacted while if the EBCT be sufficient it will be converted to the calcium and results in increasing the CO₂ efficiency.
Figure 28. The CO$_2$ efficiency versus the EBCT when the EBCT changed by adjusting the bed height for grain size 0.5-1.2mm and constant velocity

The CO$_2$ efficiency is preferably high to limit chemical consumption such as required NaOH to correct the pH. However, it could never reach 100% because:

1) The chemical equilibrium in practice is never achieved within a limited contact time. (Yamauchi et al., 1987). As CO$_2$ dissipates from the water, the kinetics of the process decreases and consequently a realistic contact time in practice is more insufficient to convert all the aggressive CO$_2$.

2) Based on a Tillman's curve given in Figure 2, part of the CO$_2$ will not participate in the reaction because it is present as non-aggressive CO$_2$. Water in chemical equilibrium always contains a certain amount of non-aggressive CO$_2$ relative to the amount of HCO$_3^{-}$ present in the water. Therefore the process becomes inefficient as the bicarbonate content in the water increases (Letterman et al., 1991)
5 Mathematical model

The calcite dissolution kinetics plays a fundamental role in the effectiveness of the remineralisation process in practice. Therefore, it is crucial to develop the kinetics model which could predict the calcite dissolution with high accuracy. This model could be utilized to predict the calcite dissolution rate as a function of design parameters and subsequently to improve design and operation condition regarding produced water quality and cost efficiency. In general the objective of using the mathematical model are:

1. To calculate the effluent water quality based on the initial water quality data after calibration of the model
2. To determine the optimal design and operational variables of a calcite filter

In order to model the remineralisation process from the beginning until the point of equilibrium, three steps were taken:

1. Simulation of chemical reactions in calcite filters using PhreeqPython
2. Determining the reaction rate based on model given by Yamauchi since the Phreeqc uses the PWP model which is not so reliable for our system with low pH value. (Hasson & Bendrihem, 2006; Bang, 2012; Shemer et al., 2013)
3. Fitting the model to pilot experiments data

5.1 Simulation of chemical reactions

The inlet water of the filters was permeate water with a low and constant ion content. In our simulation the average water quality given in Table 5 was used. The initial concentration of calcium and bicarbonate was measured for each run by the laboratory and the CO₂ concentration were measured at the pilot plant using CO₂ meter. This information was used to calculate the calcium concentration at equilibrium using the implemented Phreeqc in the PhreeqPython.

5.2 Reaction rate based on Yamauchi model

To calculate the kinetics of the calcite dissolution reaction, the Yamauchi model (Yamauchi et al., 1987) is used (see chapter 20 for extensive description). According to Yamauchi et al., the aggressive CO₂ is a driving force of reaction and the basic dissolution rate expression is:

Based on Yamauchi equation (Eq. 2.32), there is a linear relationship between \( \ln \left( \frac{[X]_e - [X]_L}{[X]_e - [X]_0} \right) \) vs. the EBCT, where X represents either [HCO₃] or [Ca] and the subscripts 0, L, and e stand for inlet, bed height and equilibrium concentrations respectively. The slope of this line gives the \(-k \left( \frac{1}{D_p \phi} \right)^{\frac{1}{6} - \epsilon_L} \). By replacing the corresponded diameter and porosity, the Ya coefficient could be calculated experimentally. It should be noted that, Ya coefficient is calcite dissolution rate coefficient which contains also the from factor and therefore there is no need to measured or calculate the form factor separately. To calculate the Ya coefficient, the results from velocity tests for both grain size were used. The result are shown in Figure 29 and Figure 30.
Figure 29. The Linear plot of \(\ln\left(\frac{[Ca]_e-[Ca]_L}{[Ca]_e-[Ca]_o}\right)\) vs. EBCT for grain size of 0.5-1.2mm at the left side and 1-2mm at right side where \(R^2 > 0.99\) for grain size 0.5-1.2mm and \(R^2 > 0.98\) for grain size 1-2mm.

Figure 30. The Linear plot of \(\ln\left(\frac{[Ca]_e-[Ca]_L}{[Ca]_e-[Ca]_o}\right)\) vs. EBCT for various grain size at the velocity of 5 m/h and 13 °C

The main observations from the figures above are:

- The experimental data confirmed the linear relation given by Yamauchi et al. as the result follows the identical straight line with correlation coefficient of \(R^2 > 98\).
- We found that filtration rate has the converse effect on calcite dissolution rate as by increasing the velocity the contact time necessary to reach equilibrium decrease; This effect can be seen from Figure 29, however the effect is more obvious in calcite grain size 1-2 mm. This observation was also found by Yamauchi et al.; however Yamauchi et al.(1987) did not take in to account the effect of velocity on Reynolds number. The turbulence of the flow increases with increasing filtration rate based on a Reynolds number equation and more turbulence accelerates the transfer of substances from solid surface to bulk solution (Lehmann et al., 2013).
- Figure 30 depicts the effect of calcite grains on dissolution rate constant which reaffirmed the model given by Yamauchi et al. It can be seen that the smaller particle has a steeper slope which corresponded to the greater Ya coefficient. This could be explained by the fact that the smaller particles has larger surface reaction which accelerate its dissolution rate.
- Ya coefficient, found from the velocity test, ranged between \(4.86 \times 10^{-3}\) to \(7.78 \times 10^{-3}\) for grain size 0.5-1.2mm and between \(4.12 \times 10^{-3}\) to \(8.24 \times 10^{-3}\) for grain size 1-2mm
when velocity range between 5 to 28.7 m/h. The difference between Ya coefficient could be explained by diversity in form factor of each grain size.

Table 8 compares the calcite dissolution rate based on the Yamauchi model derived from previous studies with the dissolution rate constant derived from our experimental data. The results show that the dissolution constant strongly affected by changing the temperature. As it is shown in Figure 31, the dissolution rate increased by factor of 2 by elevating the temperature from 22 °C to 30 °C (Shemer et al., 2013). However, the dissolution rate constant derived from study of (Shemer et al., 2013) at temperature of 22 °C is comparable with our experimental data. Since the temperature in our case was approximately constant, the temperature effect on calcite dissolution was neglected.

### Table 8: Calcite dissolution rate (Ya coefficient) from previous studies regarding their operational conditions and our experimental data

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>D_{p} (mm)</td>
<td>2.85</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1.34.137.136</td>
<td>0.5-1.2 mm</td>
<td>1.2 mm</td>
</tr>
<tr>
<td>t</td>
<td>38%</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>56%</td>
<td>56%</td>
<td>40-44%</td>
<td>53%</td>
<td>49%</td>
</tr>
<tr>
<td>Velocity (mm/s)</td>
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<td>2.75</td>
<td>4.56</td>
<td>4.56</td>
<td>4.56</td>
<td>4.16</td>
<td>2.7</td>
<td>2.1</td>
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</tr>
<tr>
<td>4.14</td>
<td>4.56</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>2.7</td>
<td>8.6</td>
<td>4.58</td>
<td>4.58</td>
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<tr>
<td>6.22</td>
<td>7.51</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.97</td>
<td>197</td>
<td>197</td>
<td>197</td>
</tr>
<tr>
<td>Column diameter (mm)</td>
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<td>98</td>
<td>98</td>
<td>98</td>
<td>980</td>
<td>100</td>
<td>198</td>
<td>198</td>
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<td>Seed size (mm)</td>
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<td>1.0</td>
<td>1.0</td>
<td>0.94</td>
<td>0.94</td>
<td>1.0</td>
<td>0.5-2.4</td>
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<td>22</td>
<td>22</td>
<td>22</td>
<td>28.6</td>
<td>28.6</td>
<td>24</td>
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</tr>
<tr>
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<td></td>
<td>122.2</td>
<td>122.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO_{2} concentration (mmol/l)</td>
<td>0.5</td>
<td>2</td>
<td>4.3</td>
<td>3.4-4.3-6.8</td>
<td>0.25-0.75</td>
<td>1.4-3.4-6.4</td>
<td>3.4-5.6-6.8</td>
<td>0.95-2.16-3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>k_{31} (mol/kg)</td>
<td>5.1E-03</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>2.3E-03</td>
<td>?</td>
<td>4.8E-03</td>
<td>4.8E-03</td>
<td>4.8E-03</td>
</tr>
<tr>
<td>E/k_{31}</td>
<td>7.1E-03</td>
<td>6.59E03</td>
<td>120E-07</td>
<td>1.01E-02</td>
<td>1.76E-03</td>
<td>8.38E-03</td>
<td>4.8E-03</td>
<td>4.8E-03</td>
<td>4.8E-03</td>
</tr>
<tr>
<td>Calcite purity</td>
<td>98%</td>
<td>96%</td>
<td>96%</td>
<td>94%</td>
<td>94%</td>
<td>97.5%</td>
<td>?</td>
<td>99%</td>
<td>99%</td>
</tr>
</tbody>
</table>

![Figure 31. Recap from previous studies on calcite dissolution rate using the Yamauchi model](image-url)
5.3 Calibration of Yamauchi model

The effect of velocity on dissolution rate constant was further investigated to find a unique relation which fit the velocity data. For this purpose the least squares method is used. The result from this fitting data are shown in Figure 32.

The calcite dissolution rate coefficients $6k/\Phi$, obtained by analysing the data from ten velocity runs (5 various velocity for each grain size) were found to fit the following correlations:

$$\frac{6k}{\Phi} \left( \frac{mm}{s} \right) = 2.96 \times 10^{-3} \sqrt{U_L (mm/s)} \quad (4.1)$$

This equation will be used to calculate the Ya coefficient in Yamauchi et al., model. However, as it can be seen from Figure 32 this correlation underestimate the dissolution rate coefficient ($6k/\Phi$) at low velocity of 5 m/h, especially for the smaller grain size. This is because when comparing the dissolution rates obtained from the 5 and 10 m/h velocity tests depicted in Figure 29, could be concluded that at such low flow rate the dissolution rate was not a function of the flow velocity since the slopes of the dissolution rate curves of both velocities were almost identical. In other words, under the conditions tested, the increase of the flow rate from 5 to 10 m/h did not have a visible effect on the dissolution rate.

By replacing the velocity correlation to the Yamauchi et al model given in 4.1 , the modified Yamauchi expression will derive:

$$ln \left( \frac{[Ca]_e - [Ca]_i}{[Ca]_o - [Ca]_o} \right) = 2.94 \times 10^{-3} \sqrt{U_L (mm/s)} \left( 1 - \frac{\epsilon_L}{D_p} \right) * \frac{z_h}{U_L} \quad (4.2)$$

The input data of the model consists of two main parts: the initial water quality before the filter to calculate the calcium concentration at equilibrium using the PhreeqPython and the operational parameters such as velocity, bed height and calcite grain size. To make all calculations more organized in one place, the model has been implemented in PhreeqPython.

5.3.1 Result from modified model

The result from the duplicated velocity test and CO$_2$ test were used to validate the modified Yamauchi model.
Figure 33 and Figure 34 show the result of calcium concentration predicted by modified Yamauchi model for grain size 0.5-1.2mm and 1-2mm respectively.

As it is shown in Figure 33 and Figure 34, the model can predict the calcium concentration at each EBCT with error less than 5% except the velocity of 5m/h which sometimes error is around 8%. This is because as it is mentioned the velocity correlation underestimated the dissolution rate as it is shown in Figure 32. Figure 35 depicts the small grain size CO₂ experiment simulation using the modified Yamauchi model in PhreeqPython. The PhreeqPython code of these simulations are given in appendix and VIII.
In conclusion, the pilot results confirmed the validity of the modified Yamauchi model for desalinated water from RO with a various operational variable such as calcite grain size, velocity, EBCT and initial carbon dioxide and calcium concentration at low temperature. The result shown only approximately 5% error. This error could be explained by several reasons explained below:

- As it is shown before, one of the important parameter affecting the calcite dissolution is initial CO₂ concentration. Therefore the accurate measurement of initial CO₂ concentration is crucial to predicting the calcium concentration using the model. However, the permeate water contains a variable amount of CO₂ concentration which was measured with a CO₂ meter at the pilot plant and this sensor has an accuracy of ±5%. This error in measurement could cause the deviation between measured and predicted data.

- Grain size: The other reason that could cause an error in simulation values is the calcite grain size. The model used the average grain size found from sieving analyses while there are a range of grain size inside the filter which could cause a small deviation between a predicted and measured data.

- Bed height: As it is mentioned in chapter 3.2.1, the bed height during the first run with grain size 0.5-1.2 mm were measured using the tape measure from the outside of the filters which may result in an inaccuracy in height measurement and consequently in the model.
5.3.2 Testing the Yamauchi assumptions

As previously mentioned, the calcite dissolution rate is proportional to the specific surface area. Yamauchi et al. (1987) assumed the calcite filter as one layer, plug flow, model in which the effect of calcite dissolution on grain size and subsequently on specific surface area was neglected. In the following part the validity of these two assumptions will be tested.

As it can be seen from Figure 36, most of the dissolution took place in first half meter of calcite filter which diminishes over the bed height. This part will be filled frequently with fresh calcite to keep the design EBCT constant. The frequency of refilling could be calculated using model based on calcite reduction. This will be explained in chapter 6. It is recommended to reload the filter by more than 10% reduction in initial calcite level to maintain the design EBCT. (Ludwig & Hetschel, 1986)

![Figure 36. Calcite dissolution simulation at constant water quality and grain size using the modified Yamauchi model](image)

To estimate the diameter reduction before refilling the filter, it is assumed that the number of calcite grains in specific volume does not change during the calcite dissolution and calcite grain assumed to be spherical to simplify the calculations. Using these assumptions the number of calcite grains in the filter could be calculated with median diameters of 0.81 mm and 1.5 mm for each grain size as follows:

\[
V_{\text{calcite packed}} = \frac{\text{No. calcite bag} \times \text{Weight of each bag} \times \text{Purity of calcite}}{\text{bulk density of calcite}}
\]

\[
\text{No. calcite grains} = \frac{V_{\text{calcite packed}}}{\frac{2}{3} \pi \left(\frac{d_p}{2}\right)^3}
\]

Subsequently, the reduction volume could be calculated based on 10% bed height drop (after 10% the filter will be reload) by:

\[
H_{\text{After reduction}} = \frac{V_{\text{calcite packed}}}{\text{Surface area of the filter}} \times \text{Porosity} \times 0.9
\]

If the number of calcite grains stay constant, the new diameter could be calculated with equation 4. 4 by replacing the volume of calcite packed after the reduction. The diameter of
calcite after 10% reduction in bed height was equal to 0.76 mm from initial diameter of 0.81 mm.

Subsequently, the calcite concentration over the bed height was simulated using modified Yamauchi model to see the effect of calculated diameter reduction on calcite dissolution.

As it can be seen from the Figure 36, the effect of diameter reduction on calcite dissolution rate is not large. This reaffirmed the assumption made by Yamauchi et al regarding the negligible effect of calcite dissolution on calcite grain size during the operation period.

In order to further examine the necessity of a more complex model based on a multi-layer concept, an existing multi-layer model is used (G. Zweere, 2016). The model was built in PhreeqPython where it has been assumed that after each backwash the stratification of grain sizes over the bed height will occur. In this model, similar as Yamauchi model (Yamauchi et al., 1987), the aggressive CO$_2$ is defined as driving force for calcite dissolution in the water and as a starting point, the first order reaction kinetics (Eq. 4.6) is used to describe the dissolution process.

$$\frac{-dc}{dt} = k (C - Cs)$$  \hspace{1cm} 4.6

Since the half-life of a first-order reaction is a constant, by calculating the aggressive CO$_2$ at half concentration the rate constant (k) from below equation could be recalculated.

$$[CO_2] = \frac{1}{2} [CO_2]_0 \rightarrow \frac{[CO_2]}{[CO_2]_0} = \frac{1}{2} = e^{-kt} \rightarrow t = \frac{\ln 2}{k} = \frac{0.693}{k} V$$  \hspace{1cm} 4.7

Subsequently, the half concentration of aggressive CO$_2$ could be calculated using 4.8.

$$\text{Aggressive CO}_2 \ 1/2 = K_{solving} * v^{0.65} * \varphi * \rho * d^{1.1} / \rho$$  \hspace{1cm} 4.8

Where:

- $\rho$ = density of calcite grains (2500-2700 kg/m$^3$)
- $\varphi$ = porosity of the bed (0.32-0.5)
\[ d = \text{grain size} \]
\[ \varphi = \text{granular shape factor} = (0.9 \text{ to } 0.665) \]
\[ V = \text{filtration velocity (contact time)} \]
\[ K_{\text{solving}} = \text{correction factor} \]

Subsequently, the particle size distribution over the bed height assumed to be from smallest to largest diameter in the downward direction. Finally, the bed height divided to about 100 layers (in this case 0.025 m each layer) in such a way that the water quality calculated for above layer become the inlet water quality for below layer. This information is used to build the model in PhreeqPython. However, the further description of model in details is beyond the scope of this research.

To compare the results from both models, the velocity experiment of 16.5 m/h for grain size 0.5-1.2 mm was chosen and the calcite dissolution rate over the bed height was simulated with both modified Yamauchi model as well the multilayer model. The simulation data are shown in Figure 38. As it can be seen, there is no considerable variation in an accuracy of results simulated by modified Yamauchi model and it can simulate the calcite dissolution with accuracy of 95% or more. Therefore, there is no need for the multilayer model.

This confirmed single layer model given by Yamauchi which is also the based model used in this study.

![Figure 38. The simulation result from multi-layer model (left); (G. Zweere, 2017) and the modified Yamauchi model from this study (right) when the velocity, water quality and grain size are same.](image)

### 5.3.3 Model application regarding operational variable

Finally the model was used to predict the final calcite concentration. Figure 39 shows the simulation of modified Yamauchi model, at average initial water quality, bed height of 2 meter and grain size of 0.5-1.2mm. This simulation illustrates the influence of operational parameters on the calcium concentration after the filter. The coloured bar shows the calcium concentration in mg/l. The elevation of velocity, diameter, and porosity cause the reduction in calcium concentration. Furthermore, replacing diameter of 0.81mm and porosity of 50% can be seen that with this carbon dioxide concentration and water quality, with velocity higher than 10 m/h the required calcium concentration of 25 mg/l could be reached. This is when there is no bypassing and 100% of water goes through the filter. For example if we want to have a 53% bypassing, the treatment water should contain the calcium concentration of 51.2 mg/l which is only possible at velocity below 10 m/h.
Figure 39: Sensitivity analyses based on Yamauchi model (Yamauchi et al., 1987) with various levels of porosity, diameter, and velocity created using python and plot.ly (https://plot.ly/create/?fid=sara.ghanbari)
6 Application and optimal design

6.1 Introduction
The design of a calcite filter should comply with a pre-defined water quality. Table 9 listed current Oasen guidelines quality of remineralized water. To reach the target values besides the calcite concentration, the required magnesium concentration will be added to the filtered water in the form of MgCl₂·6H₂O (Magnesium-chloride). The parameters affecting the design and operational costs of calcite filters consist of the EBCT, the inlet CO₂ concentration and the bypass ratio. In this chapter various design scenarios will be discussed to determine the most cost efficient design. The cost calculation only includes the calcite filtration step, not the cost for dosing of magnesium chloride.

Table 9. Oasen water quality regulations

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<th>Parameter</th>
<th>Oasen standard</th>
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<tr>
<td>Total Hardness</td>
<td>1 mmol/L</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>1.25 - 1.45mmol/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.625 mmol/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.375 mmol/L</td>
</tr>
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</table>

6.2 General process scheme
Oasen plans to build its first full scale RO plant at drinking water treatment plant (DWTP) De Hooge Boom in Kamerik. For this purpose, capital expenditures (CAPEX) and operating expenses (OPEX) of each design scenario will be estimated based on this plant to find the optimal process parameters, in which the cost are minimal. Figure 40 depicts the main water flow scheme based on reference scenario consist of four parallel unites to guarantee the required water treatment capacity and redundancy of the system. Table 10 lists the water quality and water demand data of DWTP De Hooge Boom in Kamerik.

Figure 40. General treatment process scheme for the new to build DWTP De Hooge Boom
Table 10. Design parameters for the full-scale treatment plant De Hooge Boom in Kamerik.

<table>
<thead>
<tr>
<th>Design parameter</th>
<th>value</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual production</td>
<td>2.628</td>
<td>million m³/year</td>
</tr>
<tr>
<td>Average production</td>
<td>300</td>
<td>m³/hour</td>
</tr>
<tr>
<td>Peak factor</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td>Maximum capacity</td>
<td>420</td>
<td>m³/hour</td>
</tr>
<tr>
<td>Redundancy</td>
<td>N+1</td>
<td>At average production</td>
</tr>
<tr>
<td>Number of units</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Average capacity per unit</td>
<td>105</td>
<td>m³/hour</td>
</tr>
<tr>
<td>Hydraulic capacity per unit</td>
<td>140</td>
<td>m³/hour</td>
</tr>
<tr>
<td>CO₂ in RO permeate (max)</td>
<td>1.8</td>
<td>mmol/l</td>
</tr>
<tr>
<td>CO₂ in RO permeate (min)</td>
<td>1.25</td>
<td>mmol/l</td>
</tr>
<tr>
<td>CO₂ in RO permeate (average)</td>
<td>1.5</td>
<td>mmol/l</td>
</tr>
<tr>
<td>CO₂ dose²</td>
<td>0</td>
<td>mmol/l</td>
</tr>
<tr>
<td>CO₂ efficiency</td>
<td>80%</td>
<td>-</td>
</tr>
<tr>
<td>Contact time</td>
<td>15</td>
<td>minutes</td>
</tr>
</tbody>
</table>

The total cost of an installation have a relation with the cost of the mechanical components of an installation. The cost for the mechanical components for this calculation are based on a reference values from already implemented projects. Beside the construction expenses, the investment costs known as capital expenses (CAPEX) include 35% of additional costs for project management, design, construction supervision and interest during construction. Cost for interest and depreciation and for operation and maintenance (O&M) were determined as a ratio of the construction costs. These factors were listed in Table 11. The costs used for chemicals and energy and operational parameters are shown in Table 12. The actual calculations can be found in the Excel workbook “20180105– Businesscase-Oasen.xlsx”

Table 11. Factors used for interest and depreciation, operation and maintenance (Van Der Laan et al., 2016)

<table>
<thead>
<tr>
<th>Costs</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Interest &amp; Depreciation</strong></td>
<td></td>
</tr>
<tr>
<td>Building</td>
<td>6.6%</td>
</tr>
<tr>
<td>Mechanical + Piping</td>
<td>8.7%</td>
</tr>
<tr>
<td>Electrical</td>
<td>10.3%</td>
</tr>
<tr>
<td><strong>Operation &amp; Maintenance</strong></td>
<td></td>
</tr>
<tr>
<td>Building</td>
<td>0.5%</td>
</tr>
<tr>
<td>Mechanical + Piping</td>
<td>2.0%</td>
</tr>
<tr>
<td>Electrical</td>
<td>4.0%</td>
</tr>
<tr>
<td>Additional costs</td>
<td>35%</td>
</tr>
</tbody>
</table>

Table 12. Cost for chemicals and energy (Van Der Laan et al., 2016)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite granular per ton</td>
<td>€ 74</td>
</tr>
<tr>
<td>CO₂ per ton</td>
<td>€ 102</td>
</tr>
<tr>
<td>Energy per kWh</td>
<td>€ 0.11</td>
</tr>
</tbody>
</table>

² There is at average 1.5 mmol/L CO₂ in the RO effluent, which is more than sufficient to dissolve 0.625 mmol/L of CaCO₃.
6.3 Assumptions and boundaries conditions
In this part the technical starting points of this design are be discussed.

Design capacity
The average capacity should be sufficient to achieve the maximum capacity with 4 units in operation and average capacity with 3 units in operation. This will guarantee the adequate redundancy in the case that one unit fails or needs to be maintained. In this design, to determine the filter dimensions, the capacity per unit is calculated using equation 5.1. This will prevent oversizing the filters. It is possible that one unit fails at the maximum capacity, then the capacity should be achieved by operation at shorter contact time.

\[
Q_{\text{per unit}} = \text{Max} \left( \frac{Q_{\text{max}} \times \text{treatment} \%}{\text{Number of units}}, \frac{Q_{\text{Average}} \times \text{treatment} \%}{\text{Number of units} - 1} \right)
\] 5.1

Filter dimensions
The calcite bed height should be in a range between 1.5-3 m (Voutchkov, 2013). Due to practical problems regarding transportation of filters to the production location, the diameter of filter should not be above the 3.5m. This will avoid high costs of transportation. Besides that, by decreasing the ratio of column diameter to length, the possible dispersion effect will minimize (Delgado, 2006).

Calcite grain size
From the experimental results it was concluded that calcite grain size range between 0.5-1.2mm accelerates the calcite dissolution kinetic due to the larger specific contact area (A/V). Therefore this calcite grain size will be used in the design.

CO\textsubscript{2} concentration in the RO permeate
As it is discussed before, the carbon dioxide concentration at De Hooge Boom production location fluctuates from day to day due to the various well configurations. However, in this design, the average CO\textsubscript{2} concentration of 1.5 mmol / L will be used as an available CO\textsubscript{2} concentration in permeate water. This could be done by changing the wells combination in such a way that the amount of carbon dioxide is kept as constant as possible in all configurations.

Furthermore, the modified Yamauchi model developed in this study is used to determine the minimal CO\textsubscript{2} concentration to achieve the target calcium concentration as well as to comment on various scenarios with different bypass ratio.

The CO\textsubscript{2} efficiency is another important factor to determine the optimal CO\textsubscript{2} concentration. The results from pilot research are shown that the CO\textsubscript{2} efficiency decreases by increasing the CO\textsubscript{2} concentration as well as by a reduction of the EBCT. It should also be noted that higher CO\textsubscript{2} dosage requires a higher pH correction after the filter. Here it is assumed that the aeration step provides sufficient capacity to remove the residual CO\textsubscript{2} and therefore, in order to find the optimal CO\textsubscript{2} dosage, the subsequent aeration step will be not taken into consideration.
EBCT
From a process control point of view, there are several advantages to have effluent water from the filter which has approached the equilibrium closely. From the experimental results it was observed that after 15 min EBT there is no significant change in calcium concentration which means that the equilibrium is practically reached after 15 min. There are three main advantages to achieve a complete reaction:

1. The contact time is not critical: a slight decrease in the height of the filter bed does not affect the calcium and bicarbonate concentrations of the effluent water from the filter. Therefore, the refilling of the filter bed can be less accurate and less frequent.
2. Short production interruptions or changes in the production flow rate have not noticeable influence on the calcium and bicarbonate concentrations in the effluent water from the filter.
3. The calcium and bicarbonate concentrations can be controlled with just the CO₂ dosage instead of the CO₂ dosage and the EBCT, because the EBCT is always sufficiently large. This makes the management of the process simpler and more robust.

Moreover, the EBCT less than 15 min is not desirable as the CO₂ efficiency will decrease at shorter EBCT; especially at the higher CO₂ concentrations. Therefore the design is based on EBCT of 17 min, to still reach the minimum EBCT of 15 min, at design capacity when the bed height has been dropped.

Velocity
In order to maintain the minimum EBCT of 15 min for a fix bed height of 2.7 m (10% bed reduction) at design capacity, the velocity should not be more than 10.8 m/h. This could be calculated as follows:

\[
EBCT = \frac{Volume}{Q} = \frac{Area \times H}{Area \times velocity} = \frac{H}{velocity} \Rightarrow V_{Max} = \frac{2.7}{\frac{15}{60}} = 10.8 \text{ m/h}
\]

Dispersion effect
To investigate the effect of non-plug flow on the practical scale, the results from tracer test done from at the Kolff production location of Vitens is used (Zweere & Teunissen, 2015). To determine how the water flows through the filter, a tracer test has been carried out on the filter with the packed bed height of 2.85 m, the flow rate of 220 m³/h, the surface of the filter is 23.7 m² and the porosity of 0.47. During the experiment, the EC was measured each 90 second from the 8 sample points along the filter bed. Then the results from sample point at 2.6 m from the ground was taken as starting point and the flow was modelled with the assumption of plug-flow. Subsequently, the calculated results from the model were compared with measured data. The results from two sample points at height of 2.1 and 0.6 meter are shown in Figure 41 and Figure 42 respectively. The results of this experiment confirmed the almost ideal plug-flow through the filter. As a result, the effect of dispersion will be also neglected in translating the pilot model to the full-scale.
6.4 Model application

Calculations were performed based on the modified Yamauchi model to determine the calcium concentration and subsequently to determine the percentage of bypass ratio. Furthermore a cost-effectiveness analysis was carried out. The calcium concentration at design operation was used to calculate the bed refilling frequency.

The key parameters of this design in short are:
- The design capacity of 420 m³/h
- The average capacity of 300 m³/h
- EBCT of 15-17 min
- The maximum velocity of 10.8 m/h
- The average water quality given in Table 7
- The average carbon dioxide concentration of 1.5 mmol/l
- Max filter diameter of 3.5 meter
Based on the design parameters the calcium concentration was calculated using the modified Yamauchi model. The minimum carbonate dioxide required to reach the calcium target was also determined. As it is illustrated in Figure 43, the calcium concentration almost approached the equilibrium at EBCT of 15 minutes. A minimum CO₂ concentration of 0.65 mmol/l to provide the calcium target is needed. Since there is always a higher CO₂ concentration of 1.5 mmol/l in the permeate water, a 100% treatment with calcite filtration would result in a concentration of 1.3 mmol/l calcium. Therefore, in the following cost calculations scenarios the design is based on a constant bypass flow.

The treatment percentage were calculated as follows:

\[ x \cdot 1.28 + (1-x) \cdot 0.04 = 0.625 \]

where 0.04 mmol/l is initial calcium concentration of water and 1.28 is predicted calcium concentration when the inlet CO₂ concentration is 1.5 mmol/l using model and x is the treatment percentage that is 47%. This used as treatment percentage in scenarios 1-4 where no extra CO₂ was dosed in the system.

**Refilling frequency**

To calculate the refilling frequency the following steps should be done:
First the produced calcium will be calculated using model. In our case this is 1.28 mmol/l. using this value the amount of calcite consumption could be calculated using equation 5.4.

\[ \text{CaCO}_3 \text{ consumption with } 100\% \text{ purity (mg/l)} = 1.28\text{mmolCa} \times 1 \times \frac{\text{mmolCaCO}_3}{1\text{mmolCa}} \times \frac{100 \text{ mgCaCO}_3}{1\text{mmolCaCO}_3} \]

This the calcite consumption when calcite has 100% purity. In our case we have 99.1% purity.

\[ \text{CaCO}_3 \text{ consumption with } 99.1\% \text{ purity(mg/l)} = \frac{\text{CaCO}_3 \text{ consumption with } 100\% \text{ purity (mg/l)}}{\text{purity percentage}} \]

Using the average capacity, the amount of calcite consumption per hour could be calculated as follows:

\[ \text{CaCO}_3 \text{ consumption (kg/hr)} = \text{result of 5.5 } \times \text{treatment } \% \times \text{Average capacity} \]

Figure 43. The result from Yamauchi model at minimum required concentration and average concentration of CO₂
To calculate the reduction bed per each filter equation 5.7 could be used.

\[
\text{Bed reduction (m/h)} = \frac{\text{CaCO}_3 \text{ consumption (kg/h)}}{\text{Number of filters} \times \text{specific weight of calcite (1350 kg/m}^3) \times \text{surface area of the filter}}
\]

5.7

Finally, assuming the allowed reduction of 10% the refiling frequency could be calculated.

\[
\text{Refiling frequency (day)} = \frac{\text{Allowed bed reduction (10\% of initial bed) m}}{\text{Bed reduction (m/h) \times 24h}}
\]

5.8

6.5 Design scenarios

To find out the most cost-effective design at design key parameters the following scenarios compared:

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>Parameters</th>
<th>Hypotheses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 0 (reference)</td>
<td>4 parallel units with 47% treatment percentage H = 3 m, D = 2.4m, CO(_2) = 1.5 mmol/l</td>
<td>High redundancy</td>
</tr>
<tr>
<td>Scenario 1</td>
<td>3 parallel units with 47% treatment percentage H = 3 m, D = 2.9 m, CO(_2) = 1.5 mmol/l</td>
<td>Cheaper – less redundancy</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>4 parallel units with 47% treatment percentage H = 1.7 m, D = 3.2 m, CO(_2) = 1.5 mmol/l</td>
<td>Less refilling frequency due to the larger surface area of filter. Higher production capacity (max capacity with 3 filter could be reached)</td>
</tr>
<tr>
<td>Scenario 3</td>
<td>4 parallel units with 47% treatment percentage H = 3.5 m, D = 2.3 m, CO(_2) = 1.5 mmol/l</td>
<td>Smaller filters and lower investment cost</td>
</tr>
<tr>
<td>Scenario 4</td>
<td>4 parallel units with 47% treatment percentage H = 3 m, D = 2.4m, CO(_2) = 1.5 mmol/l – with CO(_2) standby system</td>
<td>Less treatment percentage if necessary =&gt; High redundancy when max capacity with 3 filter should be obtained</td>
</tr>
</tbody>
</table>

Table 14, Figure 44 and Figure 45 present the outcome of the cost comparison of the various cost scenarios. As it can be seen, the scenario with less filters result in lower investment cost. However, this option may be less preferable due to their low redundancy. In other word, in a case that one filter fails or is maintained the design capacity should be provided only with two filters. Scenarios 4 illustrates the cost of process with the CO\(_2\) dosing installation in order to increase the redundancy of system. This will increase the investment cost by 12% and it may only useful if one filter fail at maximum capacity or more than one filter fail at the same time. In previous study done by Oasen on remineralisation techniques (Van Der Laan et al., 2016), the cost of treatment per cubic meter was found to be 0.076 € for calcite filter which is higher than all discussed scenarios here. This is because there was assumed 100% treatment percentage with a calcium concentration of 1 mmol/l compared to 0.625mmol in this study. Moreover, there is less than 1% difference between reference scenario and scenario 3 with
longer bed height and smaller filter which shows the small effect of filter dimensions on final cost. However, when one filter was eliminated the general cost of process reduced by 16%.

**Table 14. Comparison various calcite filter scenarios**

<table>
<thead>
<tr>
<th>Tested scenario’s</th>
<th>Reference scenario</th>
<th>Scenario 1</th>
<th>Scenario 2</th>
<th>Scenario 3</th>
<th>Scenario 4</th>
<th>Van der Laan(2016)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment percentage</td>
<td>47%</td>
<td>47%</td>
<td>47%</td>
<td>47%</td>
<td>47%</td>
<td>100%</td>
</tr>
<tr>
<td>Investment</td>
<td>€ 1.351.000</td>
<td>€ 1.112.000</td>
<td>€ 1.446.000</td>
<td>€ 1.332.000</td>
<td>€ 1.522.000</td>
<td>€ 1.693.000</td>
</tr>
<tr>
<td>Annual costs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interest and Depreciation</td>
<td>€ 113.000</td>
<td>€ 92.000</td>
<td>€ 119.000</td>
<td>€ 112.000</td>
<td>€ 128.000</td>
<td>€ 139.000</td>
</tr>
<tr>
<td>Operation and Maintenance</td>
<td>€ 18.000</td>
<td>€ 14.000</td>
<td>€ 18.000</td>
<td>€ 18.000</td>
<td>€ 20.000</td>
<td>€ 21.000</td>
</tr>
<tr>
<td>Energy</td>
<td>€ 8.000</td>
<td>€ 8.000</td>
<td>€ 8.000</td>
<td>€ 8.000</td>
<td>€ 8.000</td>
<td>€ 17.000</td>
</tr>
<tr>
<td>Chemicals</td>
<td>€ 12.000</td>
<td>€ 12.000</td>
<td>€ 12.000</td>
<td>€ 12.000</td>
<td>€ 14.000</td>
<td>€ 23.000</td>
</tr>
<tr>
<td>Total</td>
<td>€ 151.000</td>
<td>€ 127.000</td>
<td>€ 157.000</td>
<td>€ 149.000</td>
<td>€ 169.000</td>
<td>€ 200.000</td>
</tr>
<tr>
<td>Costs per m³</td>
<td>€ 0.057</td>
<td>€ 0.048</td>
<td>€ 0.060</td>
<td>€ 0.057</td>
<td>€ 0.064</td>
<td>€ 0.076</td>
</tr>
<tr>
<td>Deviation from reference scenario</td>
<td>0%</td>
<td>-16%</td>
<td>4%</td>
<td>-1%</td>
<td>12%</td>
<td>32%</td>
</tr>
</tbody>
</table>

**Figure 44. Cost comparison in € per year for different scenario’s**
It should be noted that all above scenarios provide the sufficient calcium concentration of 0.625 mmol/l. Since Ca:HCO3 is always 1:2, based on chapter 3.3.4, the bicarbonate concentration of 1.25 mmol/l will also be achieved.

The calcium concentration at average capacity was used to calculate the bed refilling frequency using provided calcium concentration. For this purpose it is assumed that the bed should be refilled when the bed height 10% decreased. This is because more than 10% reduction will be result in EBCT of less than 15 min which is not desirable as it eliminate the equilibrium and also reduce the CO2 efficiency. The result from the calculations shows that each calcite filter should be refilled every 17 days which means that every week one filter should be refilled and backwashed, in order to prevent the refilling of filters at the same time. In total 160 ton calcite per year is needed which should be partially stored in two silos at treatment plant.

As a result of cost analyses, scenario 3 is recommended to choose as it is the optimal scenario’s with high redundancy and lowest cost compare to scenarios with 4 parallel unites. However, as it is shown the effect of longer bed height on investment cost is not big. Therefore the reference scenario could be also a good option. This will give the operator a flexible choice for bed height and diameter of filters between these two options. The major components of this scenario are listed in Table 15.

<table>
<thead>
<tr>
<th>Design parameter</th>
<th>Value</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of contactors</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>calcite bed volume</td>
<td>14</td>
<td>m3</td>
</tr>
<tr>
<td>diameter</td>
<td>2.3-2.4</td>
<td>m</td>
</tr>
<tr>
<td>bed height</td>
<td>3-3.5</td>
<td>m</td>
</tr>
<tr>
<td>calcite silos</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>calcite use</td>
<td>160</td>
<td>ton/year</td>
</tr>
<tr>
<td>number of silos</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>volume per silo</td>
<td>30</td>
<td>m3</td>
</tr>
<tr>
<td>backwash pumps</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>capacity each</td>
<td>48.3</td>
<td>m3/h</td>
</tr>
</tbody>
</table>
6.5.1 CO₂ dosing for DWTP with higher capacity

In general extra CO₂ dosing is beneficial when the treatment capacity is high and high number of filters are needed. By increasing the inlet CO₂, the calcium dissolution also increase and it will result in higher bypass ratio and consequently fewer number of filters. However, the treatment capacity of DWTP De Hooge Boom in Kamerik is relatively low and it was not possible to reduce the number of filters to less than 4 filters as it has negative effect on redundancy of system. Therefore, to investigate the effect of extra CO₂ dosage the high design capacity of 5000 m³/h was chosen and the results are compared when there is 53% bypass versus 75% bypass. Table 16 and Figure 46 show the outcome of the cost comparison of the various cost scenarios. As it can be seen, by dosing 1.7 mmol/l extra CO₂ the investment cost of process decrease by half. This is because, the required number of filters will decrease by increasing the CO₂ concentration and it will result in increasing the bypass ratio from the filter. Another interesting finding from this comparison is the low cost of treatment per cubic meter is in compare with our case of study. This shows the higher treatment capacity reduces the treatment price per each cubic meter of treated water.

<table>
<thead>
<tr>
<th>Tested scenario's</th>
<th>Reference scenario</th>
<th>Extra CO₂ dosage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment percentage</td>
<td>53% bypass</td>
<td>75% bypass</td>
</tr>
<tr>
<td>Investment</td>
<td>€ 10.133.096</td>
<td>€ 5.810.021</td>
</tr>
<tr>
<td>Annual costs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interest and Depreciation</td>
<td>€ 827.000</td>
<td>€ 476.000</td>
</tr>
<tr>
<td>Operation and Maintenance</td>
<td>€ 121.000</td>
<td>€ 71.000</td>
</tr>
<tr>
<td>Energy</td>
<td>€ 136.000</td>
<td>€ 74.000</td>
</tr>
<tr>
<td>Chemicals</td>
<td>€ 277.000</td>
<td>€ 391.000</td>
</tr>
<tr>
<td>Total</td>
<td>€ 1.361.000</td>
<td>€ 1.012.000</td>
</tr>
<tr>
<td>Costs per m³</td>
<td>€ 0,031</td>
<td>€ 0,023</td>
</tr>
<tr>
<td>Deviation from reference</td>
<td>0%</td>
<td>-26%</td>
</tr>
</tbody>
</table>

Figure 46. Cost comparison in € per year for with and without extra CO₂ dosage at high design capacity of 5000 m³
7 Conclusions and recommendations

7.1 Conclusions

7.1.1 Pilot research and modelling

As known from the literature, the calcite dissolution rate depends on the chemical driving force and the specific surface area of the calcite grains. Among several studies investigating the calcite dissolution kinetics, the empirical model given by Yamauchi et al. (1987) was found to be the most convenient expression describing the calcite dissolution based on aggressive CO\textsubscript{2} as a driving force. Although the reliability of this model was confirmed by several authors (Hasson & Bendrihem, 2006; Shemer et al. 2013; Hasson et al. 2013; Shemer et al. 2015), none of the previous studies investigated the calcite dissolution rate at low temperature (< 22 °C) and the calcite a grain size smaller than 2 mm. Therefore, between the period of May till August 2017 various experiments were conducted to test the effect of operational parameters as well as water quality on calcite dissolution rate at a water temperature of 12 °C.

The experimental data gathered from this study confirmed the reliability of the Yamauchi et al. (1987) model to express the kinetics of calcite dissolution at low temperature of 12 °C. However, it was found that the effect of the flow rate on the diffusion boundary layer around the calcite grains has not been taken into account in the study carried out by Yamauchi et al. (1987). Therefore, the effect of velocity on calcite dissolution coefficient was investigated at five different velocities, i.e., 5, 10, 15, 20, 30 m/h. From there, a function was developed to describe the correlation between flow rate and the dissolution rate coefficient which demonstrates the influence of the filtrate velocity on the diffusion layer and subsequently on calcite kinetics coefficient. Finally, by adding this correlation to the main Yamauchi expression, the modified Yamauchi model was defined.

The experimental data from this study shows the significant reduction in CO\textsubscript{2} efficiency below 60% when the CO\textsubscript{2} concentration become more than 3 mmol/l. This is because the amount of aggressive CO\textsubscript{2} is reduced by increasing the bicarbonate concentration in the water. Moreover, high CO\textsubscript{2} concentration requires pH adjustment afterwards which may increase energy or chemical consumption.

It is shown that the calcite grain size range between 0.5-1.2 mm required a shorter EBCT than the grain size 1-2mm with EBCT in order to reach the equilibrium. In general, it was found that the necessary EBCT to reach the equilibrium is 15 minutes for grain size 0.5-1.2mm and 25 min for grain size 1-2mm. This could be explained by the fact that the smaller grain size have a larger specific area and consequently a faster dissolution reaction. Furthermore, it was found that the calcite diameter reduction, due to the effect of calcite dissolution, over the three weeks runtime of a filter, resulted only in a small effect on the dissolution kinetic and it could thus be neglected.

Comparing the modified Yamauchi model based on a single layer, with a multiple layer model, simulating a stratified bed which was developed by Zweere (2016) showed no considerable variations in the accuracy of the results. Both models can simulate the calcite dissolution with an accuracy of 95% or more. Therefore, it is concluded that there is no need to have a complex multilayer model.
It is important to have reliable sensors to measure the CO₂ concentration continuously. The results from sensor validations verified the reliability of the CO₂ sensor while the pH sensor was found to be inaccurate to measure the pH of permeate water due to the low ion content.

Lastly it was concluded from the pilot study was the linear relationship found between EC and calcium concentration as well as EC and bicarbonate concentration. Therefore, EC sensors could be used to continuously measure the Ca/HCO₃ concentration. This relation has two main advantages over any other model. First of all, the electric conductivity is easy to measure and has high accuracy. Secondly, the EC relation requires no extra data to predict the calcium and bicarbonate which makes it an easy and straightforward method.

7.1.2 Practical application

The model was used to design and optimise the calcite filtration step for the future treatment plant of Oasen located in Kamerik. De Hooge Boom treatment plant has an average capacity of 300 m³/h and it is planned to operate at full scale RO. Here the focus was only on the calcite filtration step which aims to add the target calcium and bicarbonate concentration of 0.625 mmol/l and 1.25 mmol/l respectively.

The required time to reach the equilibrium for grain size 0.5-1.2 mm was found to be 15 min which should be maintained also after bed reduction at design capacity. By assuming the 10% bed reduction, the EBCT of 17 minute was chosen as design EBCT. Another key feature of this design was the available CO₂ concentration in permeate water. Here the average CO₂ concentration of 1.5 mmol/l is used in design calculations.

To find the optimal calcite design various operating scenarios were analysed. The common feature of all of them was the bypass percentage of 53%, based on the simulation by the modified Yamauchi model. The calcium concentration in the produced water was determined based on an average CO₂ concentration in the permeate using the model at design parameters. From the results it was found that the initial CO₂ concentration of 1.5 mmol/l provides 1.28 mmol/l of calcium. Therefore, the design had to be based on partial design flow. This resulted in a bypass ratio of 53% to provide the target calcium concentration. Subsequently, several scenarios were tested to find the most cost-efficient option. In conclusion, the design with three parallel units found to be the cheapest option. However, to increase the redundancy of the process, for the given design parameters, four parallel filters with a diameter of 2.3-2.4 m and average bed height 3-3.5 m found to be optimal. The total treatment cost of this design is 0.057 €/m³ and the investment cost was found to be €1,351,000.

Furthermore, the refilling frequency was calculated based on calcite consumption as a function of a calcium dissolution. From there it was found that based on 10% reduction of filter bed and the average capacity of 300 m³/h the filters should be reloaded after around 17 days, to keep the EBCT above the 15 minutes. In order to prevent the refilling of more than one filter at the same time, every week one of filters should be refilled and backwashed.

7.2 Recommendations

This research focused on parameters which have an effect on the calcite dissolution rate. Based on results found in this report the following aspects are recommended:
• The turbidity of the effluent water could limit the maximum velocity as a high velocity may raise the turbidity above the threshold level. Therefore it is recommended to test the water turbidity based on various velocities;

• The experiments are sensitive to backwash regime since the high rate of backwash may result in breaking the particles and as a consequence increasing turbidity, which negatively effects the water quality. Therefore a further investigation should be done to find an optimal backwash flow rate and duration;

• To keep the CO$_2$ concentration constant it is recommended to change the well’s combination in such a way that the variation of water quality between configurations becomes minimized. Otherwise, it is recommended to develop a sensor which uses a model to calculate the calcium concentration based on initial CO$_2$ concentrations and subsequently determined the required bypass over the time.

• In order to determine the effect of runtime, it is recommended to test the process over a period of at least six months.

• From previous studies it was concluded that the temperature has a strong effect on the calcite dissolution. Therefore, it is recommended that the temperature dependency of the kinetic coefficient is further investigated throughout the pilot research in the case that model want to be used in other locations with a different water temperature.

• The calcite purity is another factor which may affect the kinetic coefficient. Based literature the calcite which is used for remineralisation should have a purity higher than 99%. Therefore, it is crucial to study the effect of calcite impurities on the calcite dissolution rate if the calcite source is changed with the calcite source with purity less than 99%.

• The next step for Oasen is to make an automatic sensor which uses the data from the CO$_2$ sensor, the bed height meter sensor, and the flow rate and calculate the calcium and bicarbonate concentrations using the model to provide the continues controlling on water quality.

• The EC-Calculator and EC-Bicarbonate relation could be used as the reliable and cheaper option to calculate the calcium and bicarbonate concentration continuously and developed a sensor to regulate the bypassing ratio based on the EC value.
8 Bibliography


Voughtkov. N. (2013). Desalination Engineering; Planning and Design.


Appendices

Appendix I: CO₂ Calculations methods

In order to find the most reliable way to measure the carbon dioxide concentration in the water during 17 till 20 July 2017, eight samples from permeate water were taken and the carbon dioxide concentration of each sample was measured or calculated in several ways.

The calculation steps of CO₂ concentration based on p and m alkalinity:

Assuming the maximum CO₂ concentration of 3 mmol/l and having a sample bottle with capacity of 550 ml, the required sodium hydroxide solution of 25% with a specific weight of 1300 mg/ml can be calculated as follow:

Add: 3 mmol/l \times 0.55 l = 1.65 mmol Required NaOH
1.65 * 40 (NaOH molarity) = 66 mg NaOH
NaOH_{25\%} (mg) = 66*44= 264 mg_{NaOH_{25\%}}
NaOH_{25\%} (ml) = 264(mg) /1300 mg/ml = 0.2ml (important: volume base is negligible relative to sample size)

Performance:
Take the water sample in a bottle with sodium hydroxide solution. As a result, all the CO₂ is converted into CO₃²⁻. Then by measuring p-alkalinity and m-alkalinity, the original CO₂ concentration could be calculated based on Table 17. However, because the permeate water contains a small amount of HCO₃⁻, which will also convert to CO₃²⁻, bicarbonate was measured in a sample (without NaOH) to correct the result from CO₂ calculation based on p- and m-alkalinity.

<table>
<thead>
<tr>
<th>P- and M- Alkalinity</th>
<th>Hydroxyl (OH)</th>
<th>Carbonate (CO₃)</th>
<th>Bicarbonate (HCO₃⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P = 0</td>
<td>0</td>
<td>0</td>
<td>M</td>
</tr>
<tr>
<td>P &lt; ½ M</td>
<td>0</td>
<td>2P</td>
<td>M − 2P</td>
</tr>
<tr>
<td>P = ½ M</td>
<td>0</td>
<td>M</td>
<td>0</td>
</tr>
<tr>
<td>P &gt; ½ M</td>
<td>2P − M</td>
<td>2(M − P)</td>
<td>0</td>
</tr>
<tr>
<td>P = M</td>
<td>M</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Based on (“Dow Answer Center.” 2017)

CO₂ concentration based on pH and alkalinity:

The CO₂ concentration could also be calculated using pH, alkalinity and electrical conductivity. For this purpose samples were analysed for their alkalinity and pH and using the average water composition given in Table 7, the CO₂ concentration was calculated using PhreeqPython. However, it should be noted that an inaccurate measurement of pH results in an error in CO₂ calculation. These calculations were also repeated using pH value measured at the pilot plant by pH meter at corresponding time of each sample.
Appendix II: EC vs TDS relation

A relationship between electrical conductivity (EC) and total dissolved solids (TDS) was investigated by several authors (Dahaan et al., 2016; Hubert & Wolkersdorfer, 2015; Iyasele & Idiata, 2015), who showed a positive linear relationship between TDS and EC whereby increasing TDS raises the EC value. TDS can be estimated using the equation below:

\[
\text{TDS (mg/l)} = k \times \text{EC (µs/cm)}
\]

Where \( k \) is a conversion factor with a range between 0.54-1.1 at 25 \(^\circ\)C. The conversion factor was found by plotting EC against TDS that was calculated using the sum of ions concentration in the RO permeate. For this purpose, the data from 168 samples in a large range of EC from 19 to 761 µs/cm were taken and the calcium and bicarbonate concentrations corresponding to each sample were measured in the lab. The concentration of other ions was measured over 4 different days. The laboratory analyses showed only a small concentration of sodium, chloride and bicarbonate in the water contributing to TDS.

![EC vs TDS](image)

*Figure 47. Measured data of EC against TDS fitted in python. The linear equation is equal to: TDS = 0.8801 EC + 5.227*

Figure 47 shows the \( k \) factor to be 0.88 which supports data given by (Hubert & Wolkersdorfer, 2015) for an EC-range of 70 – 16 000 µS/cm and TDS of 50 – 14 000 mg/l.

By subtracting the initial sodium, chloride and bicarbonate concentration in from total TDS in the water, the sum of calcium and bicarbonate concentration added during remineralisation is calculated. However, it should be noted that various ions had a different mobility affecting the EC (Iyasele & Idiata, 2015). This means that calcium and bicarbonate concentration contributed to the EC and subsequently to TDS concentration to a different extent. Fitting data using Excel result in the following equations for calcium and bicarbonate.

\[
\text{Ca concentration (mg/l)} = 0.245 \times (\text{TDS} - \text{Na - chloride} – \text{initial bicarbonate}) \text{ (mg/l)} \\
\text{HCO}_3^- \text{ concentration (mg/l)} = 0.775 \times (\text{TDS} - \text{Na - chloride} – \text{initial bicarbonate}) \text{ (mg/l)}
\]

It should be noted that 1:2 ratio of calcium and bicarbonate concentration could also be used to predict the final bicarbonate concentration. However, this concentration should be add by initial bicarbonate concentration which in average is an approximately 0.14 mmol/l.
However, as increasing TDS and consequently EC in effluent water from the filter is only the result of the calcite dissolution. it could be concluded that there must be a direct relationship between EC and calcium and bicarbonate dissolved in the water. Therefore, the relationships between these three parameters are further investigated using empirical data.

**EC handheld vs TDS-PhreeqPython code**

January 9, 2018

```
In [1]: from openpyxl import load_workbook
import numpy as np
import matplotlib.pyplot as plt
import pandas as pd
from sklearn.linear_model import LinearRegression
from sklearn import datasets, linear_model

%pylab inline
wb = load_workbook('EC-TDS.xlsx', data_only=True, read_only=True)
ws = wb['EC']
Populating the interactive namespace from numpy and matplotlib

In [2]: EC = []
for column in ws['G2:G169']:
    for cell in column:
        EC.append(cell.value)

TDS = []
for column in ws['K2:K169']:
    for cell in column:
        TDS.append(cell.value)

plt.scatter(EC, TDS)
plt.xlim(0.800)
plt.ylim(0.800)
plt.xlabel('EC(micro s/cm)')
plt.ylabel('TDS(mg/l)')
plt.title('EC vs TDS')```
Appendix III: EC and pH relation

The electric conductivity is strongly pH dependent when the pH level is lower than six this is because of a high mobility of the hydrogen ion. Figure 48 shows the EC values at various pH levels simulated by PhreeqPython which depicts when the pH is low, it will be affected the electric conductivity measurement. However, when pH goes above the 6-6.5, it has no effect on electric conductivity. As the pH of effluent water from calcite filter is always higher than 6.5, therefore, the effect of pH on electric conductivity could be neglected. However, this relation is not applicable when samples has low calcium concentration and subsequently low pH.

![Figure 48](image.png)

*Figure 48. pH vs EC relation when the water composition is kept constant and pH levels vary between 4 and 8.*

**pH-EC sensitivity-PhreeqPython-code**

January 9, 2018

In [1]: import phreeqpython
   import numpy as np
   %pylab inline
   pp = phreeqpython.PhreeqPython()
   def getresults(ph=5.35):
       sol = pp.add_solution_raw(
           'pH': ph,
           'temp': 13,
           'units': 'mg/l',
           'Ca': 0,
           'Alkalinity': '7.5 as HCO3',
           'Cl': 1.4,
           'Na': 3.35
       )
       # saturate to SI 0
       sol.saturate('Calcite', 0)
       EC = sol.sc
       # cleanup
       sol.forget()
       return(EC)
   ph_range = np.linspace(4.8, 100)
   results = []
   for ph in ph_range:
       results.append(getresults(ph))
   deviation = ph_range/4.5
   plt.plot(ph_range, results)
   plt.xlabel('pH')
   plt.ylabel('EC(uS/cm)')
Appendix IV: Phreeqc simulation of EC and Ca/HCO$_3$ relationship

The reliability of EC relation theoretically is investigated by simulating the reaction in the Phreeqc. The chemical reaction is simulated by applying the initial water quality before the calcite filter in the Phreeqc and forced the reaction to dissolve calcite till above saturation step by step. It should be noted that the temperature of water should be set at reference temperature of 25 °C which measurement data converted to reference temperature of 25 °C. Figure 49 shows the result from this simulation. Figure 50 shows the data from Phreeqc simulation and data derived from pilot measurement in one figure to compare both results. As it can be seen data match exactly with each other. This confirmed the reliability of EC sensor to predict the calcium and bicarbonate concentration independent of the operating conditions such as flow rate and grain size.

![Relation EC versus Ca&Alkalinity](image)

*Figure 49. Calcium/alkalinity versus various electric conductivities are plotted using Phreeqc (tony appelo’s Phreeqc version with notepad++ done by Boris van Breukelen)*

![Figure 50](image)

*Figure 50. The relation between calcium/ bicarbonate concentration and EC from measured data as well as theoretical data from Phreeqc simulation.*
# Theoretical relation between EC and Ca and HCO3 during calcite dissolution

SOLUTION 1  RO water
units mEq/l
Temp 25
Na 3.5
Cl 1.5
pH 4.56
Alkalinity 6.1 as HCO3
END

USE solution 1
REACTION # Calcite is forced being dissolved even above saturation
Calcite 1
4.3e-3 in 200 steps
USER_GRAPH 1  # plot number 1
-headings EC(uS/cm) Ca(mM) Alkalinity(mM) Ca/EC Alkalinity/EC
-chart_title "Relation EC versus Ca\&Alkalinity"
-axis_scale x_axis 0 500 100
-axis_scale y_axis 0 12 auto auto
-axis_scale sy_axis 0 0.02 auto auto
-connect_simulations true
-initial_solutions false
-start
10 graph_x sc
20 graph_y tot("Ca")*1000
30 graph_y Alk*1000
40 graph_y (tot("Ca")*1000)/sc
50 graph_y (Alk*1000)/sc
-end
SELECTED_OUTPUT
-file output.txt
-reset false
USER_PUNCH
-headings step CaCO3_reacted pH Alk(mM) Ca(mM) EC(uS/cm)
-start
10 punch step_no
20 punch RN
30 punch -la("H+")
40 punch Alk*1000
50 punch tot("Ca")*1000
60 punch sc
-end
END
Appendix V: Pilot Components

Appendix V-A: Measurement sensors information

*Table 18. pH sensor characteristics*

<table>
<thead>
<tr>
<th>Company</th>
<th>Best Instrument Analytical Solution</th>
<th>Best Instrument Analytical Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Online analyser</td>
<td>Swan</td>
<td>Swan</td>
</tr>
<tr>
<td>Type</td>
<td>pH/Redox</td>
<td>pH/Redox</td>
</tr>
<tr>
<td>Product. No</td>
<td>A.21.221.050</td>
<td>A.21.221.010</td>
</tr>
<tr>
<td>Model</td>
<td>AMI-2</td>
<td>AMI-2</td>
</tr>
<tr>
<td>Range</td>
<td>(1-13)</td>
<td>(1-13)</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.01pH</td>
<td>0.01pH</td>
</tr>
<tr>
<td>Flow range</td>
<td>4-15l/h</td>
<td>5-10l/h</td>
</tr>
<tr>
<td>Flow pressure inlet</td>
<td>1bar</td>
<td>Up to 2 bar</td>
</tr>
<tr>
<td>Temperature range</td>
<td>(-30-130 °C)</td>
<td>(-30-130 °C)</td>
</tr>
<tr>
<td>Temperature resolution</td>
<td>0.01 °C</td>
<td>0.01 °C</td>
</tr>
</tbody>
</table>

*Table 19. Electric conductivity characteristics*

<table>
<thead>
<tr>
<th>Company</th>
<th>Best Instrument Analytical Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Online analyser</td>
<td>Swan</td>
</tr>
<tr>
<td>Type</td>
<td>Powercon Specific (EC)</td>
</tr>
<tr>
<td>Product. No</td>
<td>A.23.441.100</td>
</tr>
<tr>
<td>Model</td>
<td>AMI-2</td>
</tr>
<tr>
<td>Range</td>
<td>(0.055-1000 micro μ/cm)</td>
</tr>
<tr>
<td>Resolution</td>
<td>+/- 1% reading value</td>
</tr>
<tr>
<td>Flow range</td>
<td>5-20l/h</td>
</tr>
<tr>
<td>Flow pressure inlet</td>
<td>1bar</td>
</tr>
<tr>
<td>Temperature range</td>
<td>(-30-130 °C)</td>
</tr>
<tr>
<td>Temperature resolution</td>
<td>0.01 °C</td>
</tr>
</tbody>
</table>

*Table 20. Turbidity sensor characteristics*

<table>
<thead>
<tr>
<th>Company</th>
<th>Best Instrument Analytical Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Online analyser</td>
<td>Swan</td>
</tr>
<tr>
<td>Type</td>
<td>Turbitrack</td>
</tr>
<tr>
<td>Product. No</td>
<td>A.25.4111.200</td>
</tr>
<tr>
<td>Model</td>
<td>AMI-2</td>
</tr>
<tr>
<td>Range</td>
<td>0.000-100 NTU</td>
</tr>
<tr>
<td>Resolution</td>
<td>+/- 1% Reading</td>
</tr>
<tr>
<td>Flow range</td>
<td>5-20l/h</td>
</tr>
</tbody>
</table>
Table 21. CO₂ meter characteristics

<table>
<thead>
<tr>
<th>Company</th>
<th>DKK-DOA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Turbitrack</td>
</tr>
<tr>
<td>Product. No</td>
<td>Handheld carbon dioxide meter</td>
</tr>
<tr>
<td>Model</td>
<td>CGP-31</td>
</tr>
<tr>
<td>Range</td>
<td>Liquid: 1.49-1490 mg/l / Gas: 0.1-100%</td>
</tr>
<tr>
<td>Resolution</td>
<td>(+/- 5% FS)</td>
</tr>
</tbody>
</table>

Appendix V-B : Calcite characteristics

Table 22. Calcite product characteristics

<table>
<thead>
<tr>
<th>Calcite product characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
</tr>
<tr>
<td>Purity</td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Bulk density</td>
</tr>
<tr>
<td>Porosity</td>
</tr>
<tr>
<td>Other components</td>
</tr>
</tbody>
</table>
Appendix V-C: Pilot Drawing

Figure 51. Filter draw above and A-A section of bottom

Figure 52. Filter draw with sampling points position
Appendix VI: The CO₂ experiment simulations

Appendix VII: PhreeqPython codes

Appendix VII – A PhreeqPython code-velocity test- grain size 0.5-1.2 mm

Modified Yamauchi-model-0.5-1.2mm

January 9. 2018

In [1]: import numpy as np
from math import sqrt
import matplotlib.pyplot as plt
%pylab inline

import phreeqpython
pp = phreeqpython.PhreeqPython()
from openpyxl import load_workbook

In [2]: wb = load_workbook('Yamauchi-data.xlsx'. data_only=True. read_only=True)
ws1 = wb['water-quality']
ws2 = wb['operation']
ws3 = wb['measurement-data']

In [3]: #10m/h-filter-1
sol = pp.add_solution_raw({
    'temp': ws1['D2'].value,
    'units': 'mg/l',
    'pH': ws1['D3'].value,
    'Ca': ws1['D4'].value,
    'Alkalinity': '8.78 as HCO3',
    'Cl': ws1['D6'].value,
    'Na': ws1['D7'].value,
    'Fe': ws1['D8'].value,
    'Mg': ws1['D9'].value,
    'K': ws1['D10'].value,
    'Al': ws1['D11'].value,
    'S(6)': ws1['D12'].value
})

CO2_0 = sol.total('CO2')*1e3
sol.saturate('Calcite', 0)
Cae = sol.total_element('Ca')*1e3
CO2e = sol.total('CO2')*1e3
HCO3 = sol.total('HCO3')*1e3
pH = sol.pH
soln = pp.add_solution_raw({
    'temp': ws1['D2'].value,
    'units': 'mg/l',
    'pH': ws1['D3'].value,
    'Ca': ws1['D4'].value,
    'Alkalinity': '8.78 as HCO3',
    'Cl': ws1['D6'].value,
    'Na': ws1['D7'].value,
    'Fe': ws1['D8'].value,
    'Mg': ws1['D9'].value,
    'K': ws1['D10'].value,
    'Al': ws1['D11'].value.
})
In [4]: Ca_e = sol.total_element('Ca')*1e3 #saturation ca concentration in mmol/l
Ca0 = soln.total_element('Ca')*1e3
Ca_e = ws1['D4'].value #initial ca concentration in mmol/l
e = ws2['D3'].value #prosity
z = np.arange(0.2100,1.25) #height in mm
v = ws2['D5'].value #velocity in mm/s
D = ws2['D6'].value
D_reduction = 0.7
EBCT = z/v # EBCT in s
k = 0.00296* math.sqrt(v) #reaction constant in mm/s using velocity model:
Ca = Ca_e - (exp((-k/D)*(1-e)*EBCT))**(Ca_e - Ca_0)) #end ca concentration
plt.plot(EBCT, Ca, label='velocity model with pH correction')
plt.xlabel('EBCT(s)', fontsize=15)
plt.ylabel('calcium concentration(mmol/l)', fontsize=15)
plt.xlim(0,1000)
plt.ylim(0,1.6)
EBCT = []
for column in ws3['B3:B13']:
    for cell in column:
        EBCT.append(cell.value)
ca = []
for column in ws3['D3:D13']:
    for cell in column:
        ca.append(cell.value)
plt.plot(EBCT, ca, marker='s', label='Measured data')
err = 0.05*ones(size(ca))
e = errorbar(EBCT, ca, err, ecolor='g', capsize=6)
plt.title('10 m/h', fontsize=18)
plt.legend(loc='best')

Ca_e1 = sol2.total_element('Ca')*1e3 #saturation ca concentration in mmol/l
Ca_01 = ws1['I4'].value #initial ca concentration in mmol/l
e1 = ws2['I3'].value #prosity
z1= np.arange(0.2200,125) #height in mm
v1 = ws2['I5'].value #velocity in mm/s
D1 = ws2['I6'].value
D1_reduction=0.7
EBCT1 = z1/v1 # EBCT in s
k1 = 0.00296* math.sqrt(v1) #reaction constant in mm/s using velocity model:
Ca1 = Ca_e1 - (exp((-k1/D1)*(1-e1)*EBCT1))**(Ca_e1 - Ca_01)) #end ca concentration
Ca1_reduction = Ca_e1 - (exp((-k1/D1_reduction)*(1-e1)*EBCT1))**(Ca_e1 - Ca_01))
plt.plot(EBCT1, Ca1, label='velocity model')
plt.xlabel('EBCT(s)', fontsize=15)
plt.ylabel('calcium concentration(mmol/l)', fontsize=15)
plt.xlim(0,600)
plt.ylim(0,1.6)
EBCT1 = []
for column in ws3['H3:H12']:
    for cell in column:
        EBCT1.append(cell.value)
ca1 = []
for column in ws3['J3:J12']:
ca1.append(cell.value)
plt.subplot(2,3,2)
plt.scatter(EBCT1.ca1.marker='s'.label='Measured data')
err = 0.05*ones(size(ca1))
e = errorbar(EBCT1.ca1.err.ecolor='g'.capsize=6)
plt.title('15 m/h'.fontsize=18)
plt.legend(loc='best')
Appendix VII – B PhreeqPython code-velocity test- grain size 0.5-1.2 mm

Modified Yamauchi-model-16.5 m/h
January 9, 2018

Ca_e2 = sol3.total_element('Ca')*1e3 #saturation ca concentration in mmol/l
Ca_02 = ws1['N4'].value #initial ca concentration in mmol/l
e2 = ws2['N3'].value #proosity
z2 = np.arange(0.2200, 1.25) #height in mm
v2 = ws2['N5'].value #velocity in mm/s
D2 = ws2['N6'].value
D2_reduction = 0.7
EBCT2 = z2/v2 # EBCT in s
k2 = 0.00296*math.sqrt(v2) #reaction constant in mm/s using velocity model:
Ca2 = Ca_e2 - (exp((-k2/D2)*(1-e2)*EBCT2)*(Ca_e2 - Ca_02)) #end ca concentration
Ca2_reduction = Ca_e2 - (exp((-k2/D2_reduction)*(1-e2)*EBCT2)*(Ca_e2 - Ca_02))
plt.subplot(2,3,3)
plt.plot(EBCT2, Ca2, label='velocity model')
plt.xlabel('EBCT(s).fontsize=15)
plt.ylabel('calcium concentration(mmol/l).fontsize=15)
plt.xlim(0, 600)
plt.ylim(0, 1.6)
EBCT2 = []
for column in ws3['M3:M12']:
    for cell in column:
        EBCT2.append(cell.value)
ca2 = []
for column in ws3['O3:O12']:
    for cell in column:
        ca2.append(cell.value)
plt.subplot(2,3,3)
plt.scatter(EBCT2, ca2, marker='s', label='Measured data')
err = 0.05*ones(size(ca2))
e = errorbar(EBCT2, ca2, err, ecolor='g', capsize=6)
plt.title('16.5 m/h'.fontsize=18)
plt.legend(loc='best')
plt.subplots_adjust(top=0.007, left=0.007, right=4.
hspace=0.5, wspace=0.5)
In [5]: Ca_e = sol3.total_element('Ca')*1e3 #saturation ca concentration in mmol/l
Ca_0 = ws1['N4'].value #initial ca concentration in mmol/l
e = ws2['N3'].value #porosity
z = np.arange(0.2500, 1.25) #height in mm
v = ws2['N5'].value #velocity in mm/s
D = ws2['N6'].value
D_reduction = 0.7
EBCT = z/v # EBCT in s
k = 0.00296*math.sqrt(v2) #reaction constant in mm/s using velocity model:
Ca = Ca_e - (exp((-k/D)*(1-e)*EBCT)*(Ca_e - Ca_0)) #end ca concentration in
Ca_g = Ca*40
plt.plot(Ca_g, z, '.r', label='velocity model')
zm = []
for column in ws3['N3:N14']:
    for cell in column:
        zm.append(cell.value)
    cam = []
for column in ws3['O3:O14']:
    for cell in column:
        cam.append(cell.value)
cam_g = 40*np.array(cam)
plt.scatter(cam_g, zm, s=35, label='Measured data')
plt.ylabel('Bed height (mm)', fontsize=15)
plt.xlabel('Calcium concentration (mg/l)', fontsize=15)
plt.ylim(0, 2200)
plt.xlim(0, 40)
plt.title('16.5 m/h', fontsize=18)
plt.legend(loc='best')
Appendix VII – C PhreeqPython code-velocity test- grain size 1-2mm

Modified Yamauchi-model-1-2mm
January 9, 2018
In [1]: import numpy as np
from math import sqrt
import matplotlib.pyplot as plt
%pylab inline
import phreeqpython
pp = phreeqpython.PhreeqPython()
from openpyxl import load_workbook
In [2]: wb = load_workbook('Yamauchi-data-big.xlsx'. data_only=True, read_only=True)
ws1 = wb['water-quality']
ws2 = wb['operation']
ws3 = wb['measurement-data']
In [3]: #5m/h-filter-1
sol = pp.add_solution_raw({
'temp': ws1['C2'].value.
'units': 'mg/l'.
'pH': ws1['C3'].value.
'Ca': ws1['C4'].value.
'Alkalinity': '10.19 as HCO3'.
'Cl': ws1['C6'].value.
'Na': ws1['C7'].value.
'Fe': ws1['C8'].value.
'Mg': ws1['C9'].value.
'K': ws1['C10'].value.
'Al': ws1['C11'].value.
'S(6)': ws1['C12'].value
})
CO2_0 = sol.total('CO2')*1e3
sol.saturate('Calcite').0
Cae = sol.total_element('Ca')*1e3
CO2e = sol.total('CO2')*1e3
#10m/h-filter-1
sol2 = pp.add_solution_raw({
'temp': ws1['H2'].value.
'units': 'mg/l'.
'pH': ws1['H3'].value.
'Ca': ws1['H4'].value.
'Alkalinity': '10.31 as HCO3'.
'Cl': ws1['H6'].value.
'Na': ws1['H7'].value.
'Fe': ws1['H8'].value.
'Mg': ws1['H9'].value.
'K': ws1['H10'].value.
'Al': ws1['H11'].value.
'S(6)': ws1['H12'].value
})
CO2_2_0 = sol2.total('CO2')*1e3
sol2.saturate('Calcite').0
Cae_2 = sol2.total_element('Ca')*1e3
CO2e_2 = sol2.total('CO2')*1e3
#15m/h-filter-1
sol3 = pp.add_solution_raw(
    'temp': ws1['M2'].value,
    'units': 'mg/l',
    'pH': ws1['M3'].value,
    'Ca': ws1['M4'].value,
    'Alkalinity': '10.65 as HCO3',
    'Cl': ws1['M6'].value,
    'Na': ws1['M7'].value,
    'Fe': ws1['M8'].value,
    'Mg': ws1['M9'].value,
    'K': ws1['M10'].value,
    'Al': ws1['M11'].value,
    'S(6)': ws1['M12'].value
)
CO2e_3 = sol3.total('CO2')*1e3
sol3.saturate('Calcite':0)
Cae_3 = sol3.total_element('Ca')*1e3
CO2e_3 = sol3.total('CO2')*1e3
temp = ws1['I2'].value
Ca_e = sol.total_element('Ca')*1e3 #saturation ca concentration in mmol/l
Ca_0 = ws3['D3'].value #initial ca concentration in mmol/l
e = ws2['C3'].value #prosity
z = np.arange(0.2500,125) #height in mm
v = ws2['C5'].value #velocity in mm/s
D = ws2['C6'].value
D_reduction = 1.4
EBCT = z/v # EBCT in s
k = 0.0296 * math.sqrt(v) #reaction constant in mm/s using velocity model:
Ca = Ca_e - (exp((-k/D)*((1-e)*EBCT)*(Ca_e - Ca_0)) #end ca concentration in
plt.plot(EBCT, Ca, label='velocity model')
plt.xlabel('EBCT(s)',fontsize=15)
plt.ylabel('calcium concentration(mmol/l)',fontsize=15)
plt.xlim(0.0000)
plt.ylim(0.1,6)
EBCT = []
for column in ws3['B3:B13']:
    for cell in column:
        EBCT.append(cell.value)
for column in ws3['D3:D13']:
    for cell in column:
        ca.append(cell.value)
plt.plot(EBCT,ca,label='Measured data')
err = 0.05*ones(size(ca))
e = errorbar(EBCT,ca,ecolor='g',capsize=6)
plt.title('5 m/h'.fontsize=18)
plt.legend(loc='best')

Ca_e1 = sol2.total_element('Ca')*1e3 #saturation ca concentration in mmol/
Ca_01 = ws3['J3'].value #initial ca concentration in mmol/l
e1 = ws2["H3"] value #prosity
z1 = np.arange(0.2500, 1.25) #height in mm
v1 = ws2["H5"] value #velocity in mm/s
D1 = ws2["H6"] value
D1_reduction = 1.2
EBCT1 = z1/v1 # EBCT in s
k1 = 0.00296* math.sqrt(v1) #reaction constant in mm/s using velocity model:
Ca1 = Ca_e1 - (exp(-(k1/D1)*(1-e1))*EBCT1)*(Ca_e1 - Ca_01)) #end ca concentration
Ca1_reduction = Ca_e1 - (exp((-k1/D1_reduction)*(1-e1))*EBCT1)*(Ca_e1 - Ca_01)
plt.plot(EBCT1, Ca1, label='velocity model')
plt.xlabel('EBCT(s)')
plt.ylabel('calcium concentration(mmol/l)')
plt.xlim(0, 1000)
plt.ylim(0, 1.6)
EBCT1 = []
for column in ws3["H3:H13"]:
    for cell in column:
        EBCT1.append(cell.value)

ca1 = []
for column in ws3["J3:J13"]:
    for cell in column:
        ca1.append(cell.value)
plt.plot(EBCT1, ca1, marker='s', label='Measured data')
err = 0.05*ones(size(ca1))
e = errorbar(EBCT1, ca1, err, ecolor='g', capsize=6)
plt.title('10 m/h', fontsize=18)
plt.legend(loc='best')

Ca_e2 = sol3.total_element("Ca")*1e3 #saturation ca concentration in mmol/
Ca_02 = ws3["P3"] value #initial ca concentration in mmol/l
e2 = ws2["M3"] value #prosity
z2 = np.arange(0.2500, 1.25) #height in mm
v2 = ws2["M5"] value #velocity in mm/s
D2 = ws2["M6"] value
D2_reduction = 1.4
EBCT2 = z2/v2 # EBCT in s
k2 = 0.00296* math.sqrt(v2) #reaction constant in mm/s using velocity model:
Ca2 = Ca_e2 - (exp((-k2/D2)*(1-e2))*EBCT2)*(Ca_e2 - Ca_02)) #end ca concentration
Ca2_reduction = Ca_e2 - (exp((-k2/D2_reduction)*(1-e2))*EBCT2)*(Ca_e2 - Ca_02)
Ca_plt.plot(EBCT2, Ca2, label='velocity model')
plt.xlabel('EBCT(s)')
plt.ylabel('calcium concentration(mmol/l)')
plt.xlim(0, 1000)
plt.ylim(0, 1.6)
EBCT2 = []
for column in ws3["N3:N13"]:
    for cell in column:
        EBCT2.append(cell.value)
ca2 = []
for column in ws3['P3:P13']:
    for cell in column:
        5
        ca2.append(cell.value)
plt.subplot(233)
plt.scatter(EBCT2.ca2.marker='s', label='Measured data')
err = 0.05*ones(size(ca2))
e = errorbar(EBCT2.ca2.err.ecolor='g', capsize=6)
plt.title('15 m/h', fontsize=18)
plt.legend(loc='best')
plt.subplots_adjust(top=2.007, right=4.0, hspace=0.5, wspace=0.5)

Appendix VII –D PhreeqPython code-CO2 test- grain size 0.5-1.2mm

Yamauchi-CO2-Small grain size

January 9, 2018
In [1]: import numpy as np
from math import sqrt
import matplotlib.pyplot as plt
%pylab inline
import phreeqpython
pp = phreeqpython.PhreeqPython()
from openpyxl import load_workbook
Populating the interactive namespace from numpy and matplotlib
WARNING: pylab import has clobbered these variables: ['sqrt']
'%%matplotlib' prevents importing * from pylab and numpy
In [2]: wb = load_workbook('Yamauchi-CO2.xlsx', data_only=True, read_only=True)
ws1 = wb['water-quality']
ws2 = wb['operation']
ws3 = wb['measurement-data']
In [3]: #2mole-filter-1
sol = pp.add_solution_raw(
    'temp': 13,
    'units': 'mg/l',
    'pH': ws1['D3'].value,
    'Ca': ws1['D4'].value,
    'Alkalinity': '8.113 as HCO3',
    'Cl': ws1['D6'].value,
    'Na': ws1['D7'].value,
    'Fe': ws1['D8'].value,
    'Mg': ws1['D9'].value,
    'K': ws1['D10'].value,
    'Al': ws1['D11'].value,
    'S(6)': ws1['D12'].value
)
CO2_1_0 = sol.total('CO2')*1e3
sol.saturate('Calcite', 0)
Cae_1 = sol.total_element('Ca')*1e3
CO2e_1 = sol.total('CO2')*1e3
#4mole-filter-1
sol2 = pp.add_solution_raw({
    'temp': ws1['I2'].value,
    'units': 'mg/l',
    'pH': ws1['I3'].value,
    'Ca': ws1['I4'].value,
    'Alkalinity': '7.69 as HCO3'.
    'Cl': ws1['I6'].value,
    'Na': ws1['I7'].value,
    'Fe': ws1['I8'].value,
    'Mg': ws1['I9'].value,
    'K': ws1['I10'].value,
    'Al': ws1['I11'].value,
    'S(6)': ws1['I12'].value
})

CO2_2_0 = sol2.total('CO2')*1e3
sol2.saturate('Calcite'.0)
Cae_2 = sol2.total_element('Ca')*1e3
CO2e_2 = sol2.total('CO2')*1e3

sol3 = pp.add_solution_raw({
    'temp': 13.
    'units': 'mg/l',
    'pH': ws1['N3'].value,
    'Ca': ws1['N4'].value,
    'Alkalinity': '6.71 as HCO3'.
    'Cl': ws1['N6'].value,
    'Na': ws1['N7'].value,
    'Fe': ws1['N8'].value,
    'Mg': ws1['N9'].value,
    'K': ws1['N10'].value,
    'Al': ws1['N11'].value,
    'S(6)': ws1['N12'].value
})

CO2_3_0 = sol3.total('CO2')*1e3
sol3.saturate('Calcite'.0)
Cae_3 = sol3.total_element('Ca')*1e3
CO2e_3 = sol3.total('CO2')*1e3

sol4 = pp.add_solution_raw({
    'temp': 13.
    'units': 'mg/l',
    'pH': 4.55, #ws1['S3'].value,
    'Ca': ws1['S4'].value,
    'Alkalinity': '5.85 as HCO3'.
    'Cl': ws1['S6'].value,
    'Na': ws1['S7'].value,
    'Fe': ws1['S8'].value,
    'Mg': ws1['S9'].value,
    'K': ws1['S10'].value,
    'Al': ws1['S11'].value,
    'S(6)': ws1['S12'].value
})

CO2_4_0 = sol4.total('CO2')*1e3
sol4.saturate('Calcite'.0)
Cae_4 = sol4.total_element('Ca')*1e3
\[ \text{CO}_2e_4 = \text{sol4}.\text{total('CO2')} \times 1e3 \]

```python
In [4]: Ca_e = \text{sol.total_element('Ca')} \times 1e3 \# saturation ca concentration in mmol/l
Ca_0 = \text{ws1['D4'].value} \# initial ca concentration in mmol/l
e = \text{ws2['D3'].value} \# porosity
z = \text{np.arange(0.2000,125)} \# height in mm
v = \text{ws2['D5'].value} \# velocity in mm/s
D = 0.81
D_reduction = 0.74
EBCT = z/v \# EBCT in s
k = 0.00296*\text{math.sqrt(v)} \# reaction constant in mm/s using velocity model:
Ca = Ca_e - (\exp((-k/D)*(1-e)*EBCT))*(Ca_e - Ca_0)) \# end ca concentration in
Ca_reduction = Ca_e - (\exp((-k/D_reduction)*(1-e)*EBCT))*(Ca_e - Ca_0)) \# end
plt.plot(Ca, label= 'velocity model')
plt.plot(Ca_reduction, label= 'velocity model')
plt.xlabel('EBCT(s).fontsize=15')
plt.ylabel('calcium concentration(mmol/l).fontsize=15')
plt.xlim(0.2000)
plt.ylim(0.4)
EBCT = []
for column in ws3['B3:B10']:
    for cell in column:
        EBCT.append(cell.value)
ca = []
for column in ws3['D3:D10']:
    for cell in column:
        ca.append(cell.value)
plt.subplot(2,2,1)
plt.scatter(EBCT, ca, label= 'measured data')
plt.title('2.9 mmol/l CO2'.fontsize=18)
plt.legend(loc='best')

# Ca_e1 = \text{sol2.total_element('Ca')} \times 1e3 \# saturation ca concentration in mmol/l
Ca_01 = \text{ws1['I4'].value} \# initial ca concentration in mmol/l
e1 = \text{ws2['I3'].value} \# porosity
z1 = \text{np.arange(0.2000,125)} \# height in mm
v1 = \text{ws2['I5'].value} \# velocity in mm/s
D1 = 0.81
D1_reduction = 0.74
EBCT1 = z1/v1 \# EBCT in s
k1 = 0.00296*\text{math.sqrt(v1)} \# reaction constant in mm/s using velocity model
Ca1 = Ca_e1 - (\exp((-k1/D1)*(1-e1)*EBCT1))*(Ca_e1 - Ca_01)) \# end ca concentration in
Ca1_reduction = Ca_e1 - (\exp((-k1/D1_reduction)*(1-e1)*EBCT1))*(Ca_e1 - Ca_01)) \# end
plt.plot(Ca1, label= 'velocity model')
plt.plot(Ca1_reduction, label= 'Diameter reduction')
plt.xlabel('EBCT(s).fontsize=15')
plt.ylabel('calcium concentration(mmol/l).fontsize=15')
plt.xlim(0.2000)
plt.ylim(0.4)
EBCT1 = []
for column in ws3['H3:H10']:
    for cell in column:
```
EBCT1.append(cell.value)
ca1 = []
for column in ws3['J3:J10']:
    for cell in column:
        ca1.append(cell.value)
plt.scatter(EBCT1.ca1. label='measured data')
plt.title('4.5 mmol/l CO2'.fontsize=18)
plt.legend(loc='best')

Ca_e2 = sol3.total_element('Ca')*1e3 #saturation ca concentration in mmol/l
Ca_02 = ws1['N4'].value #initial ca concentration in mmol/l
e2 = ws2['N3'].value #prosity
z2= np.arange(0.2000,1.25) #height in mm
v2= ws2['N5'].value #velocity in mm/s
D2= 0.81
D2_reduce=0.74
EBCT2 = z2/v2 # EBCT in s
k2 = 0.00296* math.sqrt(v2) #reaction constant in mm/s using velocity model:
Ca2 = Ca_e2 - (exp((-k2/D2)*(1-e2)*EBCT2)*(Ca_e2 - Ca_02)) #end ca concentration

plt.plot(EBCT2. Ca2. label='velocity model')
plt.plot(EBCT2. Ca2_max. label='velocity model')
plt.xlabel('EBCT(s)'.fontsize=15)
plt.ylabel('calcium concentration(mmol/l)'.fontsize=15)
plt.xlim(0,2000)
plt.ylim(0,6)
EBCT2 = []
for column in ws3['M3:M9']:
    for cell in column:
        EBCT2.append(cell.value)
ca2 = []
for column in ws3['O3:O9']:
    for cell in column:
        ca2.append(cell.value)
plt.scatter(EBCT2.ca2. label='measured data')
plt.title('7 mmol/l CO2'.fontsize=18)
plt.legend(loc='best')

Ca_e3 = sol4.total_element('Ca')*1e3 #saturation ca concentration in mmol/l
Ca_03 = ws1['N4'].value #initial ca concentration in mmol/l
e3 = ws2['S3'].value #prosity
z3= np.arange(0.2000,1.25) #height in mm
v3= ws2['S5'].value #velocity in mm/s
D3= 0.81
D3_reduce = 0.72
EBCT3 = z3/v3 # EBCT in s
k3 = 0.00296* math.sqrt(v3) #reaction constant in mm/s using velocity model:
Ca3 = Ca_e3 - (exp((-k3/D3)*(1-e3)*EBCT3)*(Ca_e3 - Ca_03)) #end ca concentration
Ca3_reduction = Ca_e3 - (exp((-k3/D3_reduction)*(1-e3)*EBCT3)*(Ca_e3 - Ca_03))
plt.plot(EBCT3. Ca3. label='velocity model')
plt.plot(EBCT3. Ca3_reduction. label='Diameter reduction')
plt.xlabel('EBCT(s).fontsize=15)
plt.ylabel('calcium concentration(mmol/l).fontsize=15)
plt.xlim(0.2000)
plt.ylim(0.6)
EBCT3 = []
for column in ws3['R3:R9']:
    for cell in column:
        EBCT3.append(cell.value)
ca3 = []
for column in ws3['T3:T9']:
    for cell in column:
        ca3.append(cell.value)
plt.subplot(2,2,4)
plt.scatter(EBCT3,ca3, label='measured data')
plt.title('9.5 mmol/l CO2'.fontsize=18)
plt.legend(loc='best')
plt.subplots_adjust(top=2. left=0.007. right=2.
hspace=0.5. wspace=0.5)
translate-full-scale

January 9, 2018
In [2]: import numpy as np
from math import sqrt
import matplotlib.pyplot as plt
%pylab inline
import phreeqpython
pp = phreeqpython.PhreeqPython()
from openpyxl import load_workbook

In [3]: wb = load_workbook('Yamauchi-CO2.xlsx', data_only=True, read_only=True)
ws1 = wb['water-quality']
ws2 = wb['operation']
ws3 = wb['measurement-data']
In [4]: sol = pp.add_solution_raw({
    'temp': 12.,
    'units': 'mg/l'.
    'pH': 5.77.
    'Ca': ws1['D4'].value.
    'Alkalinity': '8.5 as HCO3'.
    'Cl': ws1['D6'].value.
    'Na': ws1['D7'].value.
    'Fe': ws1['D8'].value.
    'Mg': ws1['D9'].value.
    'K': ws1['D10'].value.
    'Al': ws1['D11'].value.
    'S(6)': ws1['D12'].value
})

CO2_1_0=sol.total('CO2')*1e3
sol.saturate('Calcite'.0)
Cae_1 = sol.total_element('Ca')*1e3
CO2_1_e = sol.total('CO2')*1e3
HCO3_1 = sol.total('HCO3')*1e3
pH = sol.pH
sol2 = pp.add_solution_raw({
    'temp': 12.
    'units': 'mg/l'.
    'pH': 5.42.
    'Ca': ws1['D4'].value.
    'Alkalinity': '8.5 as HCO3'.
    'Cl': ws1['D6'].value.
    'Na': ws1['D7'].value.
    'Fe': ws1['D8'].value.
    'Mg': ws1['D9'].value.
    'K': ws1['D10'].value.
    'Al': ws1['D11'].value.
    'S(6)': ws1['D12'].value
})

CO2_2_0=sol2.total('CO2')*1e3
sol2.saturate('Calcite'.0)
Cae_2 = sol2.total_element('Ca')*1e3
CO2e_2 = sol2.total('CO2')*1e3
HCO3_2 = sol2.total('HCO3')*1e3
In [8]: Ca_e = sol.total_element('Ca')*1e3 #saturation ca concentration in mmol/l
Ca_0 = ws1['D4'].value #initial ca concentration in mmol/l
e = ws2['D3'].value #prosity
z= np.arange(0.3300,1.25) #height in mm
v= 10./3.6 #velocity in mm/s
D= 0.81
D_reduction = 0.74
EBCT = z/v # EBCT in s
k = 0.00296* math.sqrt(v) #reaction constant in mm/s using velocity model:
Ca1 = Ca_e1 - (exp((-k/D1)*(1-e1)*EBCT1)*(Ca_e1 - Ca_01)) #end ca concentration in
Ca_reduction = Ca_e - (exp((-k/D_reduction)*(1-e)*EBCT)*(Ca_e - Ca_0)) #end
plt.subplot(2,2,1)
plt.plot(EBCT/60, Ca, label= 'velocity model')
plt.xlabel('EBCT(s)',fontsize=15)
plt.ylabel('calcium concentration(mmol/l)',fontsize=15)
plt.xlim(0,30)
plt.ylim(0,2)
plt.title('0.65 mmol/l CO2',fontsize=18)
plt.legend(loc='best')

##########################################################################

Ca_e1 = sol2.total_element('Ca')*1e3 #saturation ca concentration in mmol/l
Ca_01 = ws1['I4'].value #initial ca concentration in mmol/l
e1 = ws2['I3'].value #prosity
z1= np.arange(0.3300,1.25) #height in mm
v1= 10./3.6 #velocity in mm/s
D1= 0.81
D1_reduction = 0.74
EBCT1 = z1/v1 # EBCT in s
k1= 0.00296* math.sqrt(v1) #reaction constant in mm/s using velocity model:
Ca1 = Ca_e1 - (exp((-k1/D1)*(1-e1)*EBCT1)*(Ca_e1 - Ca_01)) #end ca concentration
plt.subplot(2,2,2)
plt.plot(EBCT1/60, Ca1, label= 'velocity model')
plt.xlabel('EBCT(s)',fontsize=15)
plt.ylabel('calcium concentration(mmol/l)',fontsize=15)
plt.xlim(0,30)
plt.ylim(0,2)
plt.title('1.5 mmol/l CO2',fontsize=18)
plt.legend(loc='best')
plt.subplots_adjust(top=2, left=0.007, right=4.
hspace=0.5. wspace=0.5)
Appendix VII –F PhreeqPython code-CO$_2$-species- distribution

Distribution of CO$_2$ species at different pH level simulated in PhreeqPython

In [1]: %pylab inline
from phreeqpython import PhreeqPython
pp = PhreeqPython()
solution = pp.add_solution({'NaHCO3':1.0})
In [2]: phs = []
co2 = []
hco3 = []
co3 = []
In [3]: for pH in arange(0.14.1.0.1):
solution.change_ph(pH)
phs.append(pH)
co2.append(solution.total('CO2')*1000)
co3.append(solution.total('CO3')*1000)
hco3.append(solution.total('HCO3')*1000)
fig = plt.figure(figsize=[14.6])
plt.plot(phs,co2,label='CO2')
plt.plot(phs,hco3,label='HCO3-')
plt.plot(phs,co3,label='CO3-2')
plt.xlabel('pH')
plt.ylabel('Concentration (mmol)')
plt.title('Carbonic Acid. Bicarbonate. Carbonate distribution')
lgnd = plt.legend()