Nanofiltration with zero liquid discharge in drinking water treatment

August 2007

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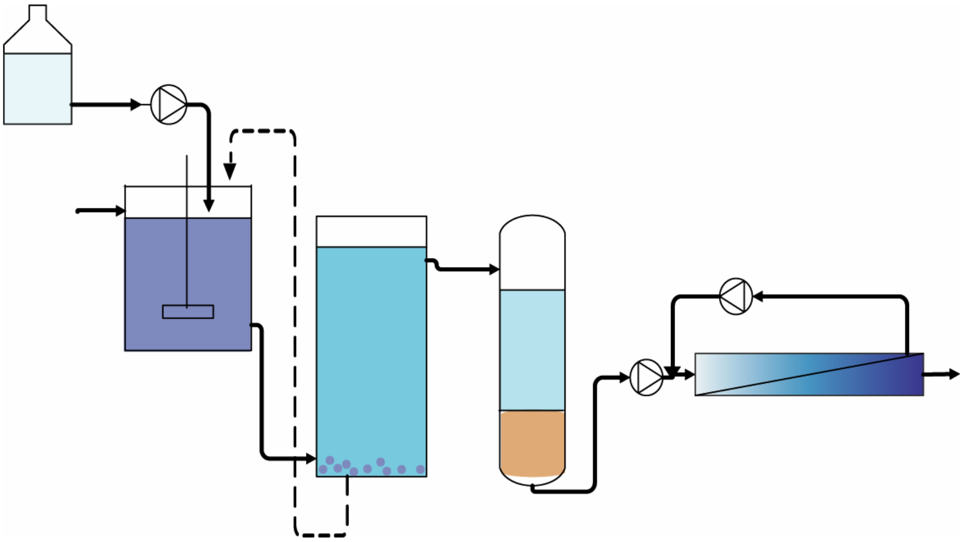

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Master of Science thesis in Civil Engineering

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Colophon

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Title
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It is the end of August in 2007. Through 8 months of research, today my thesis report comes to birth. The present report is the result of the research project as my master thesis in Water Management/Civil Engineering at Delft University of Technology. All I found, observed, thought about, experienced and obtained from my thesis and the experiment through this period are presented in this report. It is my pleasure to express my gratitude for all of them through this opportunity.

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Abstract

The topic of this thesis is a concept of zero liquid discharge for nanofiltration technology in drinking water treatment.

Nanofiltration, defined as a process between Ultrafiltration (UF) and Reverse Osmosis (RO), is a rapidly emerging technology. The origin of NF membranes can be traced back to the late 1950s when it was developed to treat sea water. Now it is applied in drinking water treatment, wastewater treatment and oil separation and also in the food industry. It is even called the future process of 21st century. However, nanofiltration is also a controversial process because of the concentrate problem, especially for inland installations. In the Netherlands, this problem is more considerable due to the need of high quality of drinking water and the decreasing quality of the surface water.

Concentrate contains high concentrations of dissolved organic and inorganic compounds in high concentration. The conventional approach of concentrate discharge to surface water becomes a growing problem due to the environmental guidelines from the authorities. The discharge of the concentrate is not the only problem. It is also a cost problem that 20% of the feed water is wasted. In the Netherlands, taxes are paid for extracted groundwater. Also the pretreatment is costly. So with every m^3 discharged concentrate money is wasted. Therefore, there is a need for a technology by which the discharge of concentrate is not necessary. That is so-called Zero Liquid Discharge Technology.

The primary problem to be solved with zero liquid discharge is the recovery. We expect through an innovative technology the nanofiltration membrane installation can be operated at very high recovery (99%) without increasing the treatment cost of drinking water. The cost for residuals treatment and disposal can be minimized because the amount of the concentrate is decreased about 20 times. A series of pretreatment processes is used for removing the scaling components from the feed water. The scaling components mainly include bivalent ions, silica and etc. Preventing fouling and scaling can guarantee a constant flux, reduce membrane area, lower chemical cleaning frequency, extend the lifespan of membrane and decrease energy consumption.

In this research, a pilot experiment was performed with sludge softening, sedimentation, weak acid cation exchange and nanofiltration at Kiwa Water Research. By using this treatment process, the recovery can be handled successfully at 99% for at least 11 days. The pretreatment concept can remove the bivalent ions completely. Sludge softening is used to remove most of the bivalent ions, like calcium, magnesium and barium. The remaining bivalent ions can be effectively removed by weak acid cation exchange. In this way, the waste stream from the ion exchange is reduced. In theory, silica can be removed by sludge softening at high pH as the co-precipitation of of $Mg(OH)_2$ and $CaCO_3$. But in this experiment the removal efficiency of silica is low probably due to the shortage of magnesium in the feed water. After this treatment process, the remaining concentrate (1%)

is evaporated, only remaining salt which can be sold or discharged to a waste facility.

In order to improve and guarantee the good performance of silica removal by sludge softening, a jar test is performed to define the influencing factor for silica removal. pH and the magnesium concentration can influence the silica removal efficiency. Higher magnesium concentration is necessary for silica removal.

Also, a ternary ion exchange model is needed to predict the breakthrough of cation concentration in order to guarantee the good quality of the feed water for nanofiltration. A ternary system is more complex than binary system. This short report can not include all the aspects of this model. This is the first step to build a ternary model. In the first phase, the basic equation has been already found. The basic model concept has been built up, but needs to be checked and improved. And some batch experiments have been done to obtain model parameters like equilibrium constants and kinetic constants. Also two groups of column experiments have been done in order to measure breakthrough curves for Ca^{2+}, Na^{+} and H^{+}(pH). The experimental result is expected to be compared with the model result in the future.

The pretreatment concept consisting of sludge softening at high pH (around 10), weak acid cation exchange in series can remove calcium, magnesium and barium completely. The calcium removal by the ion exchange is quite good. After pH breakthrough is reached, calcium still can be removed by the resin because it is exchanged with the sodium on the resin. With high magnesium concentration, silica concentration also can be reduced by the sludge softening to some extent. This combination of the treatment processes is possible to make the recovery of NF membrane reach 99% without scaling at least for 11 days.

To put this innovative concept into practice needs lots of efforts on validation and testing. Stable operation of pilot experiment at 99% for a longer time is needed to check the feasibility of this concept. It is interesting and significant work. With increasing demand of drinking water, more and more people in this world needs this kind of technology to improve their living condition and environment. We expect the occurrence of this new big step of drinking water treatment technology.

Keywords: Concentrate, Membrane filtration, Nanofiltration, zero liquid discharge, Membrane fouling/scaling, ternary ion exchange

Contents

1 Introduction

1.1 Problem statement

As water demand increases and fresh water are becoming stressed, there is an increasing need for membrane technology to treat brackish groundwater, seawater or fresh water to meet the increasing demands. Nanofiltration (NF), one of the most efficient system of membrane filtration, has excellent separation capabilities to remove both organic and inorganic compounds, including dissolved inorganic compounds, natural organic matter (NOM), bivalent ions (multivalent ions) and micro-pollutants. With nanofiltration, a permeate stream of good drinking water quality can be produced for customers. Despite this, the concentrate problem limits the application of NF in inland and arid area.

The above-mentioned components that can not pass through the membrane are concentrated and discharged with the concentrate stream. Although several concentrate disposal methods are available (such as surface water or sewer discharge, deep well injection, evaporation ponds, and thermal evaporation), they have high costs and environmental constraints [M.M.Nederlof, J.A.M.van Paassen, R.Jong. 2005]. These conventional approaches are not allowed in inland area. The concentrate problem hinders the application of NF. Therefore, there is a need for technologies that makes concentrate disposal unnecessary leading to zero liquid discharge (ZLD).

A very high recovery is preferable because it reduces concentrate losses or even results in zero liquid discharge. However, the membranes can easily be fouled and scaled at very high recovery. Currently, the operational recovery in drinking water treatment plant is only 70%~90%. That means that high recovery is limited by fouling and scaling. The fouling is formed by NOM molecules and particles on the membrane surface. The scaling is formed mainly due to the high concentration of the soluble inorganic compounds such as calcium carbonate and barium sulphate near the membrane surface. If the concentration is supersaturated, these compounds will precipitate in the membrane sheet, leading to a continuous flux decline, higher energy consumption, higher chemical cleaning frequency and a shorter life span of the membrane. In addition, silica scaling also can limit the recovery, especial for groundwater in which dissolved silica is often found.

The aim of this research is to reach a high recovery (99%) for zero liquid discharge in drinking water treatment. Groundwater is to be investigated in this research since groundwater in inland area is an important source for drinking water.

1.2 Feasible solution

In full-scale drinking water plant, zero liquid discharge can be realized by the combination of a pretreatment process scheme with a recovery of 99% and evaporation at the end.

The most efficient approach to reach a higher recovery of 99% is removing scaling components by a series of pretreatment steps. In 2006, Heijman and Sheng Li et all developed an efficient pretreatment concept to remove the scaling components of NF for surface water treatment. With that setup in pilot scale, however, the recovery can reach 97% at most mainly due to the limitation of the setup. At that time, the concentrate flow was reduced to 6 l/h and lower flows are hard to be reached with that setup. Although 97% is a great progress, a higher recovery of 99% is possible if the installations can be improved. This mechanical problem can be compensated by adding a pressure release valve and dosing pump after the concentrate flow valve. It is worthwhile to do some adjustment for the installations in this research to check on this point.

The pre-treatment concept for ground water treatment to be discussed in this research consists of sludge softening, sedimentation and weak acid cation exchange. The pretreated water is then fed to nanofiltration installation.

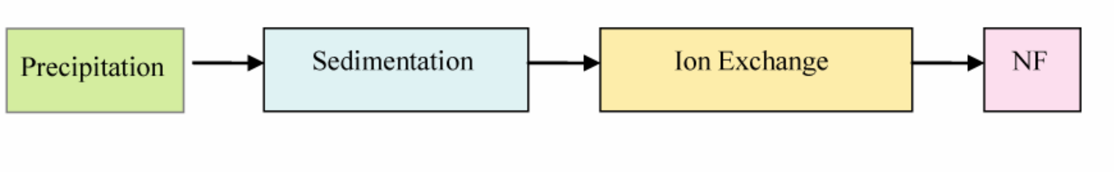


Figure 1.1 – Concept of treatment scheme

First, sludge softening at high pH (≈10) combined with sedimentation is able to remove the majority of calcium and magnesium from the feed water. Silica can be removed as a co-precipitate with magnesium hydroxide. After this, a weak acid cation exchange is added to remove the remaining calcium and other multivalent positive ions and the carry-over from the sludge softening. The combination of sludge softening, sedimentation and ion exchange is good to prepare the feed water of good quality for nanofiltration with fewer chemicals. The resin is regenerated with HCl. The effluent of the ion exchange is used for the feed of the nanofiltration. The first (Christmas) tree of nanofiltration is operating at a recovery of 90%. This is possible because the scaling ions are removed from the feed. The pressure in the second (Christmas) tree is higher, because of the high osmotic pressure. The total recovery of both trees is 99% [90%+(99% x 10%) = 99.9%]. Consequently, the concentrate volume can be reduced to almost zero. In evaporation ponds, the remaining concentrate water is evaporated and only salt is left due to its high salinity (dissolved compounds). The small concentrate volume can significantly reduce the pond construction. At the end, no liquid is to be discharged.

1.3 Objective

The objective of this thesis is to develop a new treatment concept to reach a high recovery for NF so as to realize zero liquid discharge for groundwater treatment. A high recovery of 99% is our goal. The treatment concept consists of sludge softening, sedimentation, weak acid cation exchange and nanofiltration.

Based on the treatment concept, some sub-objectives need to be investigated: 1) observe scaling and fouling phenomenon through Mass Transfer Coefficient (MTC), 2) determine silica removal efficiency with sludge softening, 3) determine calcium removal efficiency with sludge softening and weak acid cation exchange, 4) develop a preliminary ternary ion exchange model to simulate breakthrough curve.

1.4 Research approach

To reach the goal, lots of literature research needs to be studied. First, such things as the kinectics of nanofiltration, scaling and fouling, mechanisms of each treatment technology. And then a feasible treatment scheme is chosen. It includes sludge softening, sedimentation, weak acid cation exchange and nanofiltration.

Based on the literature research, a pilot setups including sludge softening vessel, sedimentation tank, weak acid cation exchange column and nanofiltration system is established at the pilot lab of Kiwa Water Research with tap water (groundwater is the source) and this experiment is operated at a recovery of 99% for more than 10 days. The membrane fouling and scaling is monitored by MTC and TMP. Everyday, the samples at five points (influent, before ion exchange, after ion exchange, concentrate, permeate) are be taken for chemical analysis. The removal efficiency of silica and calcium needs to be observed during the experiment.

For silica removal, besides pH influence, the influent water quality and hydraulic conditions are also factors influencing the removal efficiency. In order to get an idea of the optimal conditions for silica removal with sludge softening at high pH and sedimentation, an experiment with jar test apparatus is needed. The jar test can simulate sludge softening and sedimentation. From the experimental result, we can conclude on the impact of the influencing factors for silica removal so as to improve the Si removal efficiency. This experimental result is compared with the literature research and is used to further explain the result of pilot experiment.

Among the whole process scheme, the operational management of weak acid cation exchange varies with different flow rate, influent water quality, bed height and surface area. In order to manage the process and regeneration of weak acid ion exchange, an ion exchange model is necessary. It can simulate the breakthrough curve of concentration. At the beginning of this study, only three ions are considered in this model to simplify the system. In order to find the model input like equilibrium constant and LDF-constant, a batch experiment is performed. In order to compare with the model result in the further research, a column is operated to monitor pH value, calcium concentration and sodium concentration till breakthrough. The experiments are performed at the Water Lab of Civil Engineering Faculty in TUD.

1.5 Layout of this thesis

In the following part of this thesis, the theory and literature review will be presented in chapter 2 which includes general introduction about nanofiltration, kinetics of nanofiltration, detailed introduction of fouling/scaling, the description of each pretreatment process and the establishment of a new concept for removing scaling components.

The established new concept at 99% recovery is investigated by means of a pilot experiment in Kiwa Water Research. This experiment is shown in chapter 3 which shows the detail information of the experiment and results.

In chapter 4, the jar test for silica removal will be presented. From the experiment, we can conclude the optimal condition for silica removal which is helpful for the performance of sludge softening and sedimentation.

In chapter 5, the batch experiment and column experiment for ion exchange will be presented and the preliminary building up of the mathematic model will be shown.

In the final chapter, conclusions and recommendations of this research will be outlined. At the end of the report, reference literature and some appendix with experimental table and figures can be found.

2 Theory and literature research

This chapter will introduce the basic theory for this research. It starts with the introduction of nanofiltration technology including its main type used, kinetics, etc. And then the theory of membrane scaling/fouling is shown to study the mechanisms of scaling/fouling and to find the factors leading to scaling/fouling. Afterwards, relevant literature research about the three technologies for removal of scaling components, precipitation, sedimentation, and ion exchange are described. By comparing each process, a potential treatment concept is chosen and the reason of selection is finalized at the end of this chapter.

2.1 Introduction of NF

2.1.1 Definition

Nanofiltration is a pressure driven separation (filtration) process by an organic semipermeable membrane with very tiny pore size which ranges from 0.1~10 nm, normally 1~2 nm. The driving force of the separation process is the pressure difference over the membrane. From the feed solution, several components are retained by the membrane due to its selevtivity despite the driving force, while water and substances with a molecular weight < 200 D are able to permeate the semipermeable separation layer. Because nanofiltration membranes also have a selectivity for the multivalent charged ions, monovalent ions will pass the membrane partly and multivalent ions will be rejected completely.

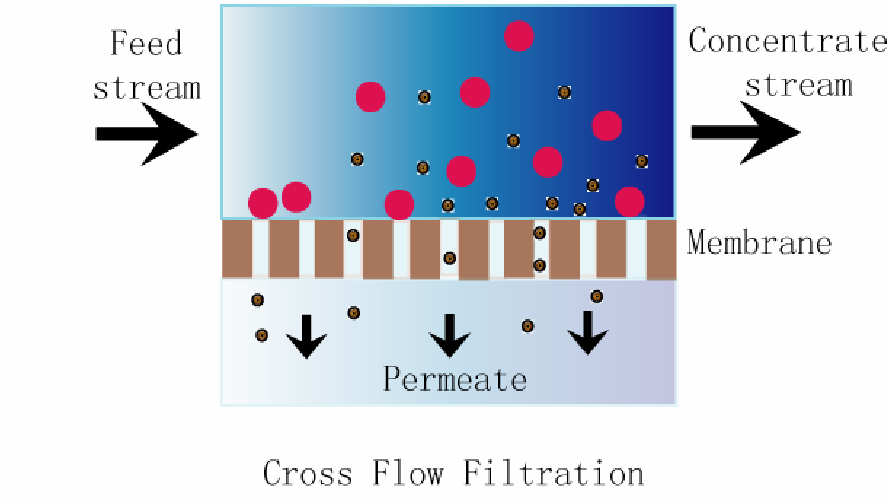


Figure 2.1 – Membrane filtration process

2.1.2 Spiral wound type of membrane

The membrane type is mainly classified into hollow fiber type, tubular type, capillary type, flat sheet type and spiral wound type depending on its construction method. For nanofiltration, spiral wound type membranes are practical because less footprint is needed to obtain the necessary production and more specific area can be obtained compared to other kinds of membrane types. Therefore, most of nanofiltration membranes are of the spiral-wound configuration. Nanofiltration membrane can be also classified into a polyamide based membrane, a polyvinylalcohol based membrane and even ceramic based membrane depending on membrane material. The first two kinds of materials in spiral-wound configuration are not backwashed. Ceramic membrane is robust enough to backwash but is too expensive.

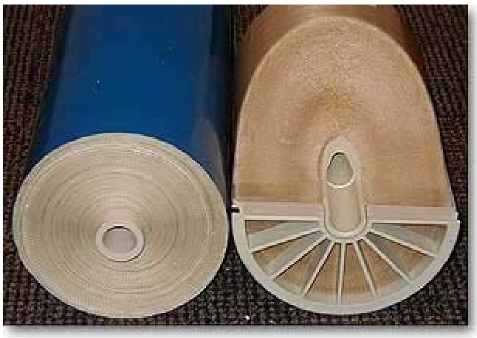


Figure 2.2– Photo of spiral wound membrane

In spiral wound membranes, several flat sheet membranes are wound around a central permeate tube. The distance between two membranes is from 0.25 to 1 mm. The feed solution enters the module and is distributed to the entire membrane area. While flowing, some water and solute flows through the membrane and enters 'permeate' manifold. The remaining flow can not pass through the membrane and enters the 'concentrate' manifold. The filtration process of spiral-wound membrane is shown in the Figure 2.3.

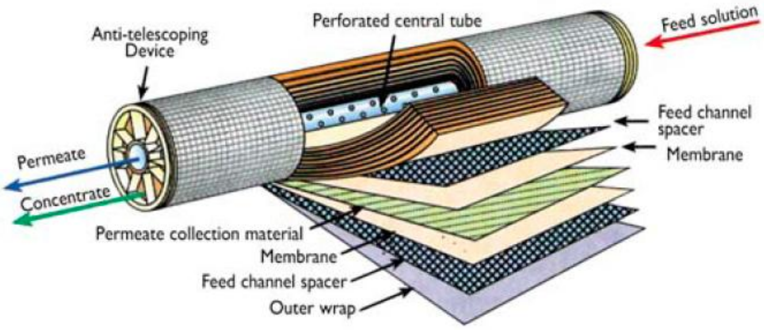


Figure 2.3 – Principle of spiral-wound NF membrane

2.1.3 Existing problems and conventional solutions

Currently, the main operational problems of nanofiltration are the low recovery (80%~90%) and concentrate problem. Traditionally, several disposal methods are used and considered. But they can be challenging, because the volume and high concentrations of dissolved components limit the solutions, particularly in areas where the large surface water body is unavailable. Their drawbacks are listed as below.

Table 2.1 – drawbacks of conventional concentrate management approaches

Concentrate management options	Drawbacks
Discharge to surface water	- Increase local salinity level, which may affect habitat in the discharge area
Discharge to sewer system	- May affect wastewater treatment performance - Elevates salinity level in wastewater effluent, which may affect discharge criteria and recycling water acceptability
Deep well injection	- Increase salinity in underground water, which may increase total dissolved solids level in the water supply source - Requires increased maintenance of injection wells due to mineral precipitation and scaling
Land application	- Affect groundwater and vegetation
Discharge to ocean or sea	- Affect marine life
Evaporation ponds	- Need extensive territory. Not cost-effective in area where land is expensive. Or no enough sun
Thermal evaperation	- Energy cost

Due to those drawbacks, conventional concentrate disposal approaches are not recommended any more. The need for zero liquid discharge exists. Fouling and scaling need to be controlled to reach a higher recovery and reduce the concentrate volume and consequently higher cost effectively and create less environmental pollution. In order to prevent scaling and fouling efficiently, the kinetics of nanofiltration and the mechanisms of scaling and fouling will be studied in the following parts.

2.1.4 Kinetics

Lots of effort needs to be done for the fouling and scaling control to reach a very high recovery. To check if fouling and scaling start to occur or not, the mass transfer coefficient (MTC) needs to be monitored. But first we should know how to calculate the basic terms, recovery and rejection based on mass balance, and transmembrane pressure (TMP).

Recovery and rejection

Recovery also can be called productivity. According to mass balance, the feed flow equal to the sum of concentrate flow and permeate flow. Recovery can be calculated by:

$$\gamma = \frac{Q_p}{Q_f} \cdot 100\% \qquad \text{[Eq. 2.1]}$$

In which,

γ – recovery [%]
Qp – permeate flow [m^3/h]
Qf – feed flow [m^3/h]

Rejection indicates the amount of components rejected by membranes. It shows the separation efficiency of the components by the membrane. It is calculated by:

$$\mathrm{Re} = 1 - \frac{C_p}{C_f} \qquad \text{[Eq. 2.2]}$$

In which,

Re – rejection
Cp – concentration of components in permeate [g/m3]
Cf – concentration of components in feed water [g/m3]

The schematic figure of mass balance, recovery and rejection is shown in Figure 2.4.

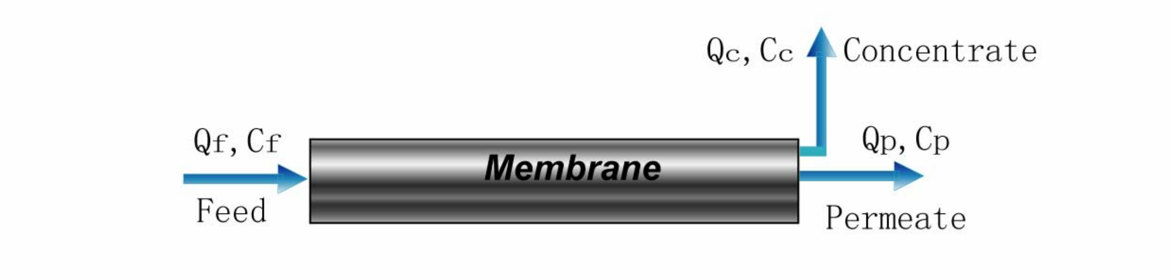


Figure 2.4 – Schematic illustration of mass balance, recovery and rejection

Transmembrane pressure (TMP)

Since the pore size of membrane is very small, water does not automatically flow through a membrane. The membrane has a resistance against filtration and this resistance has to overcome by a pressure. TMP is the net pressure difference over a membrane and acts as the driving force for the separation process. TMP is given by:

$$\begin{aligned} \mathrm{TMP} &= \Delta P - \Delta\pi = P_f - \frac{\Delta P_{hydr}}{2} - P_p - \Delta\pi \\ &= P_f - \frac{P_f - P_p}{2} - P_p - \left(\frac{\pi_f + \pi_c}{2} - \pi_p\right) \qquad \text{[Eq. 2.3]} \\ &= \frac{P_f}{2} - \frac{P_p}{2} - \frac{\pi_f + \pi_c}{2} + \pi_p \end{aligned}$$

In which,

P_f – pressure of feed [Pa]
ΔP_{hyd} – hydraulic pressure loss [Pa]
P_p - pressure of permeate [Pa]
$\Delta\pi$ – osmotic pressure difference [Pa]
π_f – osmotic pressure of feed [Pa]
π_c – osmotic pressure of concentrate [Pa]
π_p – osmotic pressure of permeate [Pa]

Osmosis pressure is a fluid property dependent on salt concentration and temperature. It is calculated by:

$$\pi = \sum \frac{R \cdot T \cdot c_i \cdot z_i}{M_i} \qquad \text{[Eq. 2.4]}$$

In which,

R – gas constant [J/K.mol]
T – temperature [K]
c_i – concentration ion [g/m3]
M_i – molecular weight ion [g/mol]
z_i – valence ion [-]

Mass transfer coefficient (MTC)

MTC indicates the permeability of a membrane. The membrane fouling and scaling is monitored by MTC. If MTC decreases against time continuously, it means scaling occurs in the membrane. It is a diffusion rate constant which is contributed by the permeate flux, membrane area, TMP and osmotic pressure.

$$MTC = \frac{Q_p \cdot TCF_{MTC}}{A_{mem} \cdot TMP} \qquad \text{[Eq. 2.5]}$$

In which:

Q_p - discharge of permeate [m^3/s]
A_{mem} - area of membrane [m^2]
TMP - transmembrane pressure [kPa]
TCF_{MTC} - temperature correction factor for MTC [-]

TCF_{MTC} and TMP varies with different real temperature, MTC should be normalized to reference temperature 20 degree.

$$TCF_{MTC} = e^{U \cdot \left(\frac{1}{273 + T_{act}} - \frac{1}{273 + Tref} \right)} \qquad \text{[Eq. 2.6]}$$

In which:

U - membrane dependent constant (3200) [-]
T_{act} - actual temperature [K]
T_{ref} - reference temperature (273+20°C) [K]

$$TCF = \frac{273 + T_{act}}{273 + T_{ref}} \qquad [Eq.\ 2.7]$$

In which:

TCF - temperature correction factor for π [-]

$$\pi_{normalized} = EGV * factor(EGV \rightarrow TDS) * factor(TDS \rightarrow \pi) * TCF \qquad [Eq.\ 2.8]$$

In which:

EGV = conductivity [μs/cm]
Factor(EGV-->TDS) = 1.0911
Factor(TDS-->п) =0.0433

The normalized osmosis pressure is substituted into the equation [2.3] to get a new TMP and then a new MTC.

2.2 Fouling and scaling

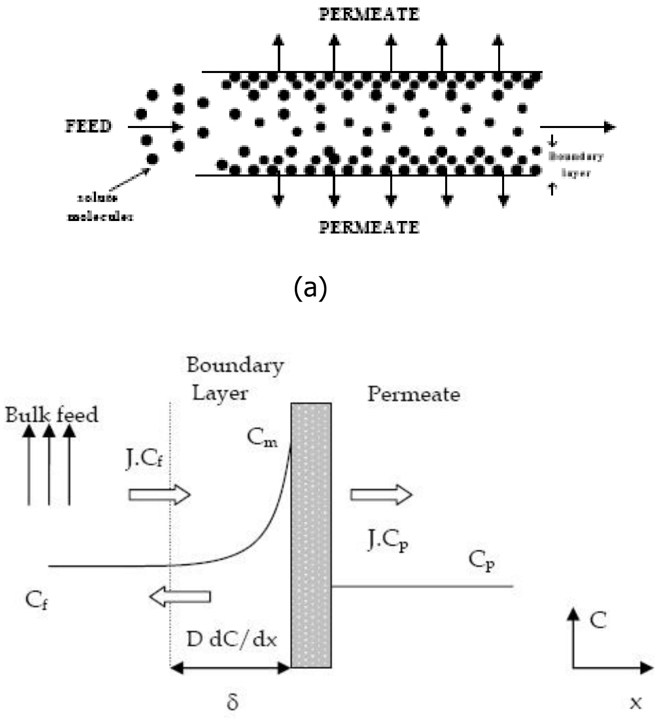
Fouling is the common name for all types of blocking of the membrane surface. The phenomenon of concentration polarization is performed in the first part of this section and afterwards several types of fouling are presented before determining the fouling components.

2.2.1 Concentration polarization

Concentration polarization is important for NF and RO, but not for UF and MF (no ions concentrated). Nanofiltration process is defined as cross flow filtration which refers to a pressure-driven separation process in which the permeate flow is perpendicular to the feed flow. The driving force for permeate flow in cross flow filtration is the pressure drop from the bulk flow to the permeate side of the membrane. Permeate flow is obtained due to the driving force.

As the liquid passes through the membrane, the accumulation of excess dissolved substances is forming in a thin layer adjacent to the membrane surface. The solute in the vicinity of the membrane surface is higher than that in the bulk flow. This phenomenon is called concentration polarization [Lianfa Song and Menachem Eiimelech, 1995]. As C.A.C van de Lisdonk said, 'Concentration polarization is the accumulation of rejected dissolved components at the membrane surface creating a local concentration higher than that of the bulk flow.'

During the past two decades, numerous theoretical investigations have been made in an effort to understand concentration polarization and to predict permeate rate since a high flux and low transmembrane pressure is most desirable. A representative achievement of these researches includes the gel-layer model [W.F.Blatt,1970], shear-induced-diffusion model [A.L.Zydney, 1986] and osmotic pressure model [W.N.Gill, 1971]. These models can give an interpretation for experimental data in cross flow filtration process. The shear-induced-diffusion model can obtain a better fit with experimental data. The osmotic-pressure model can be used in reverse osmosis systems but can not be applied to microfiltration and ultrafiltration systems since osmotic pressure is negligible in these cases.



(a)

(b)

Figure 2.5 – (a) Schematic illustration of concentration polarization (b) concentration gradient between the bulk flow and the surface of membrane [source: C.A.C. van de Lisdonk, et all, 2001]

Based on Figure 2.5, the local flux varies along the membrane. The relationship between concentration in the boundary layer and in the bulk flow is represented as follows.

$$\beta = \frac{C_m - C_p}{C_f - C_p} = \exp\left(\frac{J_v}{k}\right) \qquad \text{[Eq. 2.9]}$$

In which,

β - concentration polarization factor
Jv – local flux [$m^3/m^2/s$]
k – local mass transfer coefficient [m/s]
C_m – salt concentration on the membrane [mg/l]
C_p – permeate salt concentration [mg/l]
C_f – bulk salt concentration [mg/l]

Due to lots of variable parameters along the membrane path, the flux is difficult to be determined. In general, the flux depends on the total resistance of the system including 1) membrane resistance and 2) resistance of the retained particles. The membrane resistance is usually constant only depending on the membrane physical and chemical properties. The resistance of the retained particles determines the changing tendency of the flux. As solution passes through the membrane, solute or particles accumulate in the vicinity of the membrane surface and form a thin layer. The resulting concentrated layer increases resistance and thus reduces the initial permeate flux.

$$J = \frac{Q_p}{A_m} = \frac{TMP}{\nu \cdot R_t} \qquad \text{[Eq. 2.10]}$$

In which,

J – total flux (m3/m2/h)
Q_p – permeate flow (m3/h)
A_m – membrane surface area (m2)
TMP – transmembrane pressure (Pa)
ν - viscosity (Pa/s)
R_t – total resistance (Pa)

With the continuous supply of the feed to the inlet and the drainage of concentrated suspension from the outlet, the flux mainly decreases at the beginning of the module due to the rejection of some particles or compounds by the membrane and after a while keeps constant if no additional fouling happens. In cross-flow membrane separation, cake build-up on the membranes is reduced by applying high cross-flow velocity of the recirculated concentrate, thus building up shear forces that transport the particles away from the membranes [Chang et al., 2002].The concentration polarization can be prevented by increasing the cross flow velocity along the membrane surface.

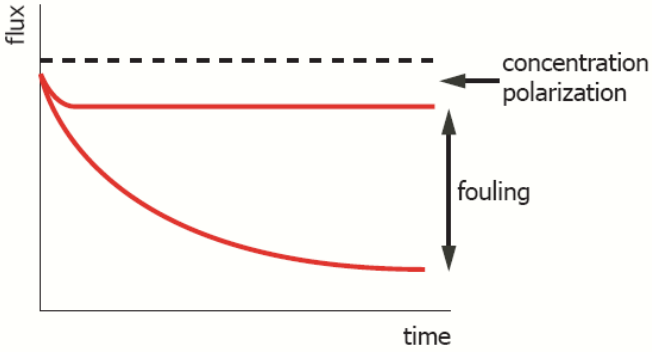


Figure 2.6 – Flux decline in cross flow filtration

2.2.2 Classification

Three types of processes and phenomena are responsible for membrane fouling: particle fouling, scaling and biofouling.

Particle fouling

Particle fouling can be defined as the accumulation of suspended and colloidal matter on the membrane surface. Clay precipitates can also result in particulate fouling. This kind of fouling is caused by the above-mentioned four mechanisms. Therefore, the particle fouling formation depends on particle properties, membrane surface properties and hydrodynamics. For nanofiltration, particle fouling can be limited by pretreatment, like MF/UF processes. For groundwater, the particle fouling is not considerable.

Scaling

Scaling is the precipitation of sparingly soluble inorganic salts on the membrane surface when their ionic concentration in the water flow exceeds the saturation concentration. Most scales to be formed are carbonate salts (e.g. $CaCO_3$), sulphate salts (e.g. $CaSO_4.2H_2O$), silica and calcium phosphate. Scaling depends mainly on the salt concentration. Under a high recovery, a large amount of salts are accumulated in the membrane leading to a high salt concentration in the bulk flow. In addition, even if the salt concentration in the bulk flow is below the saturation concentration, the salt concentration in the boundary layer close to the membrane surface can be above the solubility due to the salt accumulation caused by convection. This is so called concentration polarization. At a feasible cross flow velocity, scaling might be prevented by reducing bivalent ion concentration with pretreatment.

According to the theory of thermodynamics, precipitation of inorganic salts will occur when the solubility is exceeded. The extent of supersaturation is determined by solubility index (SI).

$$SI = \log \frac{C}{C_s} \qquad \text{[Eq. 11]}$$

In which,

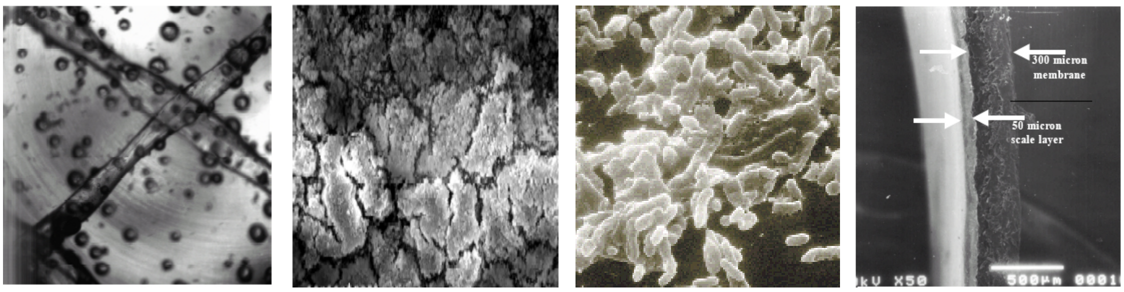
SI – saturation index
C_s – solubility product [mol/l]
C - concentration of ions [mol/l]

When scaling occurs in nanofiltration membranes, the permeability of the membranes decrease. A higher feed pressure needs to be applied to maintain the desired flux. This will cause an increase in energy consumption. Scaling can be prevented by dosing of acids or anti-scalants. Therefore, scaling causes higher chemical consumption and may result in shorter life span for membrane. Scaling also can be reduced by removal of scaling components through pretreatment and by not exceeding the solubility concentration in a optimal hydrodynamic condition. Other factors, like pH, temperature and ion strength also influence the occurrence of scaling.

Biofouling

Biofouling is influenced by biological contamination. It involves adhesion and growth of microorganisms on the membrane surface. Microorganisms can enter the system through water or air, or both. They have irreversible effects on membrane. Since the membranes can not be disinfected with chlorine to kill the microbiological bacteria, biofouling occurs in NF membranes or RO membranes after the operation of a longer period. The types of microorganisms, their growth factors and concentration in a membrane system greatly depend on critical factors, such as temperature, dissolved oxygen concentrations and the presence of organic and inorganic nutrients.

Biofouling is hard to control, even by reducing the number of microorganisms in the feed, they can multiply, and they will do so if nutrients are available [H.C. Flemming,1996, H.C. Flemming, G. Scaule, T.1997].



(a) (b) (c) (d)

Figure 2.7 – SEM micro photos of different type of fouling (a) Particle fouling on spacer (b) Scaling (c) Biofouling (d) Side view of scaling

2.2.3 Fouling and scaling components

Membrane systems are fouled by a variety of factors. The mix of fouling constituents is a function of feed water characteristics, membrane type, and system operating conditions, but typically includes:

- inorganics such as clays and silts, metal precipitates, sparingly soluble salt precipitates
- organics such as natural organic matter (NOM)
- biological matter includes microorganisms that accumulate or colonize membrane surfaces, and biofilms

Depending on the resulting factors, therefore, membrane fouling also can be distinguished as the following main types, NOM fouling, scaling due to soluble salt precipitates, silica scaling, and biofouling. NOM is generally recognized as the main foulant in UF and MF, not in NF and RO. In order to prevent non-biological membrane fouling of nanofiltration, the feed solution should be free of: particles, multivalent or bivalent ions (eg: Ca^{2+}, Mg^{2+}, Ba^{2+}), silica and etc. All of them are the key factors contributing to the membrane fouling and scaling.

Multivalent ions (bivalent ions)

The ions involved in scaling (e.g. calcium, barium and magnesium) are multivalent ions with β-factors which are higher then for monovalent ions. The difference between β-factors is caused by the more extended water shield of the multivalent ions. The back diffusion is slower with these ions compared to the monovalent ions (see Figure 2.8).

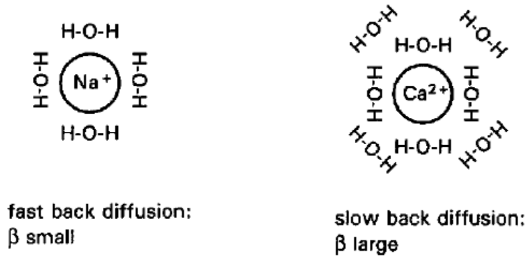


Figure 2.8 – back diffusion of multivalent ions and monovalent ions[source: C.A.C. van de Lisdonk, B.M.Rietman, et all, 2001]

Besides this, bivalent ions have been proved to be a dramatic fouling factor for membrane filtration [Cho J. Amy G., Pellegrino J. 2000; Li Q. and Elimelech M. 2004; Hong S. and Elimelech M. 1997]. With the increase of ion concentration, more bivalent ions accumulate on the surface of membrane, leading to exceeding the saturation concentration followed by scaling.

Silica

Silica is a general term, which refers to silicon dioxide (SiO_2) in all of its forms. It can be found in surface water and groundwater. In natural waters dissolved silica comes from the weathering of minerals and rocks with a normal range between 1-40 mg/l [Abdullah M. Al-Rehaili. 2003].

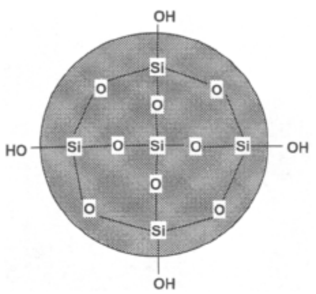


Figure 2.9 - Silica (SiO2)n formula (Source: K.D. Demadis et al., 2005)

Silica is another key scaling factor in membrane separation processes when the concentration of soluble silica exceeds the amorphous silica equilibrium solubility (The solubility limit is about 120 mg/l at ambient temperature of 25^{o}C and neutral pH of the solution [Abdullah M. Al-Rehaili. 2003; S.Chen, T. Chang and C.Lin. 2006; Ingrida Bremere, Maria Kennedy, et all, 2000].

There are three mechanisms of silica scaling: monomeric adsorption on the membrane surface, colloidal deposition on the membrane surface and the formation of biogenic amorphous silica by living organisms [R.Sheikholeslami, J. Bright. 2002]. The mechanisms of silica scaling is schematized in Figure 2.10.

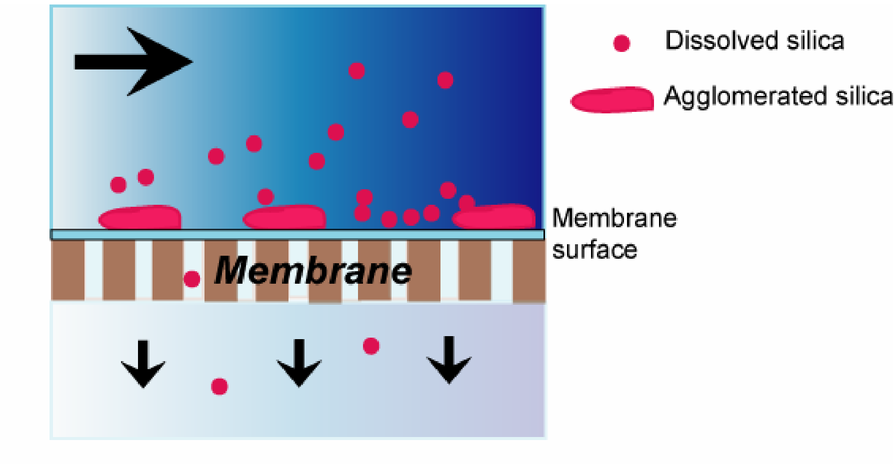


Figure 2.10 – Schematic illustration of silica scaling

Other factors resulting in fouling and scaling

Besides the water composition, NF membrane fouling is also affected by: 1) The physicochemical properties of the membrane; 2) the operational parameters (eg. TMP, flux), etc..

2.3 Solution for scaling components removal

The removal of multivalent cations has been investigated in different research projects in order to increase the recovery of nanofiltration or reverse osmosis. Van Paassen et all [Paassen J, Wessels, P.2002] used ion exchange and Long et all [B. W. Long, R. G. Bond, 2007] used pellet softening in order to reduce the scaling components. Softening by jar tests is effective for silica/hardness/barium removal [Abdullah M. Al-Rehaili. 2003; S.Chen, T. Chang and C.Lin. 2006; R.Sheikholeslami, J. Bright. 2002]. Heijman et all [Heijman, S.G.J., Li, S., Dijk, J.C. van, 2006] investigated fluidized ion exchange with surface water as the feed. In the following subsection, several technologies, softening (pellet softening and sludge softening), sedimentation, and ion exchange (weak acid cation exchange) are presented. This section will finalize with the design of an optimal pretreatment concept for nanofiltration scaling control. This concept is the combination of sludge softening, sedimentation and weak acid cation exchange in series to obtain zero liquid discharge for groundwater treatment.

2.3.1 Softening

The hardness of raw water in the Netherlands varies between 0.5~5 mmol/l. The hardness of surface water is normally from 2.0 to 3.0 mmol/l. For groundwater, the degree of hardness varies in different locations. Traditionally, in order to reduce the hardness (mainly for calcium) from the drinking water softening is applied so as to satisfy the water quality standard for public health, ethics, environmental and economy aspects. The guidline of hardness in drinking water in the Netherlands is between 1.5 mmol/l and 2.5 mmol/l. Thus originally chemical softening is applied to obtain the drinking water which is not too soft and not too hard. Here, in this study, maybe chemical softening is possible to be used as the first step for drinking water treatment because it is able to remove the majority of Ca^{2+} ions as pretreatment for nanofiltration.

Chemical softening is realized by dosing of a base, like NaOH, $Ca(OH)_2$ or Na_2CO_3 to remove calcium. Due to the shift in the calcium carbonic acid equilibrium, spontaneous crystallization occurs and precipitates. For natural water, pH is in the range of 7-8, thus mainly HCO_3^- exists. In order to produce the precipitation of calcium carbonate, the dosing of base depends on the saturation index.

Pellet softening

Pellet softening, one type of chemical softening, is often used in practice to remove hardness. It is named after its fluidized bed filled with pellets. Seed grains which have a diameter of approximately 0.2~0.6 mm are dosed into the reactor or column to fill a fluidized bed which can increase crystallized surface area. During softening, the $CaCO_3$ attaches to the surface of seed grains to form pellets.

Sludge softening

Sludge softening also belongs to chemical softening, but it needs a higher pH and dosing of seed crystal (calcium carbonate) to contribute to the precipitation of calcium carbonate and magnesium hydroxide. Sludge softening always combined with sedimentation afterwards. A big amount of dosage of a base in the softening reactor causes lots of sediments at the bottom of sedimentation tank. By recycling the precipitation of $CaCO_3$ from sedimentation tank back to softening reactor, the particle size and density of the precipitates can increase so as to settle down the precipitate more efficiently afterwards. This recycling system is preferable for the removal efficiency of bivalent ions and silica. Also, mixing in a sludge softening reactor with a certain stirring speed is necessary so as to increase the chance of attachment of particles and flocculants. Due to the presence of sediments, the water is not transparent and the color of water is milk white.

Sludge softening has two obvious functions: efficient hardness removal and silica removal.

- Function 1 Hardness removal

The precipitation of $CaCO_3$ is dominant for $pH < 9$ but for $pH>9$, $Mg(OH)_2$ also occurs. At high pH, sludge softening can remove calcium as well as magnesium to a very low concentration. In other words, it also can be called high pH softening. The precipitation of one salt influencing the precipitation of a second has been reported by [Hina, Nancollas and Grynpas 2001], and [Sudmalis, Michael and Roya Sheikholeslami, 2000]. Therefore, other bivalent cations like barium also can be removed in sludge softening [Rick Bond. 2006].

Conclusion: Sludge softening is better than pellet softening because more Ca, Mg and Ba are removed.

- Function 2 Silica removal

In addition, with sludge softening at high pH silica can be removed by three kinds of mechanisms, sweep coagulation, adsorptive coagulation and chemical reaction.

One mechanism of silica removal is called sweep coagulation. Silica can be removed as a co-precipitate with magnesium hydroxide ($Mg(OH)_2$). S.Chen, T. Chang and C.Lin. (2006) studied the effects of pH, magnesium hydroxide and calcium carbonate on silica removal. Both $CaCO_3$ and $Mg(OH)_2$ are directly correlated with silica mass removal. $Mg(OH)_2$ contributes much for silica removal, corresponding to the results reported by Sheikholeslami and Zhou (2000) and Rich Bond (2006). The precipitation of $Mg(OH)_2$ is dominate at high pH (>9). Silica concentrations decreased sharply around pH 10.2 [Rich Bond, 2006]. So high pH is necessary for $Mg(OH)_2$ precipitating and consequently for silica removal.

Another mechanism of silica removal is adsorptive coagulation. The negatively charged silica polymers ($H_3SiO_4^-$ and $H_2SiO_4^{-2}$) were dominant for pH>9.9. At lower pH, the soluble form of silica is monomer, uncharged $Si(OH)_4$. The charge on the surface of $Mg(OH)_2$ can be neutral, positive or negative depending on different pH. At high pH, the charged silica might be attracted on the surface of $Mg(OH)_2$. At high pH (10), silica removal is probably due to the formation of both the positive charged surface of $Mg(OH)_2$ and the negative charged silicate, where electrostatic attraction between them could occur.

The other mechanism of silica removal is chemical reaction between silica and magnesium at high pH ($Mg^{2+} + SiO_4^{4-} \rightarrow Mg_2SiO_4$). But the formation of Mg_2SiO_4 is impossible since SiO_4^{4-} is presented only at pH higher than 12 while Mg^{2+} has been precipitated out in lower pH (9~10) for the formation of $Mg(OH)_2$.

From the above study, silica removal either by sweep coagulation, adsorptive coagulation or chemical reaction is not clearly distinguished since the formation of $Mg(OH)_2$ and Mg_2SiO_4 was not analyzed. Further study is needed to investigate the charge on the surface of $Mg(OH)_2$ at high pH. But at least we know that all the mechanisms work at high pH.

We can make some conclusions based on the literature study. High pH softening is proven effective for silica removal. The precipitation of $Mg(OH)_2$ and the presence of magnesium is necessary for silica removal. Sludge softening is better than pellets softening because of silica removal.

2.3.2 Sedimentation

By definition, sedimentation is a treatment process where suspended particles, like flocs are moved from water by settling. Here, sedimentation can be used after sludge softening reactor that leads to the precipitation of calcium carbonate and magnesium hydroxide attached with silica. And then the sediments are pumped back to the sludge softening reactor. Sedimentation is usually used before ion exchange column or filtration process to avoid clogging of the bed.

As we know, the sedimentation efficiency is mainly influenced by settling velocity. The velocity of settling particles is controlled by gravity. When the upward force is less than the downward force, the particle starts to settle (see Figure 2.11). The larger and heavier particles will have a higher settling velocity. As mentioned before, the density and size of the particles can be increased by dosing crystal seeds ($CaCO_3$).

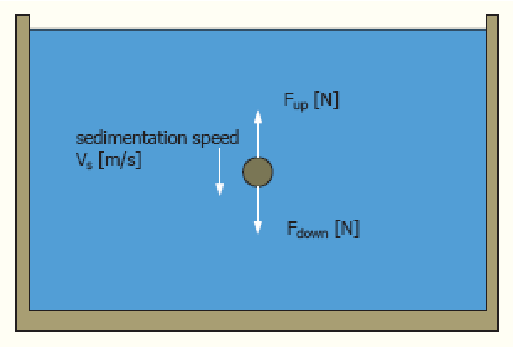


Figure 2.11 – Force on settling particles

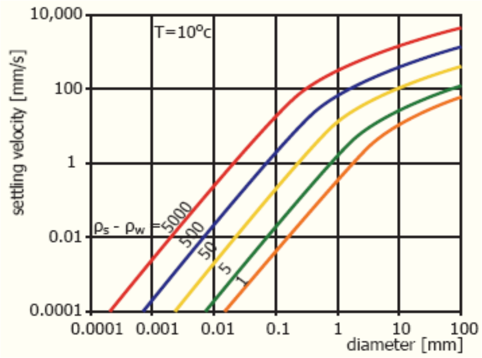


Figure 2.12 - settling velocity of discrete particles (van Dijk, 2004)

In order to guarantee enough retention time for precipitation in a shallow tank, up-flow sedimentation is a good choice comparing with down-flow sedimentation. The up-flow velocity of water should be lower than the settling velocity of particles. Experience shows the up-flow velocity normally should be controlled at less than 2 mm/s, otherwise it will exceed the settling velocity of particles and reduce the precipitating efficiency.

2.3.3 Ion exchange

Ion exchange processes are used for the removal of color, organics, nitrates, hardness (calcium and magnesium) and demineralization in drinking water treatment. It is defined as a reversible process for mass transfer of ions, usually between liquid phase (solution) and solid phase (resin). Almost all the bivalent ions are removed until breakthrough. Ion exchange is a highly effective separation technique, which can achieve complete removal of trace ionic components from dilute solutions.

Ion exchange resin

An ion exchange resin is an insoluble matrix normally in the form of small beads (<2 mm diameter), fabricated from an organic polymer substrate. The resin can consist of anion resin or cation resin. In order to remove the bivalent positive ions like calcium, magnesium and barium, cation resin is chosen. Acid cation resin is divided into strong acid cation resin and weak acid cation resin. Strong cation exchange resins contains sulfonic acid groups or the corresponding salts. Weak cation exchange resins contain carboxylic acid groups or the corresponding salts. Strong acid resin are used for deionization and softening, and weak acid resin can be used for the same purpose, but it is easily influenced by the pH. The advantage of weak acid cation resin is the lower requirement of regenerate solution. For this experiment, weak acid cation resin (H^+ form) is applied.

Ion exchange equilibrium

When the resin releases the ions to the solution, the counter-ions of solution can enter the matrix of resin. Generally, ion exchange in a binary ions system is considered as a simple stoichiometric reaction as shown in Equation 2.19. This reaction describes the transfer or removal of A^{n+} from a liquid phase to a solid phase.

$$z_b A^{z_a} + z_a \overline{B^{z_b}} \Leftrightarrow z_a B^{z_b} + z_b \overline{A^{z_a}} \qquad \text{[Eq. 2.19]}$$

In which,

A – A ion in water
$\overline{A}$ – A ion on resin
B – B ion in water
$\overline{B}$ – B ion on resin
z_a, z_b – valence of A and B

Ion selectivity

For different ions, the selectivity of the resin varies. Based on batch experiment at equilibrium condition, the selectivity can be obtained and selective sequency for different ions is found for strong cation resin and strong anion resin as shown in the following table. From the table, we can see the strong acid resin has a higher selectivity for bivalent ions than for monovalent ions. For weak acid resin, the sequency is quite the same.

Table 2.2 – ion selectivity with order of preference

Type of resin	Ion selectivity
strong cation resin	barium>lead>calcium>nickel>cadmium>copper>zinc> magnesium>potassium>ammonia/sodium>hydrogen
strong anion resin	Iodide>nitrate>bisulfite>chloride>cyanide>biocarbonate >hydroxide>fluoride>sulphate

Batch and column exchange system

Ion exchange processing can be accomplished by either a batch method or a column method. In the first method, the resin and solution are mixed in a batch tank. When the exchange comes to equilibrium, the resin is separated from solution. Because regeneration of the resin for a batch system is chemically inefficient, this method has limited potential for practical application. The batch method can be used to obtain the selectivity coefficient at equilibrium. Normally, the column exchange system is applied in a full scale installation.

Passing through a column needs a bed of ion exchange resin. The bed process can be regarded as infinite batch tanks in a series. In an ion exchange column, two kinds of bed process, fixed bed process and fluidized bed process are possible. To realize the two kinds of bed processes, two flow patterns are required. For fixed bed process, the flow direction is downwards, while upwards for fluidized bed process.

In a fixed bed ion exchange, resin particles can act as a filter medium, resulting in plugging of the column. The solution is continuously supplied to the resin phase from above and flows out below the resin phase. In such a case, at the start of the passage of solution, various ions dissolved in the solution are first exchanged and adsorbed to resins on the top layer of resin phase. After adsorption to the resins of the top layer has progressed and the exchange capacity of the top layer has been reached, ions in the solution supplied thereafter are adsorbed to the resins of the layer next to the top layer. In this way, the exchange process moves downward as the treatment progresses, and finally ion exchange phase reaches its breakthrough point.

The polymeric structure of ion-exchange resins might swell. The swelling is depended on the loading with different ions (Ca^{2+}, Na^{+}, H^{+}). The bed height can expand due to the swelling of resin depending on the solution quality.

In a fluidized bed, the resin particles are separated from each other via liquid up-flowing through the column. Thus particles are allowed to pass through the bed without causing a pressure drop. The choice of a fluidized bed depends on the characteristics of the particles in the feed solution. If the feed water (eg. surface water) contains particles or suspended solids, a fluidized bed needs to be chosen for ion exchange in order to preventing clogging of filters and diminishing the pressure drop.

2.3.4 Determination of treatment concept

The pros and cons of each process are compared in the Table 2.3.

Table 2.3 – process comparison

pellet softening and sludge softening

The choice between sludge softening and pellet softening depends on the necessity to remove silica from the feed water at high pH (around 10). While pellet softening removes calcium to a concentration of about 0.5 mmol/l and does not remove magnesium. Sludge softening removes more Ca, Mg. So the loading of the IEX is lower due to the less regenerant waste.

coagulation and sludge softening

Although both coagulation and softening process are capable of removing silica, coagulation is not chosen since it can not remove hardness and has lower silica removal (40%). Softening not only can obtain higher silica removal (80%), but also can remove hardness simultaneously.

Weak acid ion exchange and softening

Sludge softening has an advantage that it removes calcium with the use of fewer chemicals compared to ion exchange. However, it also has the drawbacks which can be compensated by ion exchange:

- Sludge softening does not remove calcium completely and the removal of barium is not efficient compared to ion exchange.
- Sludge softening is easier to bring 'carry over' of crystals to the next process. Even if a sedimentation process is used after it, the tiny carry over still can not be removed efficiently. The 'carry over' has a risk of clogging membrane. Consequently, an ion exchange column with weak acid resin is necessary to be applied after sludge softening and sedimentation. This kind of resin can offer a aggressive water environment to remove 'carry over'.
- After sludge softening, most of hardness is removed from drinking water, but the pH is changed to be 10 which is very high for NF. The pH entering NF should be controlled to much lower than 9.5 to prevent the scaling of calcium carbonate. In order to exchange the residual Ca^{2+} and Mg^{2+} and control the pH, ion exchange with acid cation resin can be used.

We can sum up the above advantages and drawbacks as follows. Sludge softening at high pH might remove silica and most of hardness. The precipitatie of the sludge softening can settle down efficiently in the up-flow sedimentation tank. To remove silica, sludge softening at high pH is necessary. Afterwards, ion exchange with weak acid resin is applied to bring some additional advantages: 1) removes the remaining calcium and magnesium; 2) removes barium efficiently, 3) removes the carry over from the sludge softening; 4) adjust the pH to a suitable level before entering NF. Since sludge softening and sedimentation is located in front of ion exchange, most of hardness has already been removed, resulting in a lower loading for ion exchange. The load on the resin can be reduced compared when only ion exchange is used. Since suspended solids and particles are removed by sedimentation, fluidized bed ion exchange is not necessary.

Therefore, sludge softening combined with sedimentation can cooperate with fixed bed ion exchange with weak acid resin. This combination concept is possible to remove the scaling components efficiently before NF with low costs. The process scheme is shown as below.

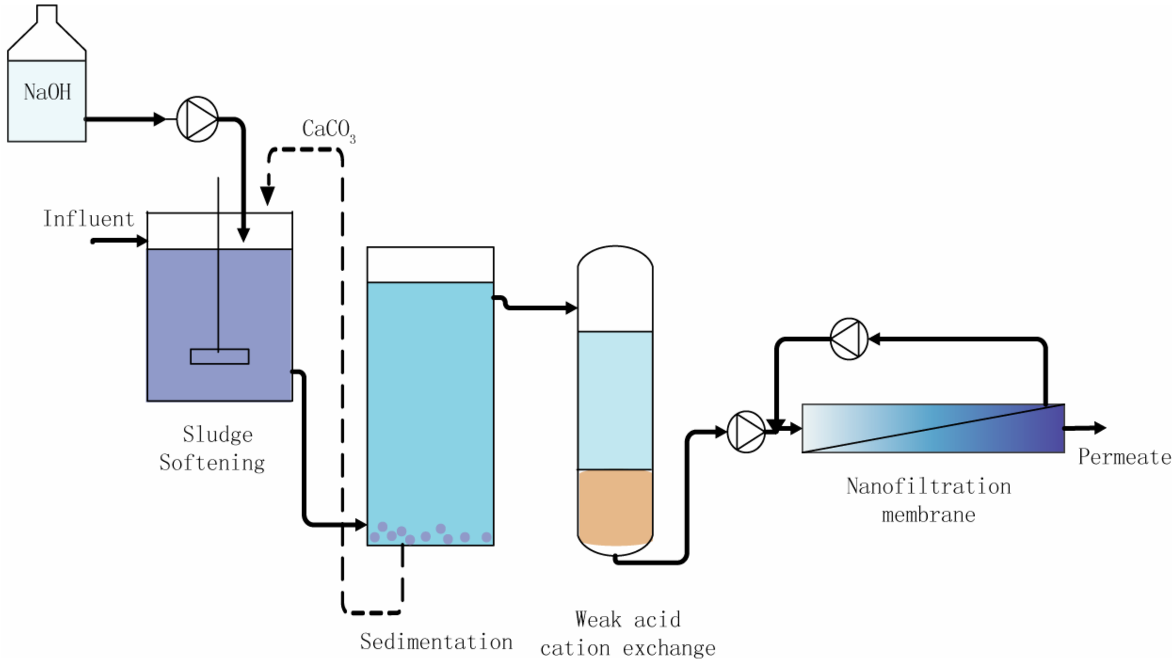


Figure 2.13: Process scheme for groundwater treatment

3 Experiment at 99% recovery

3.1 Introduction of the experiment

This is a pilot experiment executed at Kiwa Water Research. The aim of this experiment is to realize the creative treatment concept for groundwater treatment. So one sludge softening vessel with stirring equipment and NaOH dosing system, one up-flow sedimentation tank, one down-flow ion exchange column with fixed bed, a small cartridge filter and one nanofiltration installation are built up and connected together.

In this experiment, the tap water from groundwater source will be treated through the treatment steps. The high pH is raised up to 10 by dosing of NaOH (3mmol/l). Between the ion exchange and nanofiltration, a cartridge filter is used to remove some particles and precipitates. Everyday several water samples will be taken at different places, like tap water, after sedimentation, after ion exchange, concentrate and permeate. Some water quality parameters will be analyzed. In order to handle this setup operating at 99% recovery, the mechanical problem of concentrate flow control is solved by adding pressure release valve and a small dosing pump after the concentrate valve. Finally, the result shows that the treatment concept is efficient to prevent scaling at recovery of 99% for 11 days from March 19 to March 30 of 2007.

3.2 Materials and setup

3.2.1 Materials

Water to be tested

The water to be tested is the tap water at Kiwa Water Research. The water source is from groundwater which is suitable for the requirement of the test.

Table 3.1 : Tap water quality

Parameter	Concentration (mg/l)	Parameter	Concentration (mg/l)
NH_4^+	<0.04	HCO_3^-	255
K^+	1	NO_3	0.725
Na^+	12.7	Cl^-	9.495
Mg^{2+}	5.86	SO_4^{2-}	<1.0
Ca^{2+}	70.0	Si	8.55
Ba^{2+}	0.024		

The pH of tap water is about 7.8 and the water temperature is 13 °C. Calcium concentration is a little bit high which is the key factor of scaling. Barium concentration and magnesium concentration is not high. In this tap water, Si concentration is 8.55 mg/l, SiO_2 concentration is 18.2970 mg/l. The solubility limit for Si in water is estimated at approximately 120 mg/l, and that for SiO_2 is about 250 mg/l. If the retention rate of silica by NF is very high, at 98% recovery, 27% of silica should be removed before NF (a x 18.2970 / (1-98%) = 250 mg/l, a = 27%).

Sodium hydroxide (NaOH)

NaOH is dosed because it is useful for hardness removal as well as silica removal. NaOH can contribute to the precipitation of $CaCO_3$ and $Mg(OH)_2$, which can reduce the hardness. By dosing NaOH, the following reactions will occur.

$NaOH + Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H_2O + Na^+$

$2NaOH + Mg^2+ \rightarrow Mg(OH)_2 + 2Na^+$

According to the above-mentioned literature research, the target for pH value is 10. In the tap water, pH=7.86, Ca^{2+} =1.765mmol/l, HCO_3^- = 4mmol/l. In order to get the required pH value, we use Stimela to similate the carbonate acid equilibrium. As a result, 3 mmol/l (120mg/l) NaOH should be dosed in sedimentation tank.

Calcium carbonate ($CaCO_3$)

At the beginning, we dose 1 kg of $CaCO_3$ in the mixing tank. But after one night, we find the water in this tank became transparent. In this situation, the efficiency of the precipitation is low. But the problem is not due to the mixing capacity because the stirring power is already enough with a combination of one stirrer and one recycling pump. The problem is only because the amount of $CaCO_3$ is not enough for overnight working and the concentration of $CaCO_3$ is diluted during the night. At last, we dosed 2 kg of $CaCO_3$ in the mixing tank. And then the dilution effect was reduced. In full scale plant, the recycling of CaCO3 is continuous. No dilution effect will occur.

Ion Exchange Resin

Weak acidic resin is chosen just because it needs fewer chemicals for regeneration than the strong acidic resin. The weak acidic cation resin used in this experiment is the Amberlite IRC86 produced by ROHM&HAAS Company. This kind of resin is good for low salt background, which matches with the situation in this experiment. The detailed description of this resin is presented as follows.

Table 3.2 - Typical Chemical & Physical Characteristics of Resin

Functional groups	$- COO^-$
Ionic form (as shipped)	H^+
Total exchange capacity	4.1 eq/l (H^+ form)
Moisture holding capacity	47 - 53% (H^+ Form)
Specific gravity	1.17 - 1.195 (H^+ Form)
Shipping weight	790 g/l
Harmonic mean size	580-780 μm
Uniformity coefficient	1.8
Fine particle range	-0.3mm < 2%
Coarse particle range	+1.18mm < 5%
Maximum reversible swelling	$H^+ \rightarrow Na^+$: 100%

Table 3.3 - Standard Operating Conditions

Maximum operating temperature	120 ^{o}C	
Minimum bed height	700 mm	
Service flow rate	5 - 70 BV/h	
Regeneration	HCL	H2SO4
Concentration	2 – 5 %	0.5 - 0.7 %
Specific load	2 – 8 BV/h	15 – 40 BV/h
Quantity	104 - 110%	
Distorted	2 BV under regeneration condition	
Wash out	2 - 4 BV work condition	

Figure 3.1 – ion exchange resin (Amberlite IRC86)

3.2.2 Experimental setup

Figure 3.2 – Picture of the equipments 1) Sludge softening vessel; 2) Sedimentation tank; 3) Ion exchange column 4) Nanofiltration membrane module

1) Sludge softening vessel:

First, tap water is mixed continuously in this tank with NaOH and $CaCO_3$. 3 mmol/l (120mg/l) NaOH is dosed to raise the pH up to 10 and CaCO3 is added to improve the performance of precipitation which will happen in the sedimentation tank. In order to mix sufficiently, a stirrer and a recycling pump are used to stir the water. The flow at the inlet of this tank is controlled by a floating valve. The retention time for mixing is about 3 h.

2) Sedimentation tank:

Silica, hardness and barium can be removed here with the sedimentation of $CaCO_3$ and $Mg(OH)_2$ happened in this tank. The flow direction is upward. The up-flow velocity of water is about 0.3 m/h. It is lower than to 1 m/h which is the maximum up-flow velocity for sedimentation. In this case, the up-flow velocity does not exceed the particle settling velocity. The lower the up-flow velocity is, the more efficient the precipitation is. In this tank, the residence time is about 3 hours.

3) Ion exchange column:

Weak acid cation resin (10 liters) is used in this column to exchange cations. During the process, acid ions in the resin will enter the solution resulting in lower pH. The contact time (EBCT) in the column is about 14 min.

4) Nanofiltration installation:

The last step is NF membrane installation which mainly includes a feeding pump, recycling system of concentrate, a NF membrane, a concentrate flow controller, PLC control plate and etc.

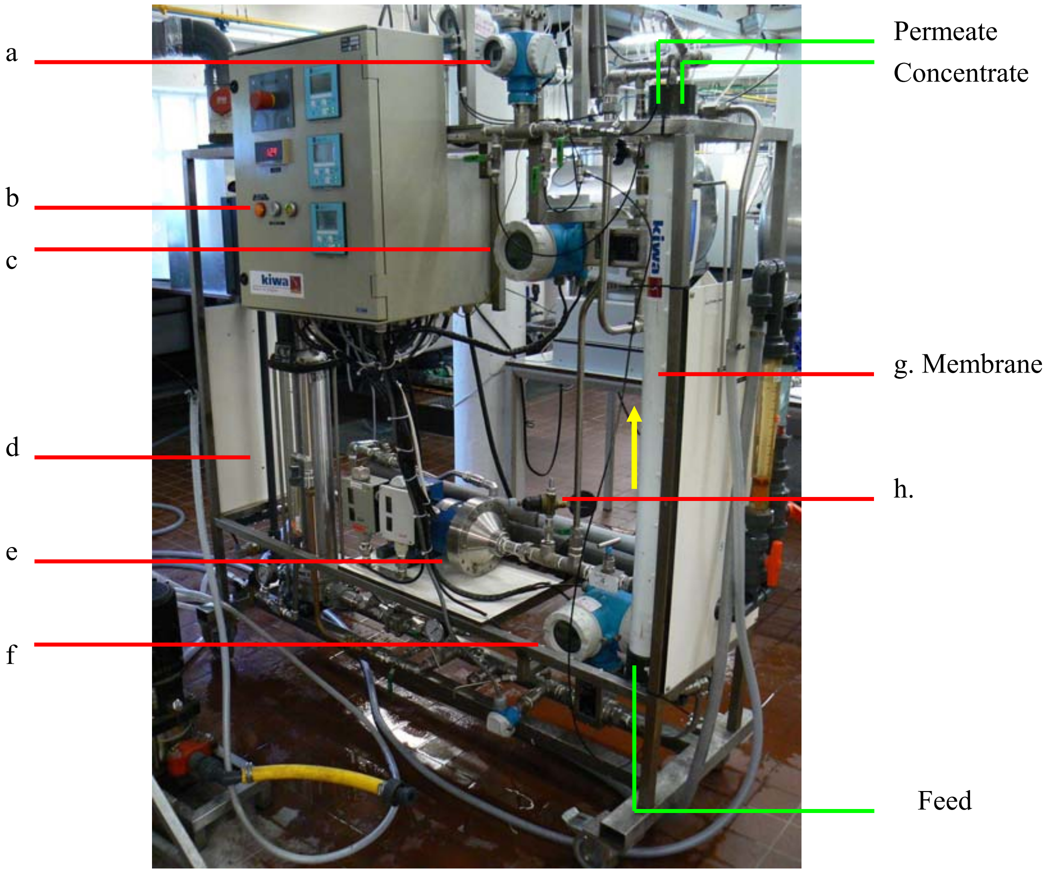


Figure 3.3 - NF installation,

a) pressure meter: It can measure the feed pressure, permeate pressure and concentrate pressure;

b) PLC Control plate: It can switch the feeding pump and show the water temperature in the bulk flow and the conductivity at feed, permeate and concentrate;

c) permeate flow rate meter;

d) speed adaptable pump for providing feed pressure;

e) recycling centrifuge pump: it can recycle the concentrate to guarantee a certain cross flow rate, for preventing concentration polarization;

f) cross flow rate meter;

g) nanofiltration membrane;

h) connected to concentrate flow controller

Nanofiltration membrane

For this experiment, one 2540-T580-TSF spiral wound membrane module from Trisep was used. The membrane was placed vertically. The detailed description of the membrane is given in Table 1.

Table 3.4 – Membrane characteristics

Manufacturer	Trisep
Membrane Type	ANM Aromatic Polyamide Advanced Nanofiltration Membrane
Configuration	Spiral Wound, Fiberglass Outer wrap
Mechanical Configuration	Filmtec Style Core Tube
Feed Spacer	0.031" thick diamond spacer
Membrane surface area	2.6 m^2
Recommended applied pressure	3-14 bar
Maximum applied pressure	41 bar
Recommended applied temperature	2-45^{o}C
Feed water pH range	2-11 continuous
Chlorine tolerance	<0.1 ppm
Maximum turbidity	1 NTU

Figure 3.4 – Picture of the NF membrane module

Concentrate flow controller

One of most important point for this experiment is that the recovery should be operated at 99% continuously. Concentrate flow is very difficult to obtain because of the small valve flow (about 0.4 l/h) and the high pressure of the concentrate (10 bar). We modified this part of the NF installation. This part of installation includes two pressure release valves, a pressure meter, a normal open/close valve, a small dosing pump with a release valve. The two pressure reduction valves were used to reduce the pressure to below 1 bar. The dosing pump is pumping against a pressure release valve of 1.5 bar. So the dosing pump is accurately controlling the concentrate flow. After several tests, the results prove that this modified installation can successfully control the concentrate flow at a very low level continuously.

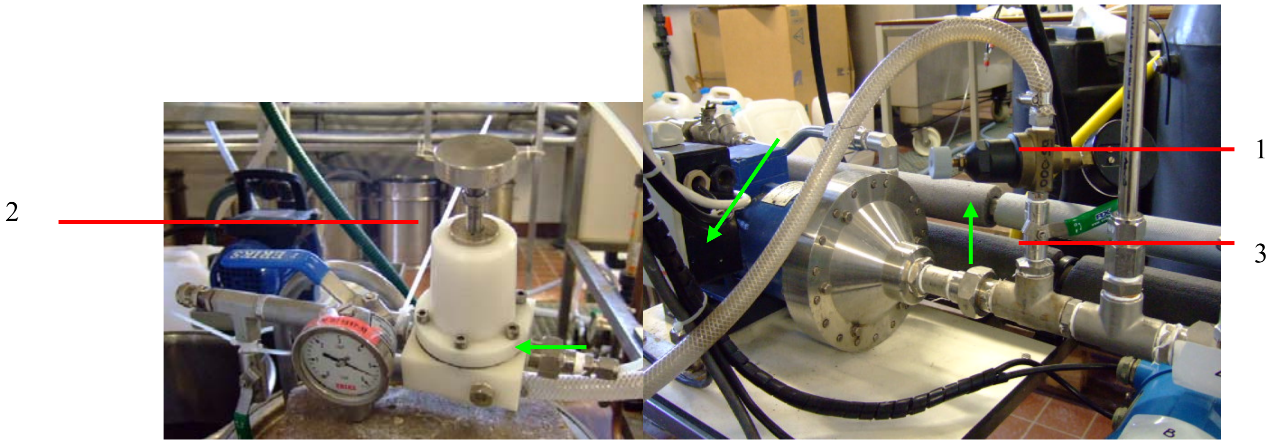


Figure 3.5 – Pressure release system, 1,2) Pressure release valve; 3) normal open/close valve

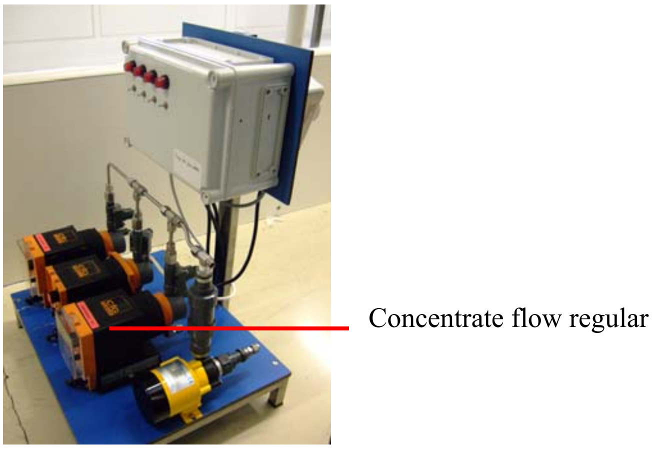
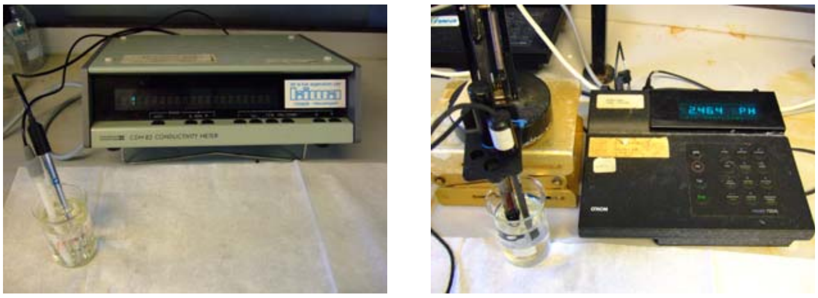


Figure 3.6 – Concentrate flow regular (dosing pump with a small pressure release valve)

pH and conductivity measurement

Since part of the NF installation is changed, the concentrate water does not flow through the location of the conductivity sensor mounted on the installation. Therefore, we can not read the concentrate conductivity directly from the PLC control plate. It has to be measured by hand. Consequently, every one hour, the pH and conductivity should be measured with the following meters.



(a) (b)

Figure 3.7 – a) pH meter; b) conductivity meter

3.3 Methodology

3.3.1 Preparatory steps

Before starting the experiment, some chemical preparation and setup adjustment is necessary.

Prepare the NaOH solution.

Weight 1200 mg of NaOH (pellet) with an electrical balance. Fill 10 liter of demi water in a plastic tank which is connected with a dosing pump. Put the weighted NaOH into the plastic tank and mix with a stirring stick sufficiently. Close the plastic tank.

Cautions: wear lab cloth, safety glasses and gloves.

Calibrate the concentrate flow regulator

Fill a 1 liter beaker with demi water. Recycle the demi water with a dosing pump with a small release valve. Collect the effluent in a 50 ml volumetric bottle. Record the time interval when the water level reaches 50 ml of the bottle. Divide the volume by the time interval to get the flow. Using this method, we can adjust the pump strike and pump frequency to obtain the required flow rate.

Regenerate the resin

If the resin is new, it does not need to be regenerated. But the resin we used is an old resin and needs to be cleaned and regenerated. We use HCl for regeneration of resin. The volume of HCl is 6-10 BV. The concentration is 2-5%. The regeneration velocity should not be too high and was set at 25 l/h for this experiment.

1) Prepare the HCl solution. Dilute the 25% HCl with demi water to 2%.
2) Fill the HCl solution in a 20 liter plastic tank.
3) With a dosing pump, dose the solution at a constant flow velocity to the resin (downward).
4) Put the end point of the effluent tube higher then the top of the resin. Then the waste solution can freely flow out from the ion exchange column and the effluent flow rate is equal to the influent flow rate.
5) Collect the waste solution with plastic tanks for waste treatment.
6) Repeat the same procedure for 3 or 4 times. The pH decreases to about 2.
7) Rinse with demi water till constant pH.

3.3.2 Experimental procedures

At the first step of the experiment, the tap water enters the sludge softening vessel. The influent flow depends on the feed flow requirement of NF installation. By a floating valve mounted on the vessel, the influent flow can be controlled at 40.4 l/h based on hydraulic level. If the hydraulic level in the vessel goes down, the floating valve will open to let more tap water come in to compensate the hydraulic level. The floating valve will not close until the required hydraulic level is reached. By this way, the influent flow rate can be controlled constantly.

At the same time 3 mmol/l of NaOH solution is dosed into the vessel continuously with 0.5 l/h of dosing rate. The pH can be raised to 10. The mixing of tap water and NaOH is generated by mechanical stirring with a stirrer and a recycling pump. The stirring speed is not adjustable. The mixing time in the sludge softening vessel is about 3 hours. The G value is about 480 s^{-1} and the GT value is about $5x10^6$. The water temperature is 13-14 ^{o}C.

Afterwards, the solution enters the bottom of the sedimentation tank and flows out from the top with an up-flow velocity of 0.3 m/h. The time for precipitation is 3 hours. Lots of precipitates will settle down on the bottom of the tank.

The experiment needs to be operated continuously overnight and there is no continuous feed of calcium carbonate as seed grains. But the sedimentation has a drawback that it has no automatic recycling system to pump the $CaCO_3$-sludge from the bottom of tank to the sludge softening vessel. During the night, the water in the sludge softening becomes transparent due to dilution of water, resulting in less turbidity not enough for silica removal. In order to prevent water to be transparent, only fast mixing is applied in the sludge softening vessel to disturb the precipitants on the bottom of the vessel (see Figure 3.8). Therefore, everyday this work needs to be done by hand two times at least.

Figure 3.8 – water in the sludge softening vessel

After the sedimentation tank, the solution goes into the ion exchange column with downwards flow direction. At night, without recycle of CaCO3 sediments from sedimentation tank to the sludge softening vessel, the CaCO3 concentration in the sludge softening vessel is diluted which will influence the efficiency of crystallization. Because the sedimentation process is not efficient enough, some precipitate is settling on the IEX. The IEX is cleaned daily.

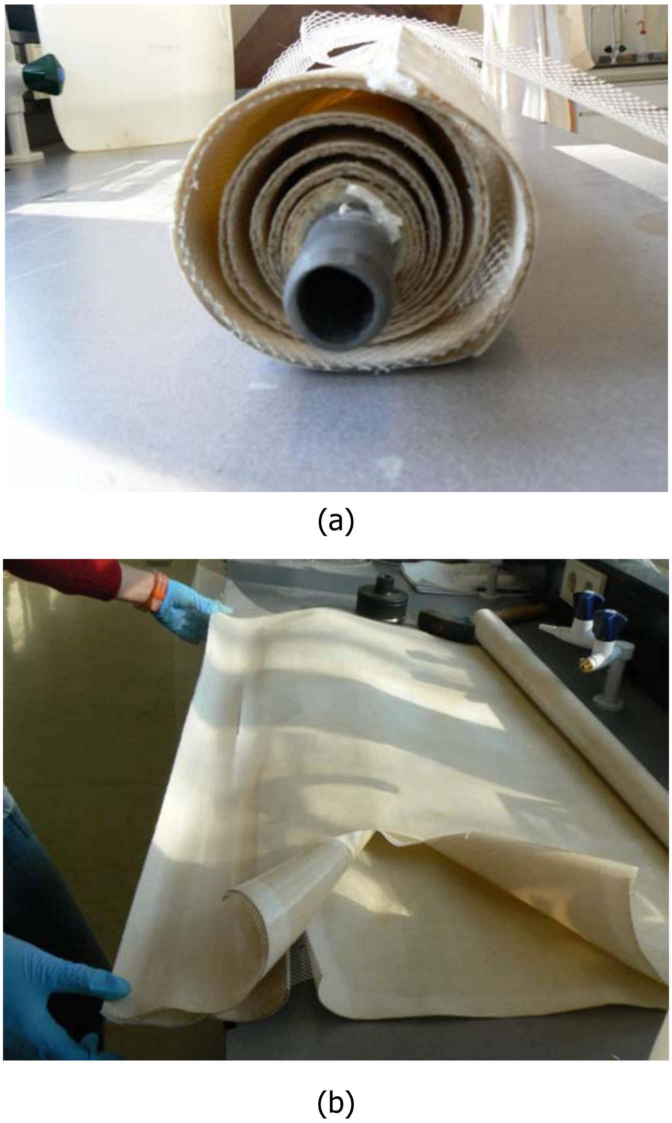
The effluent of ion exchange then fed into the NF installation by the feed pump. In order to guarantee the turbidity of the feed water is suitable for the membrane, a small cartridge filter (0.1μm) is added between ion exchange and NF installation.

At 99% of recovery, 40.4 l/h of feed flow will produce 40 l/h of permeate flow, resulting 0.4 l/h of concentrate flow. This is controlled by a feed pump and the concentrate flow control system. During the filtration process, part of the concentrate is recycled to the feed in order to reduce the influence of concentration polarization. The cross flow velocity in the bulk is around 300 l/h. During the experiment, the pressure, conductivity, flow rate at feed, permeate and concentrate and the temperature in the bulk flow are recorded every two hours in the day time. The pH during the whole process is monitored by hand every two hours. Also five samples (tap water, after sedimentation, after ion exchange, permeate, and concentrate) are taken everyday.

3.3.3 Autopsies of membrane

In order to study the deposited matters on the membrane surface, after 11-days experiment the membrane needs to be taken out of the set up for ICP-MS sample analysis. The procedure of autopsy is as follows:

1. Wear gloves and clean scissors
2. Cut the outer shell of the membrane, spread the membrane leaves carefully.
3. Cut the membrane samples at the inlet.
4. Measure the size of samples and record the location of the samples.
5. Separate the feed spacer from the membrane sheet and put all the samples in the sample utensils separately. Two samples in total: feed spacer from the inlet, membrane sheet from the inlet.


(a)

(b)

Figure 3.9 – a) Side view of the opened membrane; b) the membrane spread

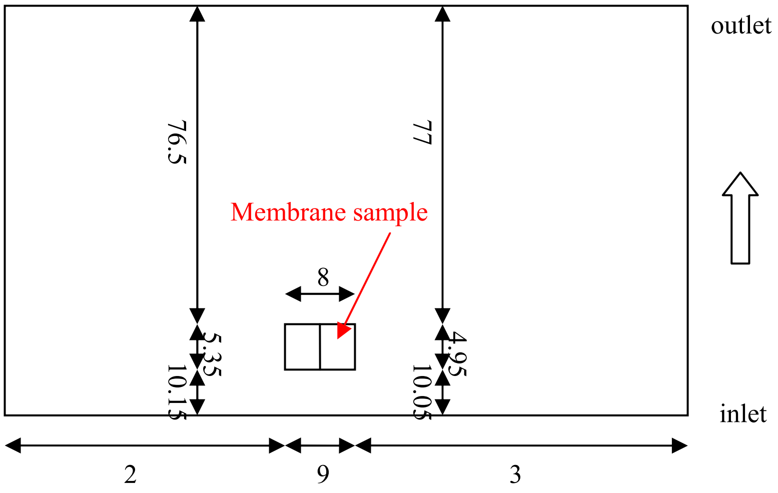


Figure 3.10 – Schematic description of the location and size of membrane sample

3.4 Results and discussion

3.4.1 Scaling components removal

As the theory illustrated, removal of scaling component before NF is the only efficient way to reach a very high recovery. From the following results to be presented, we can know the removal efficiency of bivalent ions and silica with the creative pretreatment process for an 11 days experiment.

1) Bivalent ions removal

Calcium

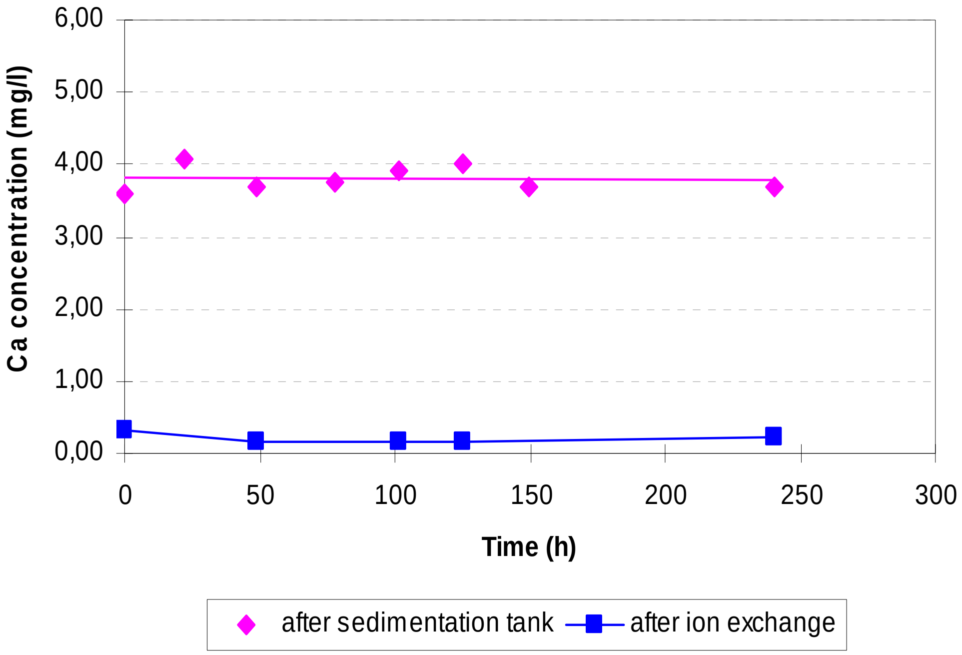


Figure 3.11 – calcium concentration after sedimentation and after ion exchange

Figure 3.11 shows a stable calcium concentration after sedimentation process and after ion exchange respectively during the 11-day operation. The calcium concentration is always kept at 0.1 mmol/l after sedimentation. According to the calcium concentration in tap water (75 mg/l, measured at 23/03/2007 at Kiwa Water Research), we can calculated that the calcium removal efficiency with sludge softening and sedimentation is very high. About 95% of calcium is removed. The flat trend line also shows a stable performance of this combination process during 11-day of continuously operation.

From Figure 3.11, we find that the calcium concentration decreases to very low level after ion exchange. The removal efficiency is more than 90%. Almost all the remaining calcium is removed by the weak acid cation exchange. During the 11 days, the product is always less than 0.5 mg/l without concentration breakthrough and without the need of regeneration. The low concentration is safe enough for nanofiltration system.

Magnesium

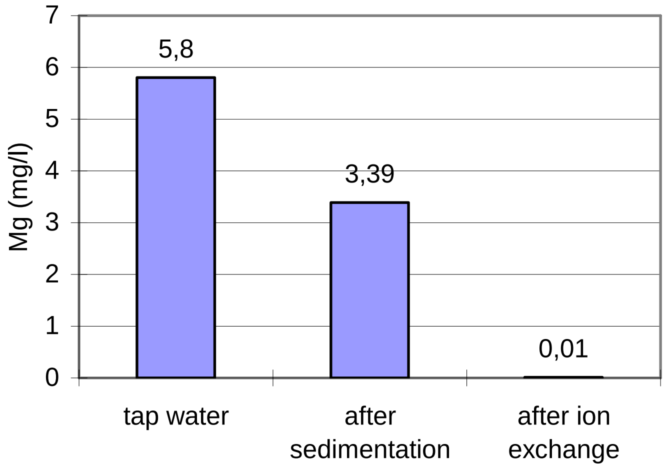


Figure 3.12 – Magnesium concentration decreases after pretreatment process

Figure 3.12 shows an obvious decreasing tendency of magnesium concentration from tap through pretreatment process. In this figure, the magnesium concentration in the tap water is only 5.8 mg/l which is not high. After softening and sedimentation, it decreases to 3.39 mg/l. The amount of precipitated magnesium is about 2.41 mg/l. Although sludge softening and sedimentation can not remove all the magnesium, almost all the remaining magnesium can be removed by ion exchange. Figure 3.12 show that only 0.01 mg/l of magnesium is left after ion exchange. This low concentration will not bring risk of membrane scaling.

Barium

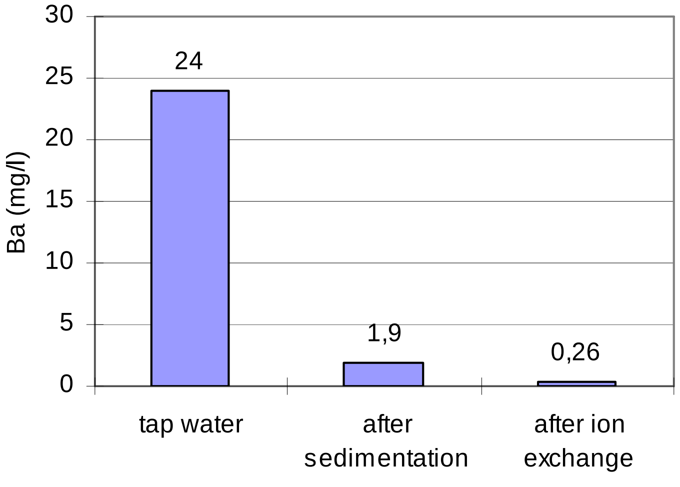


Figure 3.13 – Barium concentration decreases with pretreatment process

Figure 3.13 shows the removal of barium with sludge softening (combined with sedimentation) and ion exchange. The removal efficiency with sludge softening is about 92%. After ion exchange, only 0.26 mg/l of barium is left.

From the above experimental results, we can find that calcium, magnesium and barium can be removed completely with this setup. So this treatment concept can effectively prevent the scaling risk caused by these multivalent ions.

Silica removal

Table 3.5 – Si concentration

Si (mg/l)	tap water	after sedimentation	after IEX	concentrate	permeate
measured by Guo	9	8.6	8.3	63	7.6

Table 3.5 shows the silica concentration for the whole process in one day. In the pretreatment process, only 8% of silica is removed. It shows that the silica removal efficiency is not high by only raising pH to 10 with this tap water. However, from the report by S.Chen, T. Chang and C.Lin (2006), 80% of silica removal efficiency and 45% of magnesium removal can be obtained at pH of 11 by jar test simulation (in the raw water the silica (SiO_2) concentration is 21 mg/l and the magnesium concentration is 333.3 mg/l as $CaCO_3$).

The most important reason is that not enough $Mg(OH)_2$ is precipitating. To remove 1 mg silica 8.8 mg of magnesium is needed to precipitate [S.Chen, T. Chang and C.Lin. 2006]. However, in this experiment, the amount of precipitated magnesium with sludge softening is only about 2.41 mg/l. This is partly because of the shortage of magnesium source in tap water (5.8 mg/l of magnesium in tap water). In order to get more precipitation of magnesium, higher magnesium concentration in the tap water is required. This asks for an extra dosing of magnesium.

Another possible reason is that the mechanical mixing condition is not good. From S.Chen's report, rapid mixing was performed for 30 seconds at 100 rpm, whereas slow mixing conditions for floc formation were carried out for 15 min at 30 rpm. However, due to the limitation of our setup, only fast mixing is applied which might damage the formed flocculants and then influence the precipitation. Nevertheless, we can not conclude that the hydraulic condition is the real reason for this problem since the magnesium removal efficiency in our experiment is about 40%, same as the removal efficiency in S.Chen's research. The efficiency of the hydraulic condition is the same, only the amount of precipitated magnesium is not enough.

Although the operational condition of the pilot experiment limits the silica removal efficiency, this treatment concept still has a potential because it not only can remove most of bivalent ions, but also can remove silica if the operational condition is adjusted.

According to the process comparison in chapter 2, there is no other simple and cheaper process that can hold the two functions at the same time. From the above study, we found the bad removal efficiency of silica is probably due to the shortage of magnesium. It is worthwhile to do further research with the same tap water to define the reason. In order to simulate sludge softening process, jar test are used for this research. (see chapter 4).

Table 3.5 also tells us that the silica remove efficiency with IEX is bad. This is logical since at moderate pH (6~8) the dominant silicate species are uncharged silicate, $Si(OH)_4$, which can not be removed by the cation exchange resin. At high pH the dominated silicate species are the negative charged silicate which also can not be removed by the cation exchange resin. From the table 3.5, we found that the rejection of silica with this NF membrane is not very high. So the concentration at concentrate is moderate (63 mg/l) and does not exceed the scaling limit (120 mg/l).

3.4.2 NOM

Table 3.6 – NOM concentration [non-purgeable organic carbon (NPOC)]

	tap water	after sedimentation	after ion exchange	concentrate	permeate
2007-3-19				63	
2007-3-22			2.1	82	
2007-3-23	1.8	1.9	0.32	78	0.2
2007-3-24	1.9	1.9	1.3	73	0.21
2007-3-25			2	115	0.43
2007-3-30			2	88	

Table 3.6 shows the low concentration (less then 2 mg/l) of NOM in tap water and also in pretreated water. The cation exchange can not remove NOM. It is logical since the NOM is negative charge which can not be removed by the cation exchange. General speaking, after the pretreatment processes, there is still some NOM in the water and then enters NF installation. Figure 3.14 shows the color differences in tap water, pretreated water, concentrate water and permeate water. It is clear to see the light yellow color in the concentrate water which proves the concentrate water contains NOM compounds.

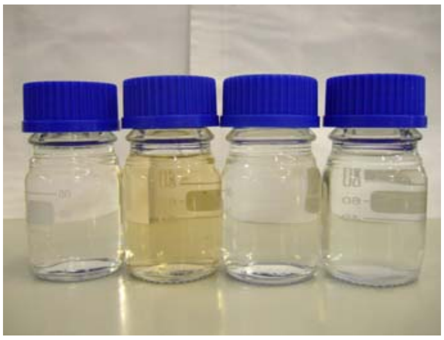


Figure 3.14 – color difference in permeate, concentrate, after ion exchange, after sedimentation (from left to right)

This pretreatment can not remove NOM completely. With the continuously feed and discharge of concentrate, most of the NOM will be retained by the nanofiltration membrane. NOM molecules have a risk of NOM fouling in the feed spacer of membrane depending on the diffusion-convection condition in the bulk flow. But NOM fouling will not cause further scaling in the membrane. So NOM removal is not very important in this experiment.

3.4.3 pH change tendency with ion exchange

During ion exchange process, pH change tendency is an important phenomenon, especial for H form resin. With different water composition and different resin, the change tendency of pH is not the same which will influence the regeneration rate with chemical. Also the pH range also influences the performance of nanofiltration membrane. That's why we take pH into account as follows.

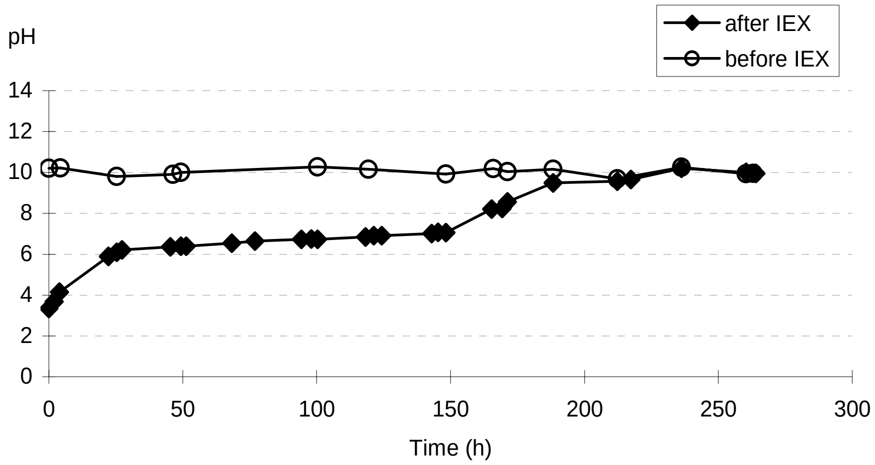


Figure 3.15 – pH before ion exchange (IEX) and after IEX for 11 days

Figure 3.15 presents the change tendency of the monitored pH before IEX and after IEX during the 11 days experiment. Before IEX, the pH is always kept at a stable level of 10. This high pH level is because of the dosing of NaOH in the sludge softening vessel. With a constant dosing rate and a stable flow rate, 3 mmol/l of NaOH can raise the pH up to 10.

After IEX, the pH is reduced to 3 at the beginning of the experiment. The decreasing pH is because the weak acid resin releases H^+ to solution with full capacity to exchange with cations from solution. The increasing hydrogen concentration results in decrease of pH. But pH does not decrease continuously. The low pH hinders the removal efficiency of the positive ions in solution (this also can be proved in chapter 5). Less H^+ is released resulting in quick increase of pH up to 6. At the pH level less than 6, CO_2 is used as pH buffer.

After one day, the pH is kept in the range between 6 and 7 for a long time (more than 100 hours) with a gently increasing tendency. During this period, CO_2 and HCO_3^- are used as pH buffer. The small increase is also caused by the trailing of releasing H^+, since the resin bed is gradually full of the exchanged cations, promoting the reaction close to the equilibrium. Compare to the first day, the capacity of releasing H^+ does not decrease fast due to the higher pH.

From 150 hour, pH starts to climb faster. Soon after, pH reaches the influent value of 10 and then keeps constant at that level. The quick rise of pH indicates that the equilibrium of the stoichiometric reaction between H^+ and cations in solution is already reached. This can be checked by the sodium analysis.

Table 3.7 – Sodium concentration

Sodium (mg/l)	**Tap water**	**Before IEX**	**After IEX**
2007-3-23 (around at 100 hours)	12	125	50
2007-3-30 (at the end)			100

From the above table, we can see during the stable phase of pH, nearly half of sodium is removed with IEX. But at the end, almost no sodium is exchanged. It means the exchange of sodium and hydrogen stopped. In the similar way, calcium as well as other cations in solution can not be exchanged with hydrogen anymore. However, according to the previous results (see Figure 3.11), we know that the calcium can be removed efficiently during the whole 11-day operation. That means the exchange capacity of the resin is still enough for Ca. After the pH breakthrough is reached, calcium will not exchange with H^+ but with Na^+ because most of the exchange places on the resin are used by Na^+. The biggest possible positive ion is sodium due to its high dosage in the previous steps and the low selectivity of sodium by the resin.

Therefore, from the above study we can conclude that the cation exchange can reduce pH and remove Ca, Mg and Ba effectively.

3.4.4 Performance of NF membrane at 99% recovery

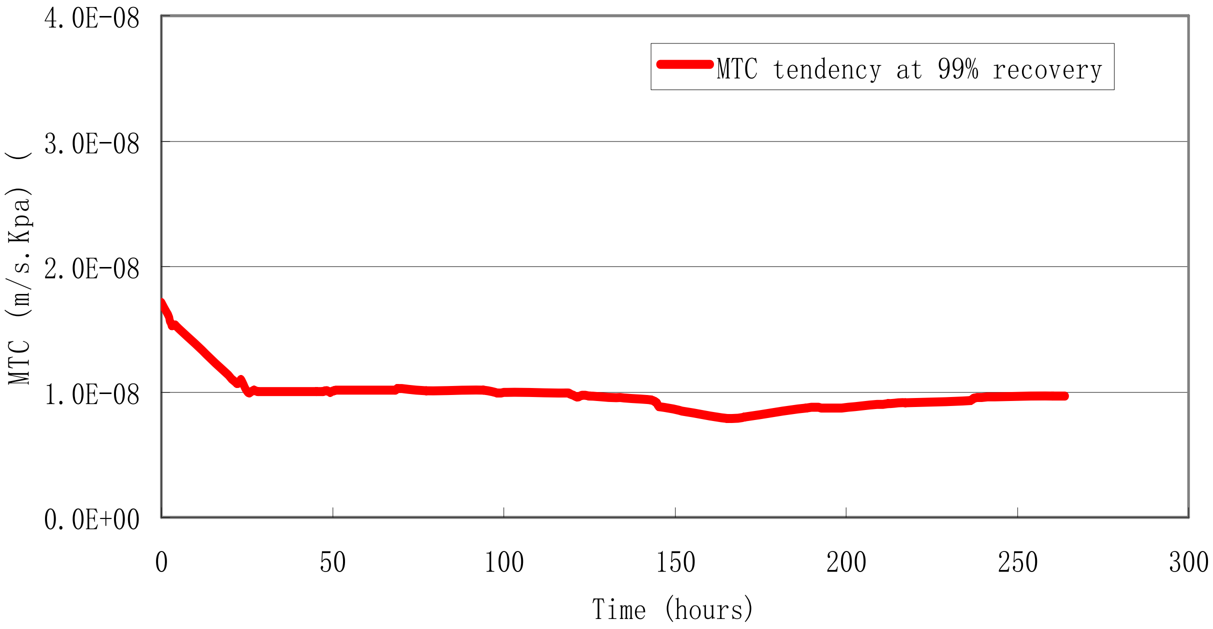


Figure 3.16– MTC with time for an 11 days experiment

From Figure 3.16, we can see a rather flat line during 11 days except for a short-term decrease at the beginning and a drop in the middle. General speaking, a constant MTC value at $1x10^{-8}$ can be obtained for about ten days and no scaling (continuous decreasing of MTC) occurs during this period. With this feed water a good performance of nanofiltration at 99% of recovery can be realized at least for 10 days. Only a quick drop at the beginning and a small falling at 160 hours (after 8 days) are found. Both of the two decreases happened in a short time and didn't develop further. Consequently they are not caused by scaling. The explanation for the two decreases is given as below.

The decrease of MTC at the first day might because of the NOM fouling in the feed spacer. Because of the very small pores of NF membranes (compact membrane at the beginning), surface fouling is the dominate fouling mechanism in nanofiltration at the initial stage of fouling. The fouling process is controlled by the interactions between the foulant and the clean membrane [Li Q. and Elimelech M., 2004.]. NOM, such as humic acid, is the major organic foulant in natural water. The concentration of NOM in the feed water is about 1 or 2 mg/l. In concentrate, the concentration of NOM is 78 mg/l which is rather high. During the beginning of the experiment, the membrane surface is clean. Therefore, the NOM accumulation on the clean feed spacer might cause initial surface fouling and consequently decrease of MTC.

The slight decrease of MTC at the middle stage of the experiment is probably the result of the particle fouling of the feed spacer. This can be seen from the Figure 3.17. During the first seven days, the pressure drop between feed and concentrate is constant indicating no particle fouling in the feed spacer. At the 170 hours, the pressure difference has a small jump, but it does not continuously increase. Therefore, the small drop of MTC after seven days does not mean the occurrence of scaling. The presence of particle fouling might be caused by the less aggressive environment (high pH) in IEX after seven days, which can not dissolve the carryover coming from the sedimentation tank.

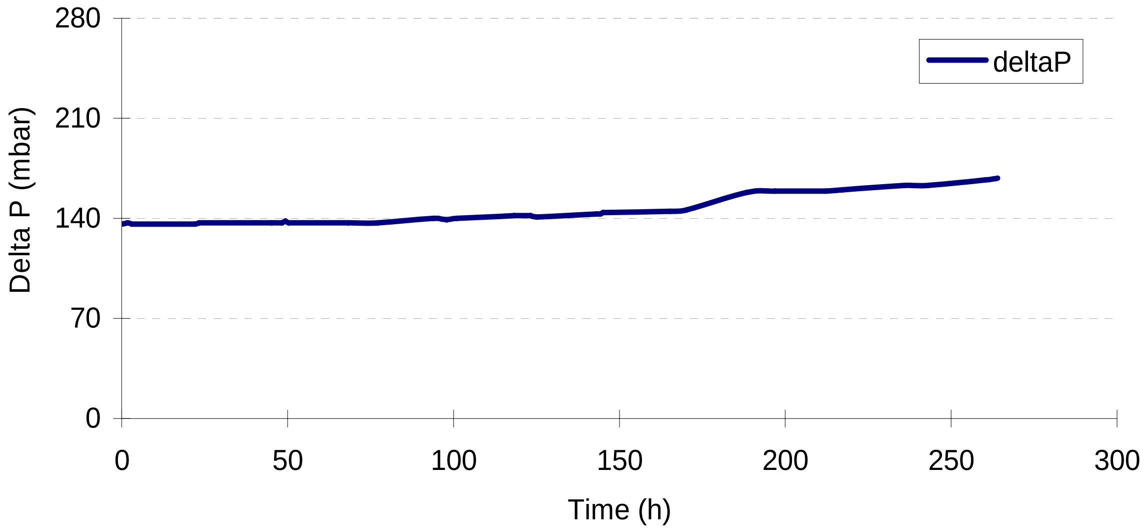


Figure 3.17 – Pressure drop change tendency with time

From the above study, we can conclude that this treatment concept can reach 99% recovery at least for 11 days without scaling. The decrease of MTC at the beginning of the experiment might be caused by the NOM fouling and the small drop of MTC after seven days might be due to the particle fouling on the feed spacer. Both of the two temporary decreases do not lead to continuous decline of MTC, which indicates no scaling.

3.4.5 Chemical analysis

1) Chemical analysis for water sample

Table 3.8 – Water quality at five sample locations in one day (unit: mg/l)

2007-3-23	tap water	after sedimentation	after ion exchange	concentrate	permeate	Rejection rate	Recovery
NPOC	1.8	1.9	0.32	78	0.2	38%	99%
Cl^-	9.5	8.5	7	230	5.5	21%	99%
SO_4^{2-}	0.13	0.07	0.03	4.2	0.03	≈ 0%	
PO_4^{3-}	0.03	0.004	0.002	0.13	0.003	≈ 0%	
Fe	0.14	0.14	<0.1	0.34	<0.1	-	
Mn	0.0031	<0.003	<0.003	0.018	<0.003	-	
Ca^{2+}	75	3.77	0.06	2.3	0.03	50%	99%
Mg^{2+}	5.8	3.39	0.01	0.23	0.01	-	
Na^+	12	125	50	1600	28	44%	99%
K^+	1	1.1	<0.9	10	<0.9	-	
Ba^{2+}	0.024	0.0019	0.00026	0.0022	0.00023	12%	99%
Si	9	8.6	8.3	63	7.6	8%	99%

Table 3.8 shows the water quality at different steps in one day. An efficient pretreatment process is shown as the result of the removal of multivalent ions. Only the silica removal needs to be improved by additional lab research. But the retention of silica by this membrane is low (8%). Although the silica removal is not efficient in the pretreatment with this setup and this water, it didn't raise the risk of scaling. The low retention is the reason that we didn't get silica scaling. If the rejection was 100%, the concentration at the feed site should be 100 times the concentration after ion exchange.

Mass balance:

$$\begin{cases} C_f \cdot Q_f = C_c \cdot Q_c + C_p \cdot Q_p \\ Q_f = Q_c + Q_p \end{cases}$$

$$C_f \cdot Q_f = C_c \cdot 0.01 \cdot Q_f + C_p \cdot 0.99 \cdot Q_f$$

So, $C_c = 100 \cdot C_f$

But actually the rejection by this NF membrane can not reach 100% for each component. We can use mass balance to check the actual recovery and retention rate for each component (See Table 3.8). For Fe, Mn and K, there are no detail data for the calculation.

The good performance of nanofiltration can produce the permeate water with good quality in which mainly sodium (28 mg/l) is left inside. The other dissolved compounds from the tap water are retained in the concentrate and just results in high salinity and high density due to the very high recovery of 99%. At the end, the water content is evaporated with evaporation and only salt is left which can be applied for other industries.

2) Chemical analysis for membrane sample

Table 3.9 – Results of chemical analysis for membrane sample

	membrane sheet		feed spacer			membrane sheet		feed spacer	
	(mg/l)*	(μg/cm^2)	(mg/l)*	(μg/cm^2)		(mg/l)*	(μg/cm^2)	(mg/l)*	(μg/cm^2)
Li	0.01	0.01	0	0	Cr	0.01	0.02	0	0.01
B	0.01	0.01	0	0	Mn	0.03	0.06	0.01	0.03
Na	7.29	14.59	0.52	1.04	Fe	14.03	28.06	3.51	7.02
Mg	0.11	0.22	0.02	0.04	Ni	0.02	0.03	0.01	0.01
Al	1.58	3.16	0.07	0.15	Cu	0.07	0.15	0.02	0.03
Si	5.25	10.5	0.33	0.67	Zn	0.17	0.33	0.02	0.03
K	0.59	1.18	0.22	0.43	Sn	0	0.01	0	0
Ca	1.43	2.87	0.26	0.52	Sb	0.11	0.22	0	0
Sc	0	0.01	0	0	Ba	0	0.01	0	0
Ti	0.01	0.01	0	0	I	0	0	0.01	0.02

Notes: The concentration (mg/l) with a * is from the analysis process. First those components need to be taken out of the membrane and dissolved in demi water before analysis. And then according to the concentration of water sample and the area of the membrane sample, the mass per each area unit of the membrane can be calculated.

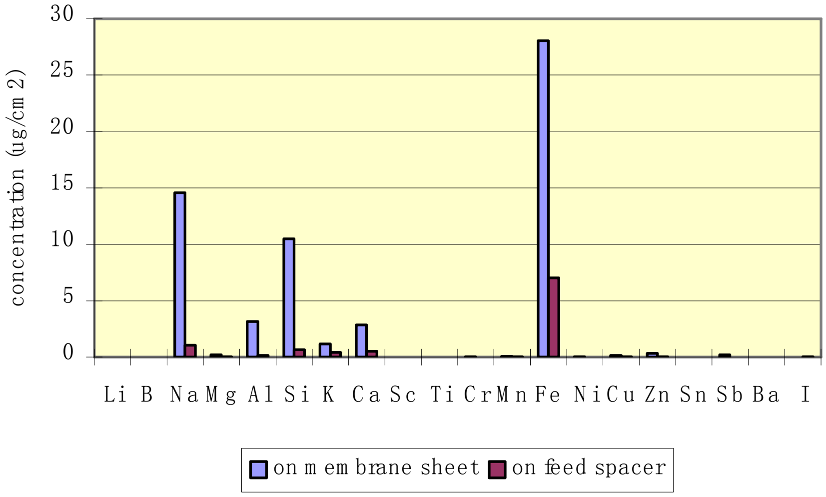


Figure 3.18 – Results of chemical analysis for membrane sample

Through membrane autopsy, two membrane samples are taken for ICP-MS analysis. One sample is membrane sheet, the other one is feed spacer. In total, 69 inorganic compounds are measured. Only more than 10 compounds are found in the feed spacer and the membrane sheet.

Membrane sheet

According to mass balance, the big amount of sodium (about 14.59 μg/cm^2 in the membrane sheet) is mainly caused by the high concentration in the feed water. The sodium concentration is 50 mg/l in the feed water, 1600 mg/l in the concentrate and 28 mg/l in the permeate. More than 15 μg/cm^2 of sodium might be retained in the membrane after 11-day experiment at 99% recovery. The silica concentration in the membrane sheet also can be checked by the mass balance. More than 10 μg/cm^2 of silica can be retained in the membrane after 11-day experiment at 99% recovery.

From the Table 3.9 and the Figure 3.18, we also found that the concentration of iron in the membrane is high (14 mg/l). In theory, we also can use mass balance to check the iron concentration. But here, we can not clearly define the reason for the high concentration of iron due to the shortage of accurate concentration in the feed water and in the permeate. However, if the retention rate of iron by the membrane is supposed to be very high, the low concentration (0.34 mg/l) in the concentrate can indicate that some iron is retained in the membrane sheet and does not go out with concentrate stream. So the high concentration of iron is probably due to the high retention rate of iron by the membrane even if the concentration in the feed water is very low (<0.1 mg/l).

The concentration of calcium, magnesium and barium is rather low which also proves that no scaling caused by the bivalent ions occurs during the experiment. The other compounds can be neglected because their concentration is almost zero.

Feed spacer

Compared to the membrane sheet, the amount of components on the feed spacer is rather less. The only component in the feed spacer is Fe. It probably means that this is the only serious foulant.

3.4.6 Cost analysis

The water price in the Netherlands is about 1~1.5 euro/m^3. The cost for drinking water treatment is about 0.32 ~ 0.62 €/m^3. The cost estimation for this treatment concept from Kiwa Water Research is presented as follows. Not only the investments, depreciation costs, operation costs, but also the costs for residual discharge and further treatment is considered in this section.

Table 3.10 - Cost calculation for the capacity of 10 million m^3 per year

Investments (€)	**7.275.100**
- Softening	2.375.000
- Chemical storage	171.100
- Ion exchange	1.003.200
- 1^e tree NF	3.378.200
- 2^e tree NF	347.500
Depreciation costs (€/year)	**752.900**
Operating cotsts (€/year)	**1.554.800**
- Energy	572.300
- Chemicals	686.700
- Maintanance	158.300
- Media	137.500
Total yaerly costs (€/year)	**2.307.700**
Totale costs (€/m^3)	**0,231**

Table 3.11 - Estimation of the discharge of the salt residuals

Total costs without residual discharge (€/m^3)	0,231
Amount residual volume (m^3)	0,015
Costs for residual evaporation (5 euro/m^3)	0,075
Total costs with residual discharge (€/m^3)	0,306

The cost for discharge of the residuals and the cost for evaporation should also be concluded in the cost analysis. Due to the use of sludge softening before ion exchange, this concept only produce spent regenerant (0.5%) from ion exchange. The volume of spent regenerant is low because the IEX is only loaded with the remaining multivalent ions from the softening. With the high recovery of 99%, only 1% of feed water is produced as concentrate. So the cost for residual disposal is not very high.

3.5 Conclusions and recommendations

3.5.1 Conclusions

- High pH sludge softening can remove most of calcium, magnesium and barium. The remaining bivalent ions can be removed completely by ion exchange. So the pretreatment process can efficiently remove the scaling components, like calcium, magnesium and barium.

- The low removal efficiency of silica with sludge softening for this tap water is probably due to the shortage of magnesium.

- The cation exchange not only can efficiently remove calcium, magnesiu and barium, but also can reduce pH which is better for dissolving the carryover coming from the sedimentation tank. When the resin has no capacity of releasing H^+, those bivalent ions still can be removed by the resin probably through the exchange with sodium.

- With the pretreatment processes including sludge softening, sedimentation, weak acid ion exchange in series, the recovery of nanofiltration membrane can reach 99% without scaling in 11-day pilot experiment.

- The modified concentrate flow regular system can successfully control the concentrate flow at a very low level without need of adjustment. For even higher recoveries, this setup also can handle.

3.5.2 Recommendations

- The pilot experiment needs to be operated for a longer period to observe the performance of nanofiltration membrane at 99% recovery. And then the final conclusion can be drawn for this treatment concept.

- Higher recovery (99.9%) also can be tested, but at higher recovery the osmotic pressure also increases requiring higher energy consumption. NOM fouling is easier to be formed resulting in lower flux. The membrane has a bigger risk to be scaled. The quality of permeate is becoming worse.

- A further research is needed to improve silica removal. The jar test experiment is used to simulate precipitation and sedimentation.

- An ion exchange model should be built up in order to predict the breakthrough of calcium concentration in a ternary system.

- For the real design of the sedimentation tank, a conical bottom and a recycling pumping system should be considered. They are used to settle the precipitation of calcium carbonate and pump it back to the sludge softening tank continuously.

4. Jar test for Si removal

The jar test experiment is a common laboratory procedure to simulate coagulation/flocculation/sedimentation with an adjustable mechanical stirring for chemical mixing. Here the jar test is used to investigate sludge softening. The experiment has two phases: precipitation with an adjustable steering rate and settling without steering.

4.1 Experimental method

4.1.1 Jar test

The jar test apparatus consists of 6 jars filled with water. For each jar, there are four baffles on the wall of the vessel. These four baffles are necessary to get a certain shear rate with a certain steering rate.

Figure 4.1 –jar test apparatus

1.5 liter of tap water (from Kiwa) is used for each jar test. This tap water contains 5.8 mg/l magnesium. The pH is about 7. 8. First, the pH of tap water is raised by dosing 3 mmol/l of NaOH. And then different amount of $MgCl_2.6H_2O$ is dosed into the tap water to increase the Mg concentration. Two tests have been done.

Test one

In this test a stirring speed of 100 rpm, a settling time of 5 minutes and a pH of 10 was used. The dosage of Mg is 0, 39, 79,158 and 394 grams respectively. The test was repeated with a pH of 10.5.

Test two

In test two, the stirring speed was 80 rpm for 60 seconds followed by a stirring speed of 30 rpm during 15 minutes. The dosage of Mg is same as the test one. The pH was kept constant at about 10.5.

(a) (b) (c) (d)

Figure 4.2 – Jar test procedure for test 2, a) fast mixing; b) slow stirring; c) sedimentation; d) after sedimentation

4.1.2 Si analysis

Sample preparation

After sedimentation, 10 ml sample at the 2-3 cm under the water surface needs to be taken from the beaker to plastic sample bottle by pipette. The sample was filtered with a 0.45 µm filter before analysis to decrease turbidity and to measure only dissolved Si. The sample temperature needs to be increased to 20-40^{o}C in the oven.

Analysis method

Si ions react with molybdate ions in acidic solution to form a yellow heteropoly acid, the concentration of which is determined photometrically by Spectroquant NOVA 60 (MERCK). The measuring wavelength is 410 nm. It has two measuring range, 0.5-50 mg/l Si and 5-500 mg/l Si.

Figure 4.3 - Spectroquant NOVA 60 (MERCK)

4.2 Results and discussion

4.2.1 Test one

Two jar tests were carried out with different pH and different magnesium concentrations but with the same hydraulic conditions. Their results are shown in figure 4.4

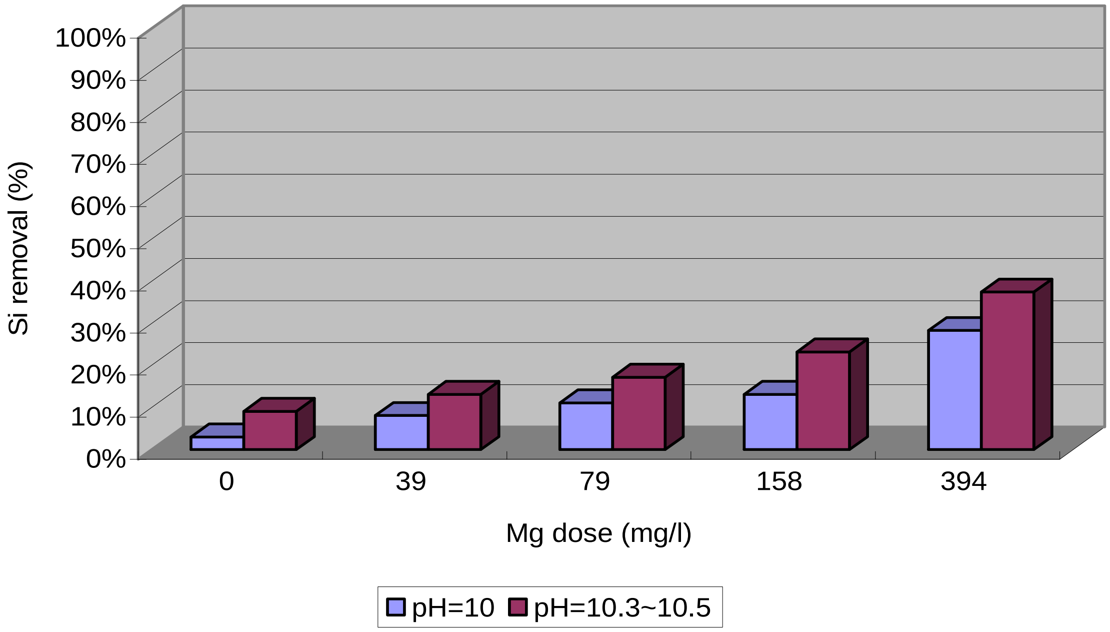


Figure 4.4 – relation of Si removal percentage and dosage of Mg influenced by pH

In the tap water, the magnesium concentration is 5.8 mg/l and the silica concentration is about 9 mg/l. According to Figure 4.4, it is clear to see that without dosage of magnesium, the Si removal efficiency is very low. The Si-removal without dosing of magnesium ions is less than 10%. The removal of Si is increased to 20% with a magnesium dosing of 158 mg/l. With the increasing magnesium concentration, the removal efficiency increases. The maximum removal efficiency only can reach 30% and 40%, otherwise lots of magnesium is needed resulting in high cost for chemicals.

T. Koo, et al. (2001) studied silica fouling and membrane cleaning of reverse osmosis membranes. They also found that increasing the concentration of calcium and magnesium also enhanced the polymerization of silica. According to S.Chen's study, high magnesium concentration is necessary for silica removal. In that experiment, the magnesium concentration in the raw water is 333.3 mg/l as $CaCO_3$ (about 80 mg/l Mg). In that case, about 45% of magnesium can be precipitated and the silica removal efficiency can reach 80% at most. That report shows that the silica removal efficiency can reach 60% at pH of 10 while at pH of around 11 it can reach 80%. For our experiment, however, only 20% of silica removal efficiency is obtained with the same amount of magnesium. The lower removal efficiency is partly because of the lower pH at around 10.

Figure 4.4 also shows that the removal efficiency at pH of 10.5 is higher than that at pH of 10. It means that higher pH is preferable to Si removal. This tendency also proves the result of other researchers [Rick Bond. 2006; S.Chen, T. Chang and C.Lin. 2006]. However in order to get a higher pH more chemicals are needed. Thus it is not cost effective to continuously use a high pH, but there can also be cost savings if the recovery can be increased further. So a total cost evaluation is necessary before the optimal pH can be concluded.

4.2.2 Test two

Additional test is added with different mixing method. This mixing method is designed according to the experiment done by S.Chen (2006).

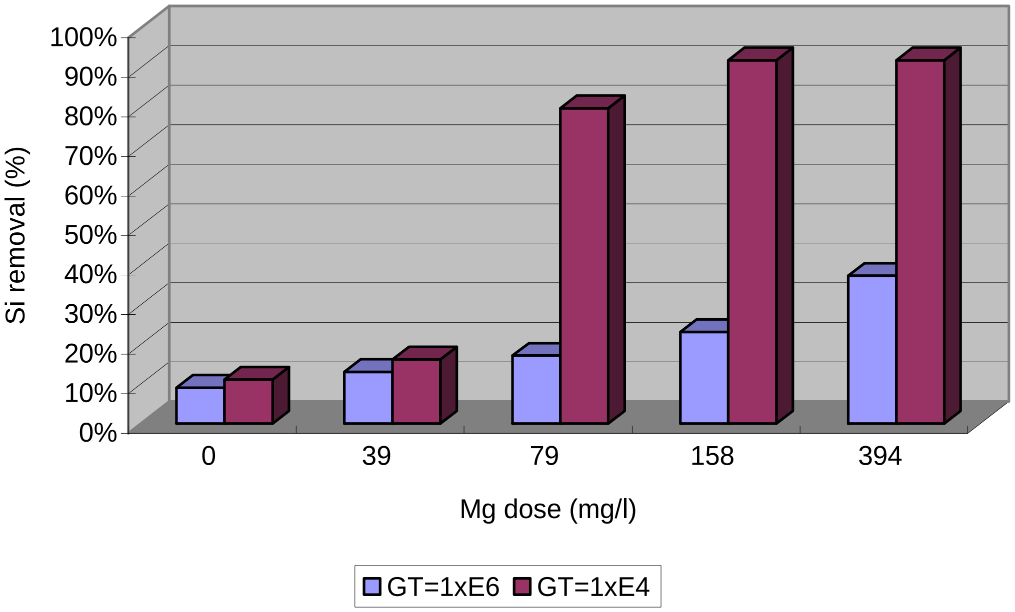


Figure 4.5 – relation of Si removal percentage and the dosage of Mg influenced by different hydraulic condition.

In Figure 4.5, the blue bar represents the Jar test at 100 rpm of stirring speed for 1 hour. The purple bar represents the jar test at 80 rpm of stirring speed for 60 second first and then at 30 rpm of stirring speed for 15 minutes. From Figure 4.5, we can see with the increase of the magnesium dosage the silica removal efficiency increased. With a magnesium dose of 79 mg/l the removal efficiency of Si is possible to reach 80%. This result is corresponding with the result of S.Chen's report.

From the figure 4.5, we found that the second mixing method has better silica removal efficiency compared to the first mixing method only with 100 rpm of stirring speed for 1 hour. But this is not likely caused by the G value (see appendix) since the measured silica is only the dissolved silica. Also, from the chapter 3, we have already known that the removal efficiency of magnesium with only fast mixing speed is enough good. So the first mixing method also can offer enough chance for the collision of particles (precipitates) and will not damage the formed flocculants.

The problem might be the shortage of magnesium. CO_3^{2-} is presented at high pH. With the first mixing method, there is enough time for the formation of $MgCO_3$. Some magnesium can be consumed by the CO_3^{2-}. But this explanation can not be determined yet since the concentration of $Mg(OH)_2$ and $MgCO_3$ is not analyzed.

According to the jar test experiment, we can make a conclusion that the high magnesium concentration is necessary for silica removal and the higher pH is preferable to silica removal. There is a balance between the chemical costs and the silica removal efficiency.

4.3 Cost estimation

According to the section of results and discussion, a certain magnesium concentration is necessary to remove silica. But higher dose rates will cost more money. Therefore, a rough cost estimation is presented here. With the dosage of 6.56 mmol/l to this tap water, 80% of silica can be removed. Therefore, we use this dosage for cost calculation.

Table 4.1 –Price of magnesium for per m^3 water

chemical	Dose	Dose (unit)	Costs	
	mg/l (Mg)	mg/l (Mg)	€/m^3 per unit dose	€/m^3
Magnesium chloride	80	1	0.0005~0.001	0.04~0.08

The cost for magnesium also depends on the influent water quality and the hydraulic condition. So in order to reach a high silica removal with minimum magnesium dosage, the design for the sludge softening reactor is very important.

4.4 Conclusions and recommendations

4.4.1 Conclusions

- The high magnesium concentration is necessary for silica removal. With the increase of magnesium concentration, the silica removal efficiency also increases. The dosage of magnesium also depends on the actual silica concentration and the magnesium concentration in the feed water.

- The higher pH is preferable to silica removal. The optimum pH value is about 10.5. Too high pH needs more chemical. Lower pH is not sufficient to remove silica.

4.4.2 Recommendations

- Since both $CaCO_3$ and $Mg(OH)_2$ can contribute to the silica removal, an extra jar test can be done with higher dosage of calcium carbonate. Calcium carbonate is reused as seed grains through a recycling system. Higher dosage will not cause cost problem. Maybe the higher calcium carbonate concentration can improve the silica removal.

- The precipitates of magnesium might contains $Mg(OH)_2$ or $MgCO_3$ or both of them. More $Mg(OH)_2$ is preferable to the silica removal. The composition of the precipitates needs to be investigated further.

5 Ternary Ion Exchange Model

5.1 Introduction

The modeling of an ion exchange process is similar to the modeling of an adsorption process in case of a simple binary system. For instance, if the IEX resin is in the sodium form, the exchange process of calcium can be modeled with the adsorption models. But for H-form resin in a multi-component system, the ion exchange process is, however, complex. When we build a model for a multi-component system, the ion equilibrium in a ternary system should also be considered.

The specific phenomena in our project are concluded as follows. Since we use H^{-}form weak acid resin for our project, the pH in the solution will decrease during experiment because the H^+ on the resin can enter the solution as a result of the by exchange with other cations in solution. The reaction of one ions pair will influence the reaction rate of other ions pair in a multi-component system. The relationship between them should hold electroneutrality balance. In order to simplify the practical system, ternary system including H^+, Ca^{2+} and Na^+ is investigated in this research.

The aim of the research is to use a mathematical model to simulate the concentration breakthrough curve in a ternary system including H^+, Ca^{2+} and Na^+ in a fixed bed with ion exchange resin. Therefore, this model has the function of replaying the history of concentration change profile and predicting the concentration change tendency.

Fundamental understating of the cations transport is particularly important to establish the basic equation for the model. Linear driving force model is applied in mass transfer. The concentration of one ion on resin (loading) depends on the concentration of other ions on resin, the equilibrium constants between them, and the total capacity of the resin.

5.2 Ion exchange equilibrium

When the resin releases the ions to the solution, the counter-ions in the solution can enter the matrix of resin. Generally, ion exchange in a binary ions system is considered as a simple stoichiometric reaction as shown in Equation 5.1. This reaction describes the transfer or removal of A^{n+} from a liquid phase to a solid phase.

$$z_b A^{z_a} + z_a \overline{B^{z_b}} \Leftrightarrow z_a B^{z_b} + z_b \overline{A^{z_a}} \qquad \text{[Eq. 5.1]}$$

In which,

A – A ion in water

$\overline{A}$ – A ion on resin

B – B ion in water

$\overline{B}$ – B ion on resin

z_a, z_b – valence of A and B

Various forms of equilibrium expressions may be used in expressing ion exchange equilibrium. Those forms include adsorption isotherm, separation factor, selectivity coefficient and thermodynamic equilibrium constant. Adsorption isotherm might express the exchange equilibrium for binary system. But for ternary system or multi-component system, the adsorption isotherm can not express all the phenomena. Separation factor does not consider the influence of valence of ions. Selectivity coefficient can provide the information of capacity of resin to the counter-ions of solution and it can be easily obtained directly from equilibrium experiment. Thermodynamic equilibrium constant also can give enough information for equilibrium expression, but this form is seldom used in practice because of the difficulties faced in determining the ionic activities. Replacing the activities with concentrations leads to the definition of the selectivity coefficient. Therefore, it is suitable to use selectivity coefficients to express the ion exchange equilibrium for the ternary system at conditions near the binary experimental conditions. Here the selectivity coefficient is called pseudo binary selectivity coefficient which has been suggested by many investigators during the past several decades.

1) Separation factor

Traditionally, the selectivity of a resin has been expressed by the separation factor. However, it does not explicitly reflect the effect of ionic valence.

$$\alpha_A^B = \frac{C_A \cdot \overline{C_B}}{\overline{C_A} \cdot C_B} \qquad \text{[Eq. 5.2]}$$

In which,

α_A^B - separation factor

C_A, C_B - concentration of A and B in solution

$\overline{C_A}, \overline{C_B}$ - concentration of A and B on resin

2) Selectivity coefficient

Instead, selectivity coefficient S can be used for the equilibrium expression according to the law of mass action [cf. Pieroni and Dranoff, 1963]. This equation provides a means of measuring the selectivity or capacity of a specific resin for a given ion. The general equation can be made to calculate the resin's selectivity of cation B over A in equilibrium system. The selectivity coefficient can be calculated directly from equilibrium experiments.

$$S_A^B = \frac{C_A^{z_b} \cdot \overline{C_B}^{z_a}}{\overline{C_A}^{z_b} \cdot C_B^{z_a}} \qquad \text{[Eq. 5.3]}$$

In which,

S_A^B – selectivity coefficient

z_a, z_b – valence of A and B

3) Thermodynamic equilibrium constant

Thermodynamic equilibrium constant depends on temperature according to the thermodynamic relationship ($\Delta G^o = -RT\ln\left(K_A^B\right)$) if the activities are properly defined. At equilibrium,

$$K_A^B = \left[\frac{\overline{a_B}}{a_B}\right]^{z_a}\left[\frac{a_A}{\overline{a_A}}\right]^{z_b} \qquad \text{[Eq. 5.4]}$$

In which,

K_A^B – thermodynamic equilibrium constant

a_A , a_B – ionic activity of A and B in solution

$\overline{a_A}$, $\overline{a_B}$ – ionic activity of A and B on resin

z_a, z_b – valence of A and B

However, this form is seldom used in practice because of the difficulties of determining ionic activities. Ionic concentration is easier to be measured. Therefore, selectivity coefficient are used in this study for ion exchange equilibrium expression instead of thermodynamic equilibrium constant.

4) Equilibrium constant (Pseudo-binary selectivity coefficient)

Klein and co-worker have suggested the use of pseudo-binary selectivity coefficients which are determined from experimental data for the analysis of multi-component ion exchange. Lots of investigators [Dranoff and Lapidus, 1957, Manning and Melshelmer, 1983] have suggested a modified and simpler version of these pseudo-binary selectivity coefficients, assuming that other ions have no significant effect on the equilibrium between the ion pair to be studied. In other words, selectivity coefficients determined from ternary system or binary experimental data are identical. Hence, these coefficients from binary experiment can be used to predict the ternary-system ion exchange equilibrium at conditions near the experimental conditions. For this study, pseudo-binary selectivity coefficients are used as the equilibrium constants.

5.3 Electroneutrality balance

No matter how many ions to be exchanged or how different selectivity each ion has, the total capacity of resin should hold the electroneutrality balance.

For H^+ form weak acid resin, H^+ is released from the resin and decreases the pH of solution. At the same time, counter-ion like sodium in solution changes with H^+ in the resin matrix. After the equilibrium of this reaction is reached, the exchange between sodium and H^+ stops and this resin can not remove sodium any more. But the total capacity of the resin is still the same. After regeneration with acid, the locations occupied by sodium in resin will be replaced by H^+.

For binary system (Na^+ and H^+):

stoichiometric reaction: $\mathrm{Na^+ + \overline{H^+} \Leftrightarrow H^+ + \overline{Na^+}}$

Electroneutrality balance: $\overline{C_{Na}} + \overline{C_H} = Q_{total}$

In which,

Q_{total} – total capacity of resin (eq/l)

After the equilibrium with sodium is reached, the resin still has capability to exchange calcium by the exchanged sodium,. The process of calcium removal will not stop until the equilibrium between Ca-Na is achieved. The reaction process and the electroneutrality balance for both of tenary system are shown below. For multi-component system, the theory is the same as the ternary system but more reactions are involved.

For ternary system (Ca^{2+}, Na+ and H^+):

stoichiometric reaction: $\mathrm{Na^+ + \overline{H^+} \Leftrightarrow H^+ + \overline{Na^+}}$;

$$\mathrm{Ca^{2+} + 2\overline{H^+} \Leftrightarrow 2H^+ + \overline{Ca^{2+}}} ;$$

$$\mathrm{Ca^{2+} + 2\overline{Na^+} \Leftrightarrow 2Na^+ + \overline{Ca^{2+}}}$$

Electroneutrality balance: $2\overline{C_{Ca}} + \overline{C_{Na}} + \overline{C_H} = Q_{total}$

5.4 Building up of the model

5.4.1 Basic equations

The aim of the ion exchange model is to simulate changes in the concentration of ions as they move through the resin bed continuously. A popular way to model the water quality change profile through a column is the application of transportation model. The flow direction is downward and the fixed bed is considered here. Four mechanisms during transportation are to be considered, 1) transfer of ions to solid phase (resin); 2) flow of solution containing ions through the column (advection and dispersion); 3) decay in water phase during transport (neglected); 3) Mass balance between water phase and solid phase. Swelling of resin can be neglected in this model in order to simplify the model concept.

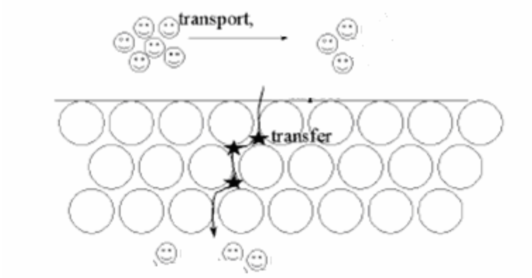


Figure 5.1 – Mechanisms in treatment process [source: L.C.Rietweld 2005]

Based on mass balance, the above-mentioned mechanisms are added to obtain the total change of concentration with time. Hence, the basic equation for ion exchange column is as follows:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial y^2} - u\frac{\partial C}{\partial y} - f_1(C) - \rho_r \frac{\partial q}{\partial t} \qquad \text{[Eq. 5.5]}$$

In which,

C - concentration of ions in water phase (mmol/l)

$u\frac{\partial C}{\partial y}$ - advection term due to the movement of the water

$D_x \frac{\partial^2 C}{\partial y^2}$ - dispersion term due to the turbulence of the water and velocity shear

$f_1(C)$ - decay term

$\rho_r \frac{\partial q}{\partial t}$ - transfer term

q - loading on resin (Mass of exchanged ions/Mass of resin)

ρ_r - wet density of resin in natural state (kg/m^3)

u - velocity of water through column (m/s)

5.4.2 Simplification of basic equation

All the cations are conservative during transport. Hence, we can neglect the decay effect. In order to simplify the model, the dispersion term also can be neglected assuming the flow is ideal plug flow and there is no turbulence or diffusion/dispersion. Then the basic equation is simplified as follows:

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial y} - \rho_r \frac{\partial q}{\partial t} = -u\frac{\partial C}{\partial y} - \frac{\partial \overline{C}}{\partial t} \qquad \text{[Eq.5.6]}$$

In order to define the transfer term, we assume a linear driving force model [Peel and Benedek, 1981] (LDF-model). This gives us a relation between the speed of mass transfer and the LDF-constant K. LDF-model is the popular method to simplify the complex phenomena like film dispersion, mass adsorption, etc. The LDF-constant can be obtained through equilibrium batch experiment [S.G.J.Heijman, A.M.van Paassen, 1999].

$$\frac{\partial q}{\partial t} = k\left(q_e - q\right) \qquad \text{[Eq.5.7]}$$

In which,

q_e – loading in resin at equilibrium (Mass of exchanged ions/Mass of resin)

q - actual (accumulated) loading in resin ((Mass of exchanged ions/Mass of resin)

Finally, the equation [Eq.6] can be simplified as:

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial y} - k\left(\overline{C_e} - \overline{C}\right) \qquad \text{[Eq.5.8]}$$

In which,

$\overline{C}$ - actual (accumulated) concentration of the exchanged ion in resin (mmol/l)

$\overline{C_e}$ - concentration of the exchanged ion in resin phase at equilibrium (mmol/l)

For each ion in this ternary system, the change of concentration in time can be expressed as follows:

$$\begin{cases} \dfrac{\partial C_{Ca}}{\partial t} = -u\dfrac{\partial C_{Ca}}{\partial y} - k\left(\overline{Ce_{Ca}} - \overline{C_{Ca}}\right) & \text{[Eq.5.9]} \\[2ex] \dfrac{\partial C_{Na}}{\partial t} = -u\dfrac{\partial C_{Na}}{\partial y} - k\left(\overline{Ce_{Na}} - \overline{C_{Na}}\right) & \text{[Eq.5.10]} \\[2ex] \dfrac{\partial C_{H}}{\partial t} = -u\dfrac{\partial C_{H}}{\partial y} - k\left(\overline{Ce_{H}} - \overline{C_{H}}\right) & \text{[Eq.5.11]} \end{cases}$$

The equlibrium concentration on resin can be calculated according to the mean value of equilibrium constant obtained from batch equilibrium experiment of binary system and the actual concentration in solution. The equilibrium constant is given as follows:

$$K_{Ca}^{H} = \frac{{C_H}^2}{\overline{C_H}^2} \cdot \frac{\overline{C_{Ca}}}{C_{Ca}} \qquad \text{[Eq.5.12]}$$

$$K_{Na}^{H} = \frac{C_H}{\overline{C_H}} \cdot \frac{\overline{C_{Na}}}{C_{Na}} \qquad \text{[Eq.5.13]}$$

$$K_{Ca}^{Na} = \frac{{C_{Na}}^2}{\overline{C_{Na}}^2} \cdot \frac{\overline{C_{Ca}}}{C_{Ca}} = \frac{K_{Ca}^{H}}{\left(K_{Na}^{H}\right)^2} \qquad \text{[Eq.5.14]}$$

The equation of concentration on resin can be obtained by combing [Eq.5.12], [Eq.5.13], [Eq.5.14] and the following electroneutrality restriction.

$$2 \cdot \overline{C_{Ca}} + \overline{C_{Na}} + \overline{C_H} = Q$$

Therefore, $\overline{C_{Ca}}$, $\overline{C_{Na}}$ and $\overline{C_H}$ are expressed by following equations [Lis Marcussen 1986]. And then substitute them back to [Eq.5.9], [Eq.5.10], [Eq.5.11].

$$\overline{C_{Ca}} = \frac{Q}{2} + \frac{\left[\sqrt{K_{Ca}^{H}} \cdot C_H + \sqrt{K_{Ca}^{Na}} \cdot C_{Na}\right]^2}{8 \cdot C_{Ca}} \cdot \left[1 - \sqrt{1 + \frac{8 \cdot Q \cdot C_{Ca}}{\left[\sqrt{K_{Ca}^{H}} \cdot C_H + \sqrt{K_{Ca}^{Na}} \cdot C_{Na}\right]^2}}\right] \qquad \text{[Eq.5.15]}$$

$$\overline{C_{Na}} = \frac{-C_{Na} \cdot \left(C_H \cdot K_{Na}^{H} + C_{Na}\right)}{4\left(\dfrac{C_{Ca}}{K_{Ca}^{Na}}\right)} \cdot \left[1 - \sqrt{1 + \frac{8 \cdot Q \cdot \dfrac{C_{Ca}}{K_{Ca}^{Na}}}{C_H \cdot K_{Na}^{H} + C_{Na}}}\right] \qquad \text{[Eq.5.16]}$$

$$\overline{C_H} = \frac{-C_H \cdot \left(C_{Na} \cdot K_{Na}^{H} + C_H\right)}{4\left(\dfrac{C_{Ca}}{K_{Ca}^{H}}\right)} \cdot \left[1 - \sqrt{1 + \frac{8 \cdot Q \cdot \dfrac{C_{Ca}}{K_{Ca}^{H}}}{C_{Na} \cdot K_{Na}^{H} + C_H}}\right] \qquad \text{[Eq.5.17]}$$

The accumulated concentration on resin can be calculated based on the granule activated carbon model of Stimela. The breakthrough of a compound in the effluent of a GAC column is divided into for instance 5 layers. In the similar way, the resin bed is divided into several layers. The effluent concentration of the top layer is calculated as the influent concentration for the next layer. The ions will not accumulate in the resin until the equilibrium is reached.

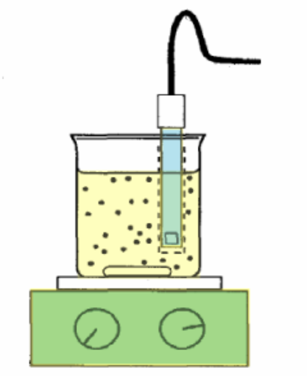
5.4 Experiment

5.4.1 Batch experiment

This experiment aims to determine the equilibrium constant of each ion pair in binary system. Several batch experiments have been done with different amount of resin.

1) Procedure of batch experiment

K(H,Ca)



In order to obtain K(H,Ca) from the batch experiment, the binary system including H and Ca should be established. First, prepare a solution consisting of calcium ion by dosing calcium chloride into 1.5 liter of demi water in a beaker. Take 50ml of sample to measure the initial concentration of calcium. And then put the H-form resin in the same beaker. Mix the solution with magnetite stirrer. Soon after, the pH of solution decreases to around 3 since the resin releases H^+. In order to raise the pH up to 6 or 7, titrate 4g/l of $Ca(OH)_2$ to the solution. If pH starts to below 6, titrate the $Ca(OH)_2$ and record the amount of titration. After 5 hours, the equilibrium can be reached. So the experiment is ended after 6 hours. When the equilibrium is achieved, the pH does not change and keeps at 6 or 7. There is no need for titration of $Ca(OH)_2$. And then take 50 ml of sample to measure the equilibrium concentration of calcium.

Repeat the same experiment with the same initial calcium concentration but with different amount of resin. The resin is weighted by electronic balance before the batch experiment. Since the resin is a little bit wet, some water is inevitable to be included in the weight of the resin.

K(H,Na)

The method is same as that for K(H,Ca). The only difference is that the chemical is different. This solution is made by dosing sodium chloride and H form resin. The pH is controlled at 6 or 7 by dosing 15 g/l NaOH in order to avoid introducing the third kind of ion in the binary system.

K(Na,Ca)

First the H form resin needs to be changed to be Na form resin by regenerating the resin with NaCl in the column apparatus. After the pH of effluent keeps constant, rinse the resin bed with demi water till a constant pH.

And then start the batch experiment. First prepare a solution consisting of calcium ion by dosing calcium chloride in a beaker. Take 50 ml of sample to measure the initial concentration of calcium. And then put the Na form resin in the solution. Mix the solution with magnetite stirrer. At the same time, another 50 ml of sample is taken for sodium analysis. But this sample only can be sent to other lad for sodium analysis afterwards. So at that time, we don't know the sodium concentration. During this batch experiment pH does not change and is always kept at 7 constantly. So there is no need to dose a base. Every two hours, the calcium concentration is measured. The experiment is ended after 6 hours. We suppose the equilibrium is reached at that time. And then take the water samples to measure the equilibrium concentration of calcium and sodium.

Figure 5.2 – Mixing beakers with resin inside (batch experiment)

2) Calcium analysis and sodium analysis

The calcium concentration is measured at the Water Lab of TU Delft with the method of EDTA titration. When the indicator shows that the color of the solution changes from pink to purple, all the calcium is combined with EDTA. Record the amount of EDTA to calculate the calcium concentration. The sodium concentration is measured at the micro-lab of Civil Engineering Faculty of TU Delft.

Figure 5.3 – Setup for calcium analysis

3) Calculation method of the equilibrium constants

K(H,Ca):

Volume of solution: 1.5 [liter]
$[Ca(OH)_2]$: 4 [g/l]
Volume of resin : V [liter]
At the beginning of the batch experiment:
$[Ca^{2+}]$ in solution: a [mg/l] (measured), a’=a/40 [mmol/l]
Ca(OH)2 dosage : 0 [ml]
$[H^+]$ from the resin: 0 [mmol/l]
$[Ca^{2+}]$ on resin : 0 [mmol/l]
$[H^+]$ on resin : 4100 [mmol/l]
At the end of the batch experiment:
$[Ca^{2+}]$ in solution: b [mg/l](measured), b’=b/40 [mmol/l]
$Ca(OH)_2$ dosage : c [ml]
$Ca(OH)_2$ dosage : d = c x 4 g/l [mg]
$[H^+]$ from the resin: e = d x 2 / 74 [mmol/l]
$[Ca^{2+}]$ on resin : f = (a x 1.5 + e - b)/ V [mmol/l]
$[H^+]$ on resin : g = 4100 – 2 x f [mmol/l]

$$K(H,Ca) = \frac{f \times e}{g \times b'}$$

K(H,Na):

Volume of solution: 1.5 [liter]
[NaOH]: 15 [g/l]
Volume of resin : V [liter]
At the beginning of the batch experiment:
$[Na^+]$ in solution: a [mg/l] (measured), a’=a/23 [mmol/l]
NaOH dosage : 0 [ml]
$[H^+]$ from the resin: 0 [mmol/l]
$[Na^+]$ on resin : 0 [mmol/l]
$[H^+]$ on resin : 4100 [mmol/l]
At the end of the batch experiment:
$[Na^+]$ in solution: b [mg/l](measured), b’=b/23 [mmol/l]
NaOH dosage : c [ml]
NaOH dosage : d = c x 15 g/l [mg]
$[H^+]$ from the resin: e = d / 40 [mmol/l]
$[Na^+]$ on resin : f = (a x 1.5 + e - b)/ V [mmol/l]
$[H^+]$ on resin : g = 4100 – f [mmol/l]

$$K(H,Ca) = \frac{f \times e}{g \times b'}$$

K(Na, Ca):

Volume of solution: 1.5 [liter]
Volume of resin : V [liter]

At the beginning of the batch experiment:

$[Ca^{2+}]$ in solution: a [mg/l] (measured), a’=a/40 [mmol/l]
$[Na^{+}]$ from the resin: 0 [mmol/l]
$[Ca^{2+}]$ on resin : 0 [mmol/l]
$[Na^{+}$ on resin : 4100 [mmol/l]

At the end of the batch experiment:

$[Ca^{2+}]$ in solution: b [mg/l](measured), b’=b/40 [mmol/l]
$[Na^{+}]$ from the resin: e [mg/l] (measured), e’ =e/23 [mmol/l]
$[Ca^{2+}]$ on resin : f = (a - b) x 1.5 / V [mmol/l]
$[Na^{+}]$ on resin : g = 4100 –f [mmol/l]

$$K(H,Ca) = \frac{f \times e'}{g \times b'}$$

5.4.2 Column experiment

1) Setup description

This experiment aims to measure the change of ionic concentration in effluent solution with time using a transparent small scale ion exchange column shown in Figure 5.4. The diameter of the column is 5 cm and the total height is 40 cm. The cotton on the bottom is used to prevent the resin flowing out from the column. The flow direction in the column is downwards. The resin is same as the resin used in pilot experiment. The solution is fed by a pump which also gives a constant flow rate.

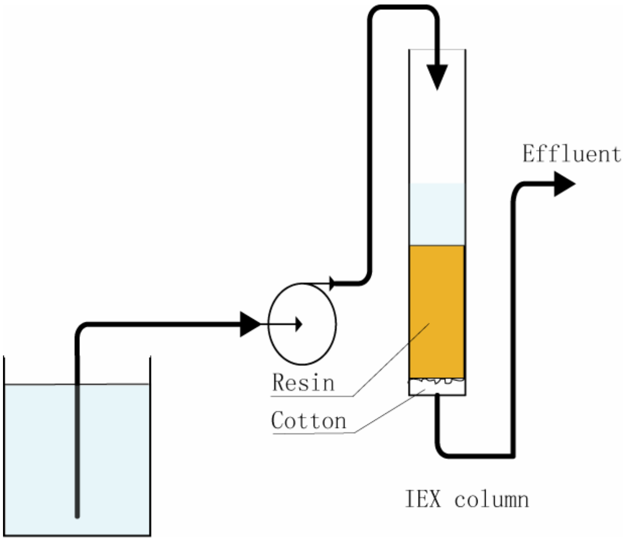


Figure 5.4 – schematic illustration of ion exchange column

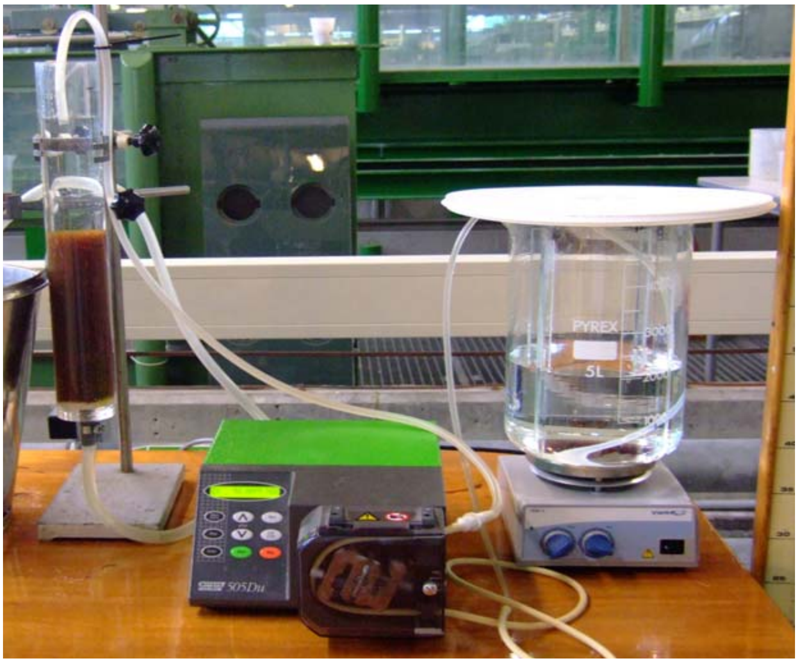


Figure 5.5– setup for regeneration and production

2) Regeneration

Before starting the column experiment, the resin needs to be regenerated in this column. The applied bed height is 20 centimeters. 2~5% of HCl is dosed through the resin bed with 1 l/h of flow rate. After regeneration with HCl, the pH is below 1. And then use demi water to rinse the resin with slow flow rate first and then with fast flow rate to get rid of the H^+ from the solution till the pH keeps constant value.

3) Production

Feed solution passes through the resin bed downward with a constant flow rate of 2 m/h (EBCT=0.5 h). Every two or three hours, take water sample from the effluent to measure the concentration of calcium and sodium and hydrogen. Two groups of tests have been done with different type of water in order to realize the operation at different pH enviornment. This first one is to test a simulated water at the moderate pH range (around 6). The second one is to test tap water at lower pH range (around 4).

Test with the model water (pH = 5~6)

Since the batch experiment to obtain the equilibrium constants is operated at pH of 6 to 7 and those equilibrium constants will be used in the model, we expect that if the experiment is operated at this pH range the experimental results are more close to the model results. In order to raise pH to a higher level, we made the simulated water by dosing 5.5 mmol/l NaOH and 2.5 mmol/l of $CaCl_2$ in demi water. In this model water, HCO_3^- is not involved since it will precipitate with Ca^{2+} as $CaCO_3$. The bed height is 10 cm and flow rate is 2 m/h (4 l/h).

Test with tap water (pH = 3~4)

The experiment method is same as the test with model water, but with tap water as the feed water. In tap water, the pH is 8. Saturation index is low. Since the tap water contains HCO_3^- which can buffer the decrease of pH, it is not necessary to dose extra base in the water. After regeneration, the pH of the effluent is in the range of 4~5. With the passage of Ca^{2+} and Na^+ through the resin bed, the pH of effluent will decrease to 1 or 2. The pH only can keep at 3~4 before breakthrough. The bed height is about 10 cm and the flow rate is 2 m/h (4 l/h). The tap water quality is presented in table 5.1.

Table 5.1 – main parameters of tap water quality (at TU Delft)

Parameter	**unit**	**3^e kwartaal 2005**	**4^e kwartaal 2005**	**1^e kwartaal 2006**	**2^e kwartaal 2006**	**3^e kwartaal 2006**
Temperature	°C	20,2	12,0	4,1	13,0	20,9
pH	pH	8,11	8,08	8,10	8,15	8,10
Saturation Index	SI	0,47	0,28	0,02	0,25	0,46
Conductivity (20 °C)	mS/m	48,7	50,2	51,3	48,7	47,6
Biocarbonate	mg/l HCO3	125	117	107	113	128
Sodium	mg/l Na	45	46	48	44	43
Calcium	mg/l Ca	50	50	50	48	49
Magnesium	mg/l Mg	7,6	7,7	7,8	7,5	7,5

5.5 Experimental results

5.5.1 Determination of equilibrium constants

According to the calculation method mentioned in section 5.4.1, we can calculate the equilibrium constants for different amount of resin. The equilibrium constant K are generally reported as a function of the ionic fraction of given ion in a diagram of K and x. Based on the diagram, the mean value of the equilibrium constant will be obtained.

The ionic fraction x is the mole fraction of the exchanged ion and the ions on the resin. it can be obtained by the following formulas. The unit of all the concentration is mmol/l.

H/Ca:

On the resin: $\overline{C} = 2 \cdot \overline{C_{Ca}} + \overline{C_H}$

Calcium: $\overline{x} = \frac{2 \cdot \overline{C_{Ca}}}{\overline{C}}$

H/Na:

On the resin: $\overline{C} = \overline{C_{Na}} + \overline{C_H}$

Sodium: $\overline{x} = \frac{\overline{C_{Na}}}{\overline{C}}$

Na/Ca:

On the resin: $\overline{C} = 2 \cdot \overline{C_{Ca}} + \overline{C_{Na}}$

Calcium: $\overline{x} = \frac{2 \cdot \overline{C_{Ca}}}{\overline{C}}$

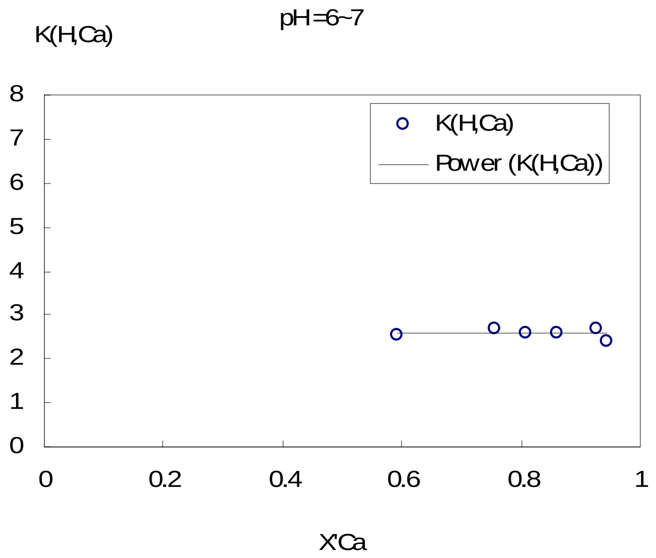


Figure 5.6 – K(H, Ca) as a function of fraction of calcium

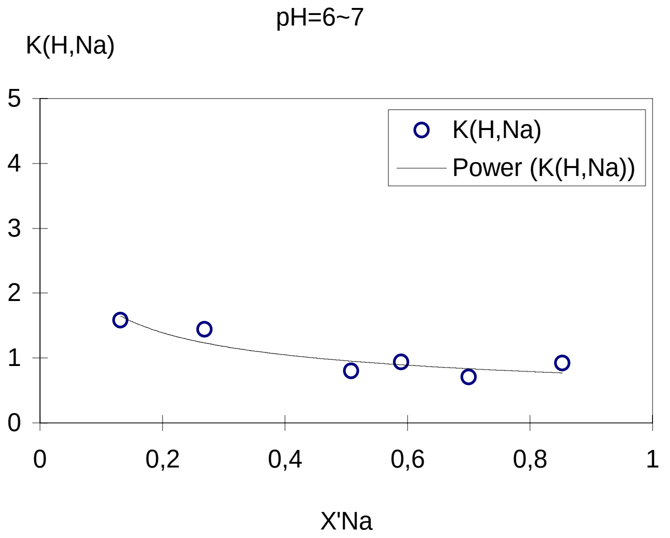


Figure 5.7 – K(H, Na) as a function of fraction of sodium

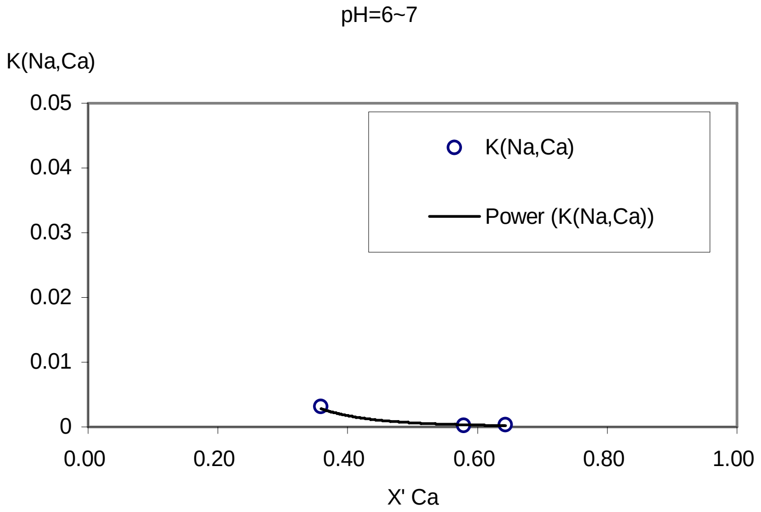


Figure 5.8 – K(Na,Ca) as a function of fraction of calcium

From the batch experiment, the function of ionic fraction and the equilibrium constants is obtained for different loadings (see Figure 5.6~5.8). Figure 5.6 shows a flat line of equilibrium constants for the fraction of calcium higher than 0.5. Although Figure 5.7 shows a decreasing tendency at lower ionic fraction, a stable tendency of K is presented at higher ionic fraction. It is better to use the average value of the equilibrium constants for the model. The average value of the equilibrium constants are given in Table 5.2:

Table 5.2 – Average equilibrium constants for three pairs of ions

	K(H,Ca)	**K(H,Na)**	**K(Na,Ca)**
Ave	2.580	1.066	0.0012

According to Figure 5.6, 5.7, 5.8 and Table 5.2, we can see that K(H, Ca) is more than two times higher than K(H,Na). It indicates that the selectivity of calcium by hydrogen is higher than that of sodium by hydrogen. Therefore, we can know that the hydrogen prefer calcium then sodium. This is coincidence with the statement in theory part that the resin has higher selectivity for bivalent ions than monovalent ions.

From Figure 5.8, we find that the K(Na, Ca) is rather low compared with the constants for H-Ca and H-Na. It shows that the preference of calcium compound to sodium is very high. But this accuracy of the K(Na, Ca) value is doubtful possibly due to the too high initial concentration of sodium or the equilibrium is not achieved yet. After regeneration of H -form resin by sodium, demi water is used to rinse the Na form resin bed to wash the additional sodium out from the bed till the sodium concentration keeps constant. However, since we can not measure the sodium concentration during the experiment, we don’t know if the sodium concentration already reaches the constant level or not.

5.5.2 Determination of LDF-constants

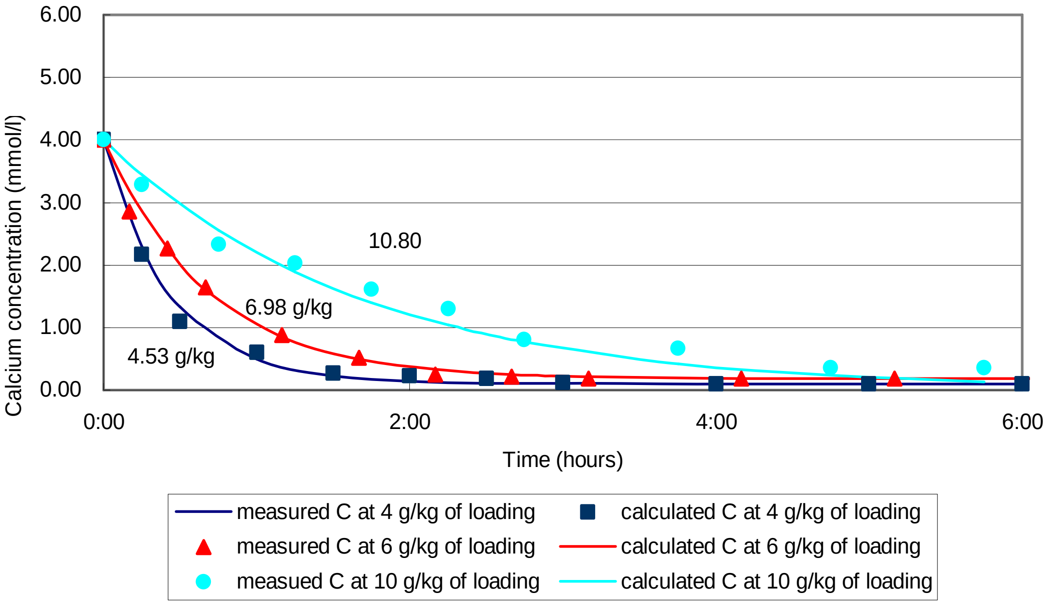


Figure 5.9 – Fitting of LDF-constants with the calcium equilibrium curve for different loadings at pH range of 6 to 7

From the batch experiment in binary system (Ca and H), the calcium concentration is measure every one or two hours till the reaction reach equilibrium. And then the equilibrium curve is obtained (see Figure 5.9). In Figure 5.9, the calcium concentration for low loading (4.53 g/kg) decreases from 4.0 mmol/l to 0.1 mmol/l, while for higher loading (10.8 g/kg) it starts from the same initial concentration but decreases slowly till 0.35 mmol/l at the end. This means that the removal efficiency with low loading is higher compared to high loading. Figure 5.9 also shows that with lower loading the equilibrium can reach quicker than higher loadings, because only 3 hours is needed before the equilibrium for lower loadings while 5 hours is needed for higher loading and the slope of the concentration curve for lower loading is steeper than the slope for higher loading.

The other important significance of this batch experiment is that it can be used to find the LDF-constant k through the following formula. By using the formula, we can find a calculated concentration curve fitting with the measured concentration equilibrium curve by a suitable LDF-constant k.

$$C(t) = \left(C_o - C_{eq}\right)e^{k\cdot t} + C_{eq} \qquad \text{[Eq. 5.18]}$$

Table 5.3 – LDF-constant values for three loadings

Loading of Ca on resin	4.53 g/kg	6.98 g/kg	10.8 g/kg
Ratio of Ca and resin	4.80 g/kg	8 g/kg	16 g/kg
LDF-constant k	2.3	1.5	0.6

From the table, we find that the transfer rate varies with different loadings. k< 0.6 (the loading is 10.8 g/kg) can be used for H/Ca to model our experiments, because the loading of 10.8 g/kg is most close to the loading of calcium in the column experiment. The loading of calcium for tap water test is about 20 g/kg when the equilibrium of H/Ca is almost reached (The calculation of loadings is based on the results of the next section). Similarly, the k for H/Na and Na/Ca also can be obtained using the same method.

5.5.3 Breakthrough curve

1) Test with model water

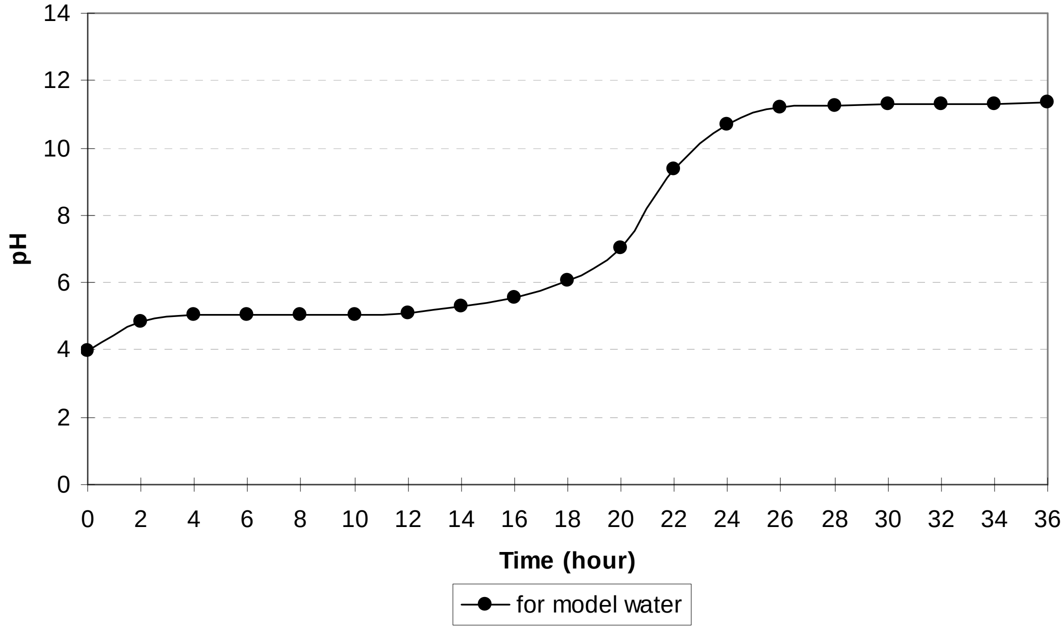


Figure 5.10 - pH with time for the model water

The change tendency of pH

In Figure 5.10, there is a fast increase of pH from 4 to 5 in the first 2 hours due to less H^+ releasing from the resin at low pH. During the following 16 hours, a moderate pH range between 6 and 7 is kept. In this period, Hydrogen exchanges with sodium and calcium continuously. The resin bed is slowly full of calcium and sodium. Afterwards, pH breakthrough occurs, showing that the exchange between calcium and hydrogen and the exchange between sodium and hydrogen has reached equilibrium. No extra H^+ comes out from the resin resulting in the quick increase of pH. After breakthrough, pH value is kept constant at 11.3, close to the pH of the feed (11.5). After breakthrough there is still exchange between Na and Ca. So the sodium loading of the resin decreases but this of course is not influencing the pH. The exchange process between Na and Ca can be illustrated by the concentration chancy tendency of sodium and calcium n in the next paragraph.

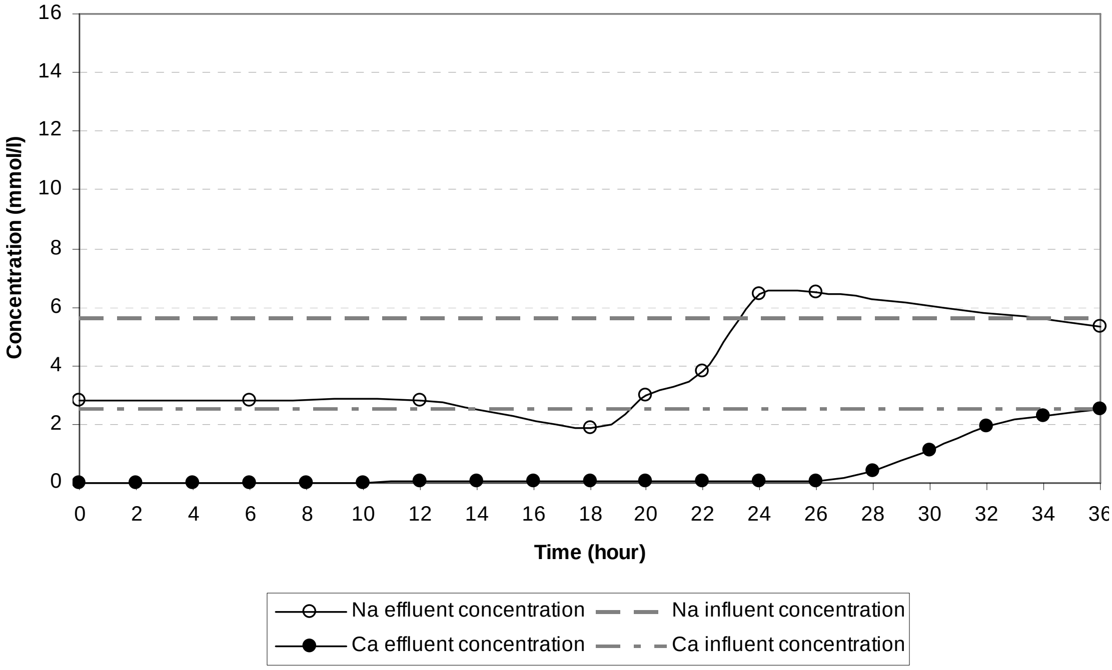


Figure 5.12– Sodium and calcium concentration with time for the model water

The change tendency of sodium concentration

In Figure 5.12, the sodium concentration during the first 18 hours is kept in the range between 2 and 3 mmol/l. In this period, only half of sodium is removed. It is because of its lower selectivity by the H-form resin. At the end of this period, there is a small drop. This drop might be due to the pH change. From Figure 5.12, we can see that at the same time pH started to increase faster. The higher pH improves the removal efficiency. Soon after, the sodium breakthrough occurs. Also, the pH breakthrough is also observed at the same time (Figure 5.10). The sodium concentration climbs up to 6.5 mmol/l which exceeds the feed concentration of 5.6 mmol/l. The high sodium concentration is because that some sodium is released from the resin by the exchange with calcium. And then the sodium concentration decreases to the same level as the feed concentration which indicates that the exchange between sodium and calcium stops.

The change tendency of calcium concentration

From Figure 5.12, we can see that the calcium concentration is kept at a very low level in a very flat form during the first 24 hours and afterwards a slow breakthrough starts. Again, the calcium breakthrough happened later than the breakthrough of pH and sodium. This is the same trend as in the pilot experiment. The exchange of calcium and sodium is involved which hinders the occurrence of calcium breakthrough. So, calcium still can be exchanged by sodium after pH breakthrough. When the equilibrium between calcium and sodium is reached, calcium can not be exchanged by sodium anymore and the breakthrough is 100%.

Comparison between sodium and calcium

From the Figure 5.12, we can see that the calcium removal is more efficient than the sodium removal before breakthrough. This is mainly due to the higher selectivity of calcium by the resin. After about 36 hours, both of the calcium concentration and the sodium concentration become the same as the feed concentration. The resin has no capacity to remove sodium and calcium anymore. This can be proved by the following calculation.

Surface area of the column: A= 0.002 m^2
Height of the resin bed: H= 0.10 m
Bed volume : BV= 0.0002 m^3
Flow rate : Q = 4 l/h
Time : T= 38 hours
Total capacity of the resin: 4.1 eq/l (4.1 mol/l for Na)
Sodium concentration at the feed : C_{Na} = 5.5 mmol/l
Calcium concentration at the feed : C_{Ca} = 2.5mmol/l
Thus, the actual capacity of the resin which has been used during the 38 hours is :
q = T x Q x C / BV = 38x4x5.5/0.0002 = 4.18 mol/l

2) Comparison between the model water test and the tap water test

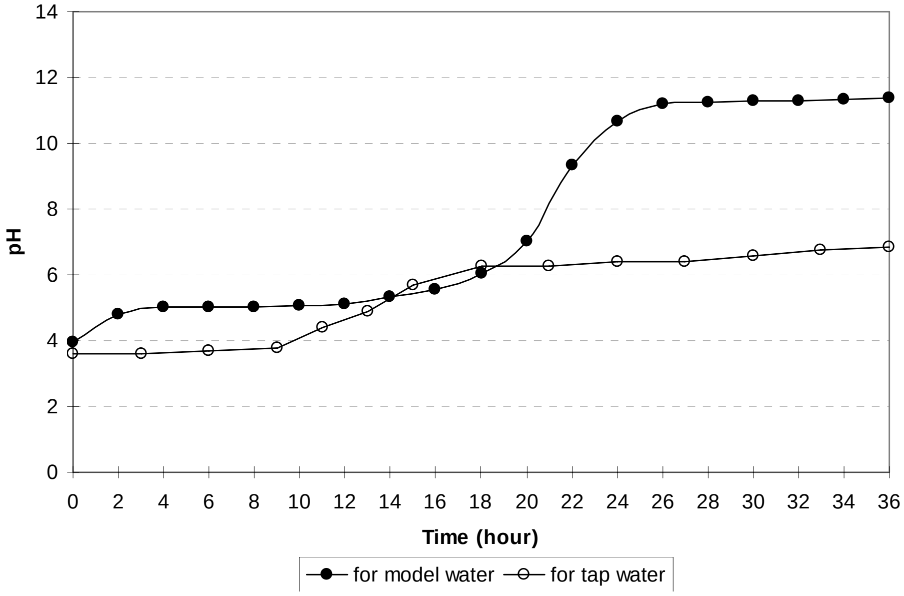


Figure 5.13 - pH with time

The change tendency of pH

For tap water, figure 5.13 shows a stable pH in a range between 3 and 4 in the first 6 hours. The pH does not increase quickly since the resin bed is gradually full of calcium and sodium. And then pH breakthrough occurs and climbs up to above 6. After 9 hours later, pH starts to increase very slowly. It has an increasing tendency to the pH of the feed (pH=8). The breakthrough for tap water test occurs earlier compared to the model water test. This might be because of the less bed height for the tap water test.

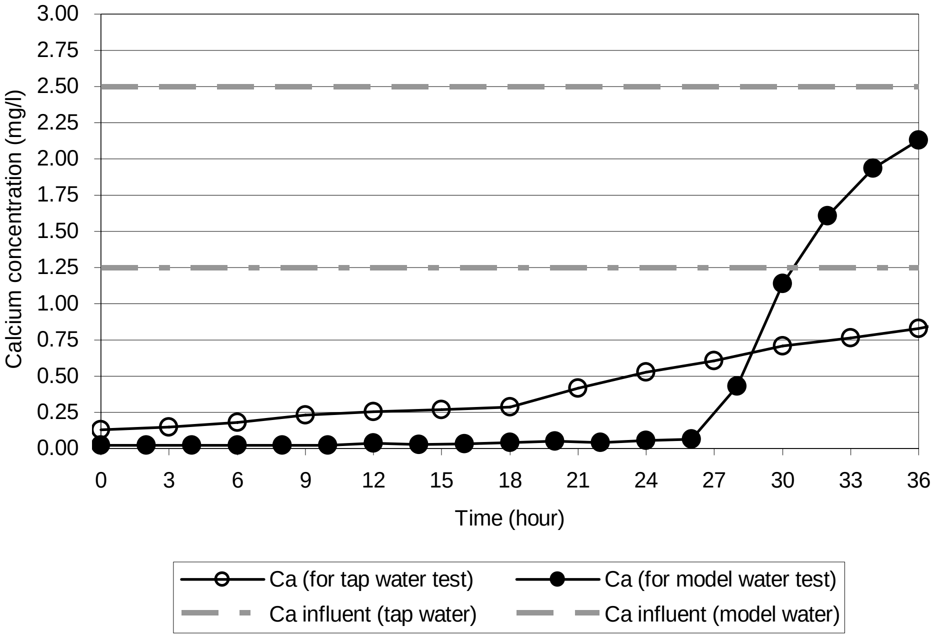


Figure 5.14 – calcium concentration with time

The change tendency of calcium concentration

For tap water test, Figure 5.14 shows two phases of calcium concentration change. During the first 18 hours, the calcium concentration keeps stable in the range between 0.03 and 0.28 with a gently increasing tendency. Afterwards, the second phase starts in which the slope of the increasing tendency becomes steeper which means the calcium concentration goes up faster. The second phase indicates that the resin bed is gradually full of calcium and the calcium breakthrough becomes obvious.

Before breakthrough, the calcium removal efficiency in tap water is 97% - 77%. While for the model water, the removal efficiency is 99% - 98%. So the calcium removal efficiency for tap water is lower compared to the model water. This is probably because of the lower pH hindering the removal efficiency.

According to the increasing tendency of the calcium concentration, we can assume that after about 50 hours the calcium concentration will become the same as the feed concentration for tap water test. At that time the resin has no capacity to remove calcium. Through calculation, we can check the actual volume of the resin bed. The volume should be about 0.13 m^3. The bed height, therefore, is 0.07~0.08 m which is a little bit lower than the bed height for the model water test. The lower bed height might be the reason why the calcium breakthrough in the tap water test occurs earlier then the breakthrough in the model water test.

3) Discussions

➢ Exchange process in resin matrix of ternary system

The exchange process can be illustrated in the following example. If we feed the solution of NaOH and $CaCl_2$ through a H-form resin bed. Three counter ions, H^+, Ca^{2+}, Na^+ are involved in the system. The co-ions are OH^- and Cl^-. At the beginning, H^+ comes out from the resin and neutralize with OH^- to form water (H_2O). The ionic site of H^+ is replaced by other counter-ions. Gradually, the original H form resin becomes a mixture matrix including H^+, Na^+ and Ca^{2+}. Co-ions are largely excluded by the negative charges on the matrix. The Na^+ and Ca^{2+} are stored in a much higher concentration than that of the feed on the resin. So the column only fills up slowly. After all the H^+ are exchanged by Na^+ and Ca^{2+}, the pH will breakthrough and the concentration of Na^+ will be saturated through the whole column. Calcium can be exchanged by sodium further and its breakthrough is postponed.

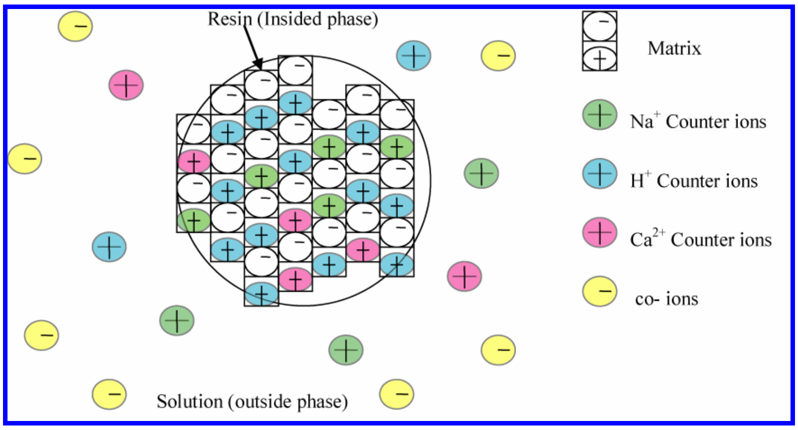


Figure 5.13 – ion exchanger with co- and counter- ions

➢ pH change through the resin bed

The ion exchange column can be regarded as a plug flow reactor. When the solution enters the resin bed, in the first layer of the bed, the exchange of H^+ and Na^+ is quick. Lots of H^+ ions are released from the resin resulting in the quick decreasing pH of the solution. The pH of the feed solution for the second layer is lower than the feed solution of the first layer. At lower pH, less H^+ is released from the resin. The pH will not decrease further. The pH profile as a function of the bed height is not constant. The pH of the effluent is lower than the pH of the feed. It will take some time to make the pH reach the value of the feed. That's why we observed a stable phase before pH breakthrough [see Figure 5.9]. pH is an important factor influencing the actual loadings of other ions. For the future research, it is worthwhile to measure the pH change through the bed by taking samples as a function of the height in the column.

5.6 Model parameters

Table 5.4– Model parameters

Input (for tap water test)			
Operational and hydraulic parameters	Flow rate = 2 m/h (4 l/h)		
	Fixed bed height L= 0.07 m		
	Surface area A=0.02m^2		
	Run time t = 50 hours		
Initial concentration		In solution(mmol/l)	On resin(mmol/l)
	Ca2+	1.25	0
	Na+	1.96	0
	H+	0	4100
	HCO_3^-	1.95	0
	Total capacity of resin = 4100 mmol/l		
	Temperature T= 16~18 (^oC)		
	LDF-constant $k<0.6$		
Equilibrium	Equilibrium constant K for each ion pair (measured)		
	K(H,Ca) = 2.58		
	K(H,Na) = 1.066		
	K(Na,Ca) = 0.0012		
Input (for simulated water)			
Operational and hydraulic parameters	Flow rate = 2 m/h (4 l/h)		
	Fixed bed height L= 0.10 m		
	Surface area A=0.02m^2		
	Run time t = 50 hours		
Initial concentration		In solution(mmol/l)	On resin(mmol/l)
	Ca2+	2.5	0
	Na+	5.6	0
	H+	0	4100
	HCO_3^-	0	0
	Total capacity of resin = 4100 mmol/l		
	Temperature T= 16~18 (^oC)		
	LDF-constant $k<0.6$		
Equilibrium	Equilibrium constant K for each ion pair (measured)		
	K(H,Ca) = 2.58		
	K(H,Na) = 1.066		
	K(Na,Ca) = 0.0012		
Output			
	actual concentration change in of Ca, Na and pH in effluent of ion exchange column with time (breakthrough curve)		

5.7 Conclusions and recommendations

5.7.1 Conclusions

- In the ternary system consisting of Ca^{2+}, Na^{+} and H-form resin bed, pH breakthrough occurs earlier than calcium. After breakthrough, all the hydrogen is exchanged by sodium. Calcium is still exchanged with the sodium on the resin after pH breakthrough.

- The removal efficiency of calcium and sodium can be influenced by pH. Lower pH might hinder the removal efficiency.

5.7.2 Recommendations

- During the batch experiment, sodium concentration needs to be monitored to check if the equilibrium is really reached. Only in this way, the measured K(Na,Ca) can be trusted.

- Since we only measured the equilibrium constants at pH of 6 to 7 and we don’t know if the equilibrium constants are different at different pH, a pH measurement along the column should be done and an extra batch experiment needs to be operated at lower pH.

- For the next step research, the important step is to build up the model and validate it compared with the measured results. Through comparison, the post-check is needed for the model parameters, like LDF-constants (kinetic constants) and the equilibrium constants.

6 Conclusions and Recommendations

6.1 Introduction

This research is to establish a potential treatment technology to realize zero liquid discharge for nanofiltration. The goal of 99% recovery is obtained with a pilot setup at Kiwa Water Research during a short period of 11 days.

In order to predict and improve the performance of this treatment concept, two extra studies have been done. One is a jar test for silica removal, from which we find that the magnesium concentration and pH value can influence silica removal efficiency. The other one is to build a ternary ion exchange model predict breakthrough curve. In order to create this model, some batch experiments are performed to obtain some model parameters, like equilibrium constants and LDF-constants. The other experiments are column experiments which are used to monitor the breakthrough curve of ions. The result of the column experiments are used for model validation in the further research work.

6.2 Conclusions

- The pretreatment process consisting of sludge softening (combination of precipitation at high pH and sedimentation) and weak acid cation exchange in series can efficiently remove scaling components, like calcium, magnesium and barium. Sludge softening can remove most of the bivalent ions. The remaining bivalent ions are removed by ion exchange.

- In the pilot experiment, Si removal efficiency is low probably due to the shortage of magnesium in the tap water. According to the jar test, we can conclude that the magnesium concentration and the pH value influence the silica removal efficiency. Higher magnesium concentration is necessary for silica removal.

- With this pretreatment concept, the recovery of nanofiltration membrane can reach 99% without scaling in an experiment of 11 days. This is the first time to reach such a high recovery. The modified setup can successfully control the concentrate flow at a very low level without the need of adjustment. For even higher recoveries, this setup also can be used.

- In the ternary system consisting of Ca^{2+}, Na^{+} and H-form resin bed, pH breakthrough occurs earlier than calcium. After breakthrough, all the hydrogen is exchanged by sodium. Calcium is still exchanged with the sodium on the resin after pH breakthrough.

- The removal efficiency of calcium and sodium can be influenced by pH. Lower pH might hinder the removal efficiency.

6.3 Recommendations

- Although the pilot experiment can reach 99% recovery for 11 days, the final conclusion for this treatment concept can not be drawn by this short-term experiment. The experiment needs to be operated for a longer period to observe the performance of the nanofiltration membrane at 99% recovery.

- Higher recovery (99.9%) can also be tested, but at higher recovery the osmotic pressure also increases lot requiring higher energy consumption. NOM fouling is easier to be formed resulting in lower flux. The membrane has a bigger risk to be scaled. Also the permeate quality will be growing worse.

- In order to guarantee enough turbidity in the sludge softening, the design of the sedimentation tank with a conical bottom and with a recycling pumping system should be considered in full-scale plant.

- More batch experiments of ion exchange can be done in order to obtain the equilibrium constants at lower pH and to check if the measured K(Na,Ca) is accurate or not.

- We only measured the equilibrium constants at pH of 6 to 7. Along the resin bed the pH might be changeable. I suggest to measure the pH along the resin and to do the extra batch experiment at lower pH to check if the equilibrium constants are different at different pH level.

- The further work for the ion exchange model is to build up the model by simulation program and validate it by comparing with the measured results. Through comparison, the post-check is needed for the model parameters calibration, such as the LDF-constants (kinetic constants) and the equilibrium constants.

Literature

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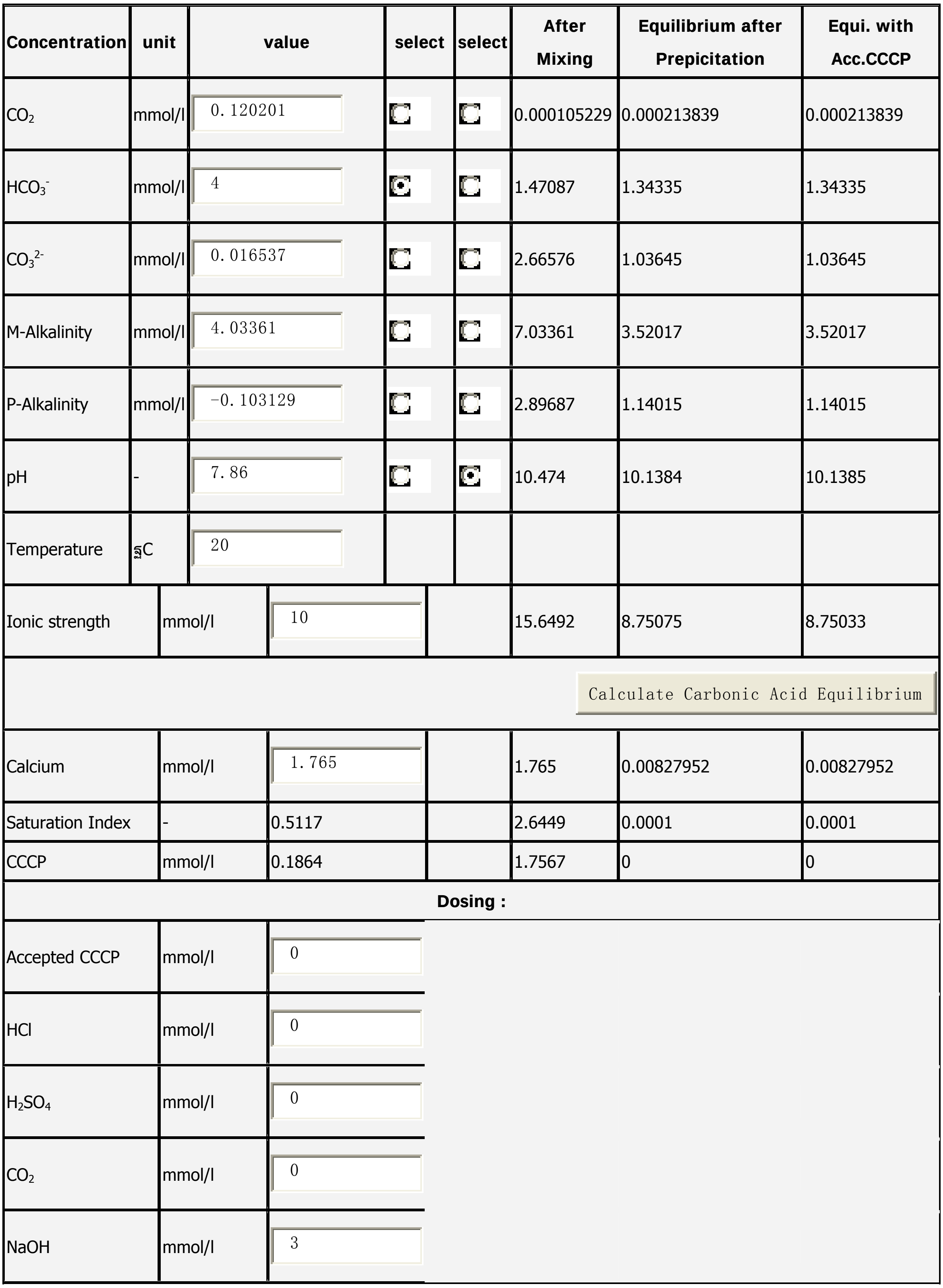
Appendix:

List of appendix:

I. Calculation of NaOH dosage for pilot experiment (The form of carbonate acid equilibrium by Stimela)



Concentration	unit	value	select	select	After Mixing	Equilibrium after Prepicitation	Equi. with Acc.CCCP
CO_2	mmol/l	0.120201	○	○	0.000105229	0.000213839	0.000213839
HCO_3^-	mmol/l	4	●	○	1.47087	1.34335	1.34335
CO_3^{2-}	mmol/l	0.016537	○	○	2.66576	1.03645	1.03645
M-Alkalinity	mmol/l	4.03361	○	○	7.03361	3.52017	3.52017
P-Alkalinity	mmol/l	-0.103129	○	○	2.89687	1.14015	1.14015
pH	-	7.86	○	●	10.474	10.1384	10.1385
Temperature	នC	20					
Ionic strength	mmol/l	10			15.6492	8.75075	8.75033
							Calculate Carbonic Acid Equilibrium
Calcium	mmol/l	1.765			1.765	0.00827952	0.00827952
Saturation Index	-	0.5117			2.6449	0.0001	0.0001
CCCP	mmol/l	0.1864			1.7567	0	0
Dosing :							
Accepted CCCP	mmol/l	0					
HCl	mmol/l	0					
H_2SO_4	mmol/l	0					
CO_2	mmol/l	0					
NaOH	mmol/l	3					

$CaOH_2$	mmol/l	0
Na_2CO_3	mmol/l	0
$CaCO_3$	mmol/l	0
$Fe^{2+}SO_4^{3-}$	mmol/l	0
$Al^{2+}SO_4^{3-}$	mmol/l	0

II. Mechanisms of carbonate acid equilibrium for softening

$CO_2 + H_2O \leftrightarrow H_2CO_3$, $H_2CO_3 + H_2O \leftrightarrow H_3O^+ + HCO_3^-$

$$K_1(T = 10^\circ C) = \frac{[H_3O^+]\cdot[H_2CO_3]}{[CO_2]} = 3.44\times10^{-7} \qquad \text{[Eq. 1]}$$

$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$

$$K_2(T = 10^\circ C) = \frac{[H_3O^+]\cdot[CO_3^{2-}]}{[HCO_3-]} = 3.25\times10^{-11} \qquad \text{[Eq. 2]}$$

$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$

$$K_s = \frac{[Ca^{2+}]\cdot[CO_3^{2-}]}{[CaCO_3]} \qquad \text{[Eq. 3]}$$

$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$

$$K_a = \frac{[Ca^{2+}]\cdot[HCO_3^-]^2}{[CO_2]} \qquad \text{[Eq. 4]}$$

Combine the above equations, it will result in:

$$[H_3O^+] = \frac{[HCO_3^-]^2\cdot K_2}{2K_s} \qquad \text{[Eq. 5]}$$

Thus,

$$pH_s = -2\log[HCO_3^-] - pK_2 + pK_s + \log[2] \qquad \text{[Eq. 6]}$$

Saturation Index is given by:

$$SI = pH - pH_s \qquad \text{[Eq. 7]}$$

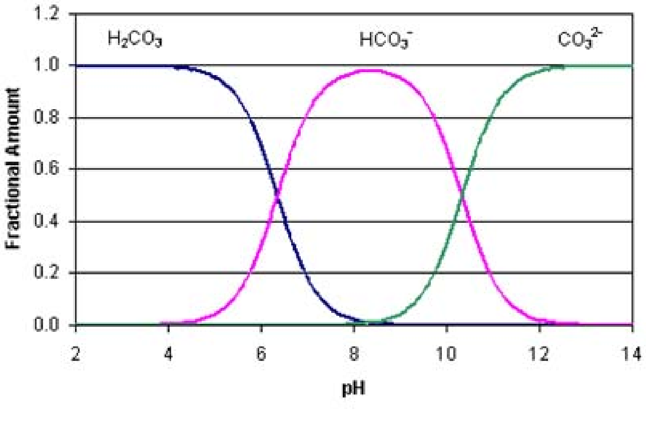
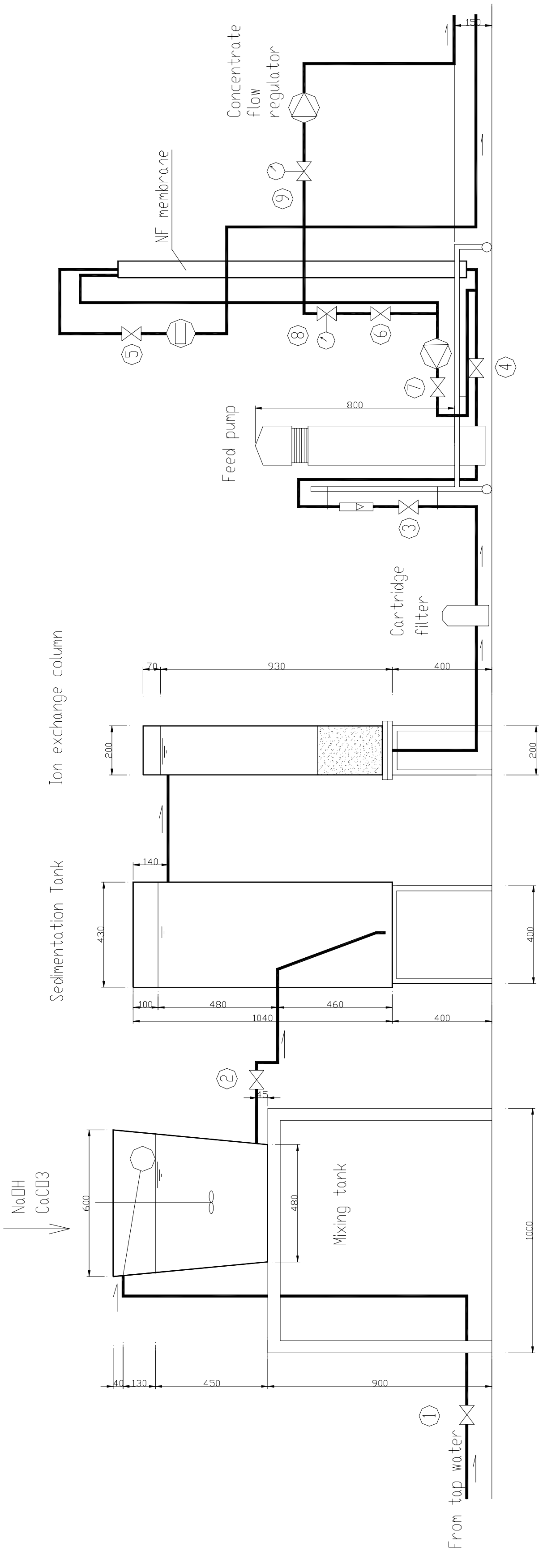


Figure 1 – total carbonate as a function of pH



III. Figure 2 - Design drawing of the pilot equipment

IV. Run protocol of the pilot experiment

Based on Figure 2, the run protocol is shown as below:

1. Open the valve (1) to fill the mixing tank with tap water.
2. Dose NaOH (pellet) carefully into the tap water to increase the pH up to 10.
3. After one-hour mixing, open the valve (2) to let the solution flow into the sedimentation tank. At the same time, start the NaOH dosing pump.
4. After few hours, the water can flow into the ion exchange column and then pass through a cartridge filter.
5. Open the valve (3), (4), (5), (6), (7) totally.
6. Switch on the feed pump to pump the water into the NF membrane.
7. Press the green button on the electrical plate to recycle the concentrate back to the feed.
8. Adjust the permeate flow by the controlling the feed pump capacity.
9. Switch on the concentrate flow regulate system. Due to the high water pressure, leakage from the concentrate flow can be found at the effluent of the flow regulate system.
10. Close the valve (6) gradually and adjust the two pressure release valves (8), (9) at the same time until there is no leakage from the concentrate flow. According to the pressure meter beside the pressure release valves, the pressure can be set at around 6 bars during the whole experiment.
11. Repeat the step 8 and 10 until the permeate flow and the concentrate flow keep at the required level.
12. Every two hours, record the pressure, flow rates, conductivities at the feed, permeate, concentrate and the temperature in the bulk flow and the pH for the whole process.
13. Everyday, take the water sample from the following points: tap water, after sedimentation tank, feed (after ion exchange), concentrate and permeate.
14. Next day, the $CaCO_3$ concentration will be diluted and there will be some precipitation of fine $CaCO_3$ particles on the top of resin. Pump the sediments back to the mixing tank and remove the $CaCO_3$ from the top of resin.
15. Continuously operate those equipments for 11 days and repeat the step 12 and 13 everyday.

V. Result of calcium analysis for pilot experiment

Table 1 – Calcium concentration after sedimentation

after sedimentation						
day	time	sample	EDTA	TH	Ca	time
dd/mm/yy	min/hour	ml	ml	mmol/l	mg/l	hour
19/03/2007	11:30	50	0.45	0.09	3.60	0.0
20/03/2007	10:00	50	0.51	0.10	4.08	22.5
21/03/2007	10:00	50	0.46	0.09	3.68	48.5
23/03/2007	15:00	50	0.47	0.09	3.76	77.5
24/03/2007	15:00	50	0.49	0.10	3.92	101.5
25/03/2007	15:00	50	0.5	0.10	4.00	125.5
26/03/2007	15:00	50	0.46	0.09	3.68	149.5
30/03/2007	16:00	50	0.463	0.09	3.70	240.5

Table 2 – Calcium concentration after ion exchange

after ion exchange						
day	time	sample	EDTA	TH	Ca	time
dd/mm/yy	min/hour	ml	ml	mmol/l	mg/l	hour
19/03/2007	11:30	50	0.040	0.008	0.320	0.0
21/03/2007	10:00	50	0.020	0.004	0.160	48.5
24/03/2007	15:00	50	0.020	0.004	0.160	101.5
25/03/2007	15:00	50	0.020	0.004	0.160	125.5
30/03/2007	10:00	50	0.030	0.006	0.240	240.5

VI. Calculation sheet of MTC

time hour/min	Qp l/h	Qc l/h	Qr l/h	Pf bar	kPa	Pc bar	kPa	Pp bar	kPa	delta P mbar	T ℃	ECf uS/cm	ECc uS/cm	ECp uS/cm	TCF for Π	Πf kPa	Πc kPa	Πp kPa	A ㎡	TCFw	MTC m/s.kPa
0:00:00	61	0.6	320	5.14	514	5.01	501	0.91	91	136	19.5	78.1	709	80.8	1.00	33.4	33.4	3.8	2.6	1.0	1.716E-08
2:00:00	59	0.6	320	5.19	519	5.05	505	0.91	91	137	20.1	55.8	752	55.6	1.00	35.5	35.5	2.6	2.6	1.0	1.618E-08
3:00:00	60	0.6	320	5.54	554	5.41	541	0.91	91	136	20	50.7	846	49.5	1.00	40.0	40.0	2.3	2.6	1.0	1.53E-08
4:00:00	60	0.6	320	5.53	553	5.4	540	0.91	91	136	20.2	46.4	905	43.8	1.00	42.8	42.8	2.1	2.6	1.0	1.534E-08
22:00:00	40	0.6	305	6	600	5.87	587	0.99	99	136	19.9	116.6	2010	60.7	1.00	94.9	94.9	2.9	2.6	1.0	1.066E-08
23:30:00	40	0.4	308	5.98	598	5.84	584	0.99	99	137	20.2	141.2	2300	59.8	1.00	108.7	108.7	2.8	2.6	1.0	1.099E-08
25:30:00	39	0.4	310	6.39	639	6.26	626	0.99	99	137	20.2	145.3	2580	71.8	1.00	122.0	122.0	3.4	2.6	1.0	9.968E-09
27:00:00	38	0.4	310	6.42	642	6.3	630	0.99	99	137	20.1	128.3	2990	75.8	1.00	141.3	141.3	3.6	2.6	1.0	1.013E-08
28:30:00	38	0.4	306	6.43	643	6.3	630	0.96	96	137	20.6	151.5	3160	79.6	1.00	149.6	149.6	3.8	2.6	1.0	1.006E-08
45:30:00	37	0.4	305	6.45	645	6.32	632	0.99	99	137	20.1	162.7	3200	71.6	1.00	151.2	151.2	3.4	2.6	1.0	1.006E-08
47:30:00	36	0.4	305	6.45	645	6.31	631	0.99	99	137	20.2	176.2	3450	80.5	1.00	163.1	163.1	3.8	2.6	1.0	1.005E-08
48:30:00	38	0.4	305	6.71	671	6.58	658	1	100	137	20.2	180.2	3550	80.4	1.00	167.8	167.8	3.8	2.6	1.0	1.006E-08
49:30:00	37	0.4	305	6.69	669	6.55	655	0.99	99	138	20.2	176.8	3690	84.3	1.00	174.5	174.5	4.0	2.6	1.0	9.996E-09
50:30:00	37	0.4	305	6.69	669	6.55	655	1	100	137	20.2	177.1	3760	84.6	1.00	177.8	177.8	4.0	2.6	1.0	1.011E-08
52:30:00	37	0.4	305	6.69	669	6.57	657	0.99	99	137	20.2	178.3	3840	85.9	1.00	181.5	181.5	4.1	2.6	1.0	1.015E-08
68:30:00	36	0.4	304	6.71	671	6.58	658	1.01	101	137	20	187.1	4000	86.8	1.00	189.0	189.0	4.1	2.6	1.0	1.016E-08
69:00:00	40	0.4	306	7.11	711	6.97	697	1	100	137	20	259	4050	80.3	1.00	191.3	191.3	3.8	2.6	1.0	1.026E-08
77:30:00	38	0.4	305	7.11	711	6.97	697	1	100	137	20.4	201	4500	90.4	1.00	212.9	212.9	4.3	2.6	1.0	1.012E-08
94:00:00	37.5	0.4	304	7.14	714	7	700	1	100	140	20.1	206	4600	92.5	1.00	217.4	217.4	4.4	2.6	1.0	1.013E-08
98:00:00	40	0.4	306	7.59	759	7.46	746	1.01	101	139	20	216	4780	90.5	1.00	225.8	225.8	4.3	2.6	1.0	9.94E-09

101:00:00	40	0.4	306	7.59	759	7.46	746	1	100	140	20	195.3	4820	97.4	1.00	227.7	227.7	4.6	2.6	1.0	9.953E-09
118:30:00	39	0.4	305	7.6	760	7.47	747	1.02	102	142	19.6	222	4850	98.7	1.00	228.8	228.8	4.7	2.6	1.0	9.897E-09
119:30:00	40	0.4	306	7.78	778	7.65	765	1.01	101	142	19.3	220	4870	93.2	1.00	229.5	229.5	4.4	2.6	1.0	9.85E-09
121:30:00	39	0.4	306	7.78	778	7.65	765	1.01	101	142	19.6	234	5000	93.9	1.00	235.9	235.9	4.4	2.6	1.0	9.633E-09
123:30:00	39	0.4	304	7.78	778	7.65	765	1.01	101	142	19.4	230	5020	99.2	1.00	236.7	236.7	4.7	2.6	1.0	9.718E-09
125:00:00	39	0.4	304	7.8	780	7.67	767	1.02	102	141	19.7	220	5100	99.5	1.00	240.7	240.7	4.7	2.6	1.0	9.675E-09
143:00:00	37	0.4	303	7.83	783	7.69	769	1.03	103	143	19.3	234	5200	105.3	1.00	245.1	245.1	5.0	2.6	1.0	9.374E-09
144:30:00	36	0.4	303	7.83	783	7.69	769	1.03	103	143	19.3	247	5250	110.9	1.00	247.4	247.4	5.2	2.6	1.0	9.165E-09
145:00:00	38	0.4	303	8.11	811	7.98	798	1.02	102	144	19.3	247	5200	106.1	1.00	245.1	245.1	5.0	2.6	1.0	9.012E-09
145:30:00	37	0.4	303	8.11	811	7.98	798	1.02	102	144	19.5	247	5350	107.2	1.00	252.3	252.3	5.1	2.6	1.0	8.847E-09
165:30:00	37	0.4	303	8.82	882	8.68	868	0.97	97	145	20.8	264	6250	113.8	1.00	296.1	296.1	5.4	2.6	1.0	7.874E-09
170:30:00	37.5	0.4	302	9.1	910	8.95	895	0.96	96	146	20.9	314	6890	127	1.00	326.5	326.5	6.0	2.6	1.0	7.972E-09
188:30:00	37	0.4	296	9.1	910	8.94	894	0.96	96	158	20.7	366	7850	165.5	1.00	371.8	371.8	7.8	2.6	1.0	8.712E-09
197:00:00	38.5	0.4	295	9.31	931	9.16	916	0.9	90	159	22.1	390	8530	192	1.01	405.9	405.9	9.1	2.6	0.9	8.714E-09
212:30:00	39	0.4	296	9.32	932	9.17	917	0.93	93	159	21	375	8380	184.5	1.00	397.3	397.3	8.7	2.6	1.0	9.063E-09
217:30:00	38	0.4	295	9.33	933	9.19	919	0.95	95	160	20.7	430	8600	186	1.00	407.3	407.3	8.8	2.6	1.0	9.145E-09
236:30:00	37	0.4	293	9.35	935	9.2	920	0.96	96	163	20.8	492	9040	191	1.00	428.3	428.3	9.0	2.6	1.0	9.307E-09
237:30:00	40	0.4	293	9.62	962	9.47	947	0.96	96	163	20.8	514	9100	197	1.00	431.1	431.1	9.3	2.6	1.0	9.498E-09
243:30:00	40	0.4	290	9.62	962	9.47	947	0.97	97	163	21.6	548	9470	219	1.01	449.8	449.8	10.4	2.6	0.9	9.634E-09
260:30:00	40	0.4	293	9.63	963	9.46	946	0.95	95	167	21.4	534	9490	215	1.00	450.5	450.5	10.2	2.6	0.9	9.678E-09
264:00:00	40	0.4	295	9.65	965	9.48	948	0.91	91	168	21.3	494	9620	229	1.00	456.5	456.5	10.9	2.6	1.0	9.699E-09

VII. Average velocity gradient (G value)

Camp and Stein (1943) studied the establishment and effect of average velocity gradient G in coagulation tanks of various types and developed the following equations for use in mechanical mixing devices. The formation of flocculants strongly depends on the G and GT value. T is the mixing time.

$$G = \sqrt{\frac{P}{\mu V}} \qquad \text{[Eq. 8]}$$

$$P = 14.35 d^{4.38} n^{2.69} \rho_0^{0.69} \mu^{0.31} \qquad \text{[Eq. 9]}$$

In which,

d – width of stirrer (m)
n – rotation speed (r/min)
ρ_0 - density of water (1000kg/m^3)
μ_0 - dynamic viscosity of water (kg.s/m^2)
V – volume of water (m^3)

VIII. Data of jar tests

Test 1:

volume of water	1.5 liter
rotation speed	100 r/min
Mixing time	1hour
Sedimentation time	5min
G	$470s^{-1}$
GT	$1.7x10^{6}$
Temperature	$14^{o}C$
pH	10-10.5

Table 4.1 Si concentration and removal percentage in test 1

			pH=10		**pH=10.3-10.5**	
	MgCl2.6H20 (mg)	**Mg (mg/l)**	**Si (mg/l)**	**removal**	**Si (mg/l)**	**removal**
tap water			9.9		9.9	
	0	0.0	9.6	3.0%	9	9.1%
	500	39.41	9.1	8.1%	8.6	13.1%
	1000	78.82	8.8	11.1%	8.2	17.2%
	2000	157.64	8.6	13.1%	7.6	23.2%
	5000	394.09	7.1	28.3%	6.2	37.4%

Test 2:

volume of water	1.5 liter	
rotation speed	fast mixing(80r/min)	slow mixing(30r/min)
Mixing time	fast mixing(60s)	slow mixing(15min)
Sedimentation time	5min	
G	fast mixing(30$s^{-1)}$	slow mixing($350s^{-1}$)
GT	fast mixing($2x10^{4}$)	slow mixing($3x10^{4}$)
pH	10.3-10.5	

Table 4.2 Si concentration and removal percentage in test 2

	MgCl2.6H20 (g)	**Mg (mgl/l)**	**Si (mg/l)**	**removal**
tap water			9.9	
	0	0.0	8.8	11.1%
	500	39.41	8.3	16.2%
	1000	78.82	2	79.8%
	2000	157.64	0.8	91.9%
	5000	394.09	0.8	91.9%

IX. Calculation form of equilibrium constants

1) Selectivity coefficient of Ca^{2+} by H^+(Dosing 4 mg/ml of $Ca(OH)_2$ to raise pH at 6.0~7.0)

1.

ratio Ca/resin	18.46	g/kg
loading	89.20	g/kg
fraction of Ca	0.86	

Time	Ca^{2+} in solution		$Ca(OH)_2$		H^+ from resin	Ca^{2+} on resin	H^+ on resin	K(H,Ca)
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
9:45	160.0	4.00	0	0	0			
15:45	104.8	2.62	498	1992	35.98	1761.63	576.73	2.604

2.

ratio Ca/resin	34.29	g/kg
loading	96.08	g/kg
fraction of Ca	0.93	

Time	Ca^{2+} in solution		$Ca(OH)_2$		H^+ from resin	Ca^{2+} on resin	H^+ on resin	K(H,Ca)
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
10:10	160.0	4.00	0	0	0			
16:10	142.6	3.57	299	1196	21.55	1897.65	304.69	2.663

3.

ratio Ca/resin	48	g/kg
loading	97.90	g/kg
fraction of Ca	0.94	

Time	Ca^{2+} in solution		$Ca(OH)_2$		H^+ from resin	Ca^{2+} on resin	H^+ on resin	K(H,Ca)
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
10:10	160.0	4.00	0	0	0			
16:10	133.5	3.34	208	832	14.99	1933.44	233.11	2.396

4.

ratio Ca/resin	12.63	g/kg
loading	83.83	g/kg
fraction of Ca	0.81	

Time	Ca^{2+} in solution		$Ca(OH)_2$		H^+ from resin	Ca^{2+} on resin	H^+ on resin	K(H,Ca)
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
9:45	160.0	4.00	0	0	0			

15:45	104.3	2.61	698	2792	50.31	1655.61	788.78	2.583

5.

ratio Ca/resin 9.23 g/kg

loading 78.58 g/kg

fraction of Ca 0.76

Time	**Ca^{2+} in solution**		**$Ca(OH)_2$**		**H^+ from resin**	**Ca^{2+} on resin**	**H^+ on resin**	**K(H,Ca)**
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
9:45	160.0	4.00	0	0	0			
15:45	98.2	2.46	902	3608	65.01	1551.87	996.26	2.692

6.

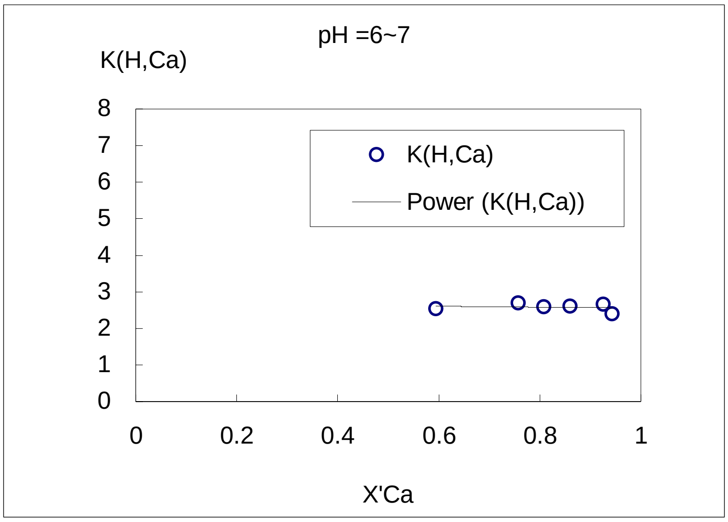
ratio Ca/resin 4.80 g/kg

loading 61.62 g/kg

fraction of Ca 0.59

Time	**Ca^{2+} in solution**		**$Ca(OH)_2$**		**H^+ from resin**	**Ca^{2+} on resin**	**H^+ on resin**	**K(H,Ca)**
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
9:45	160.0	4.00	0	0	0			
15:45	66.2	1.66	1360	5440	98.02	1217.09	1665.82	2.546

fraction of Ca	**K(H,Ca)**
0.59	**2.546**
0.76	**2.692**
0.81	**2.583**
0.86	**2.604**
0.93	**2.663**
0.94	**2.396**
Ave	**2.580**



2) **Selectivity coefficient of Na^+ by H^+** (Dosing 15 mg/ml of NaOH to raise pH at 6.0~7.0)

1.

ratio Na/resin	11.50	g/kg
loading	13.88	g/kg
fraction of Na	0.13	

Time	**Na^+ in solution**		**NaOH**		**H^+ from resin**	**Na^+ on resin**	**H^+ on resin**	**K(H,Na)**
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
9:45	230.0	10.0	0	0	0			
15:45	29.4	0.74	53.4	801	13.35	476.83	3146.33	1.583

2.

ratio Na/resin	34.5	g/kg
loading	61.5	g/kg
fraction of Na	0.27	

Time	**Na^+ in solution**		**NaOH**		**H^+ from resin**	**Na^+ on resin**	**H^+ on resin**	**K(H,Na)**
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
10:10	230.0	10.0	0	0	0			
16:10	61.5	2.67	42	630	10.5	868.14	2363.72	1.442

3.

ratio Na/resin	49.29	g/kg
loading	40.22	g/kg
fraction of Na	0.51	

Time	**Na^+ in solution**		**NaOH**		**H^+ from resin**	**Na^+ on resin**	**H^+ on resin**	**K(H,Na)**
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
10:15	230.0	10.0	0	0	0			
16:15	189.0	8.22	25.51	382.65	6.38	1381.39	1337.22	0.802

4.

ratio Na/resin	69.0	g/kg
loading	44.29	g/kg
fraction of Na	0.59	

Time	**Na^+ in solution**		**NaOH**		**H^+ from resin**	**Na^+ on resin**	**H^+ on resin**	**K(H,Na)**
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
10:15	230.0	10.0	0	0	0			
16:15	237	10.30	26.89	403.35	6.72	1521.10	1057.80	0.938

5.

ratio Na/resin	172.5	g/kg
loading	49.15	g/kg
fraction of Na	0.70	

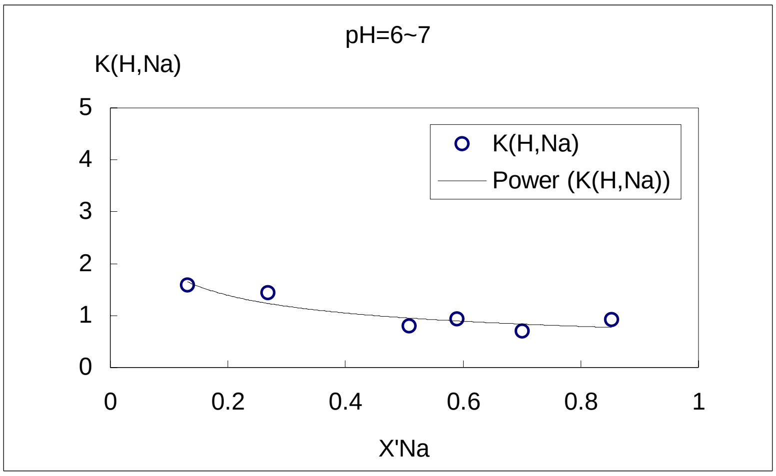
Time	Na^+ in solution		NaOH		H^+ from resin	Na^+ on resin	H^+ on resin	K(H,Na)
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
10:15	230.0	10.0	0	0	0			
16:15	236	10.26	12.44	186.0	3.11	1688.11	723.78	0.707

6.

ratio Na/resin	345.0	g/kg
loading	54.94	g/kg
fraction of Na	0.85	

Time	Na^+ in solution		NaOH		H^+ from resin	Na^+ on resin	H^+ on resin	K(H,Na)
	mg/l	mmol/l	ml	mg	mmol/l	mmol/l	mmol/l	
10:15	230.0	10.0	0	0	0			
16:15	230	10.0	6.37	95.55	1.59	1887.11	325.78	0.922

fraction of Na	K(H,Na)
0.13	1.583
0.27	1.442
0.51	0.802
0.59	0.938
0.70	0.707
0.85	0.922
Ave	1.066



3) Equilibrium constant of Ca^{2+} by Na^+ (pH at 6.0~7.0 without dosing base)

1.

ratio Ca/ resin(Na form)	48.0	g/kg
loading	37.27	g/kg
fraction of Ca	0.36	

Time	Ca^{2+} in solution		Na^+ from resin	Ca^{2+} on resin	Na^+ on resin	K(Na,Ca)
	mg/l	mmol/l	mmol/l	mmol/l	mmol/l	
9:45	160.0	4.00	0			
15:45	35.76	0.89	5.13	736.12	2627.76	0.00314

2.

ratio Ca/ resin(Na form)	120.0	g/kg
loading	66.72	g/kg
fraction of Ca	0.64	

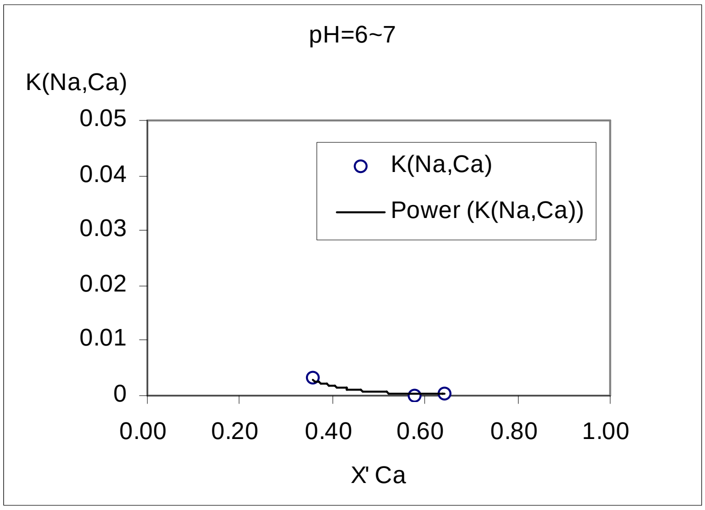
Time	Ca^{2+} in solution		Na^+ from resin	Ca^{2+} on resin	Na^+ on resin	K(Na,Ca)
	mg/l	mmol/l	mmol/l	mmol/l	mmol/l	
9:45	160.0	4.00	0			
15:45	71.04	1.78	1.0	1317.72	1464.56	0.00034

3.

ratio Ca/ resin(Na form)	240.0	g/kg
loading	60.12	g/kg
fraction of Ca	0.58	

Time	Ca^{2+} in solution		Na^+ from resin	Ca^{2+} on resin	Na^+ on resin	K(Na,Ca)
	mg/l	mmol/l	mmol/l	mmol/l	mmol/l	
9:45	160.0	4.00	0			
15:45	119.92	3.00	1.17	1187.37	1725.26	0.00018

fraction of Ca	K(Na,Ca)
0.36	0.0031
0.64	0.0003
0.58	0.0002
Ave	0.0012



X. Drinking water quality at TU Delft

(http://www.evides.nl/cijfergegevens/Tabel%20Drinkwaters.htm)

Parameter	**eenheid**	**3e kwartaal 2005**	**4e kwartaal 2005**	**1e kwartaal 2006**	**2e kwartaal 2006**	**3e kwartaal 2006**
Temperatuur	°C	20,2	12,0	4,1	13,0	20,9
Zuurstof	mg/l	11,9	13,6	17,0	13,1	10,4
Troebelingsgraad	FTE	0,06	0,06	0,07	0,07	0,07
Geur		geen afwijking	geen afwijking	geen afwijking	geen afwijking	geen afwijking
Smaak		geen afwijking	geen afwijking	geen afwijking	geen afwijking	geen afwijking
Zuurgraad	pH	8,11	8,08	8,10	8,15	8,10
Verzadigingsindex	SI	0,47	0,28	0,02	0,25	0,46
Geleidingsvermogen (20 °C)	mS/m	48,7	50,2	51,3	48,7	47,6
Anionen	meq/l	5,2	5,3	5,4	5,0	5,1
Kationen	meq/l	5,3	5,3	5,5	5,1	5,1
Waterstofcarbonaat	mg/l HCO3	125	117	107	113	128
Chloride	mg/l Cl	57	61	64	60	58
Sulfaat	mg/l SO4	62	69	77	61	52
Natrium	mg/l Na	45	46	48	44	43
Calcium	mg/l Ca	50	50	50	48	49
Magnesium	mg/l Mg	7,6	7,7	7,8	7,5	7,5
Totale hardheid	mmol/l	1,55	1,56	1,57	1,52	1,54
Totale hardheid	° Duitse hardheid	8,7	8,7	8,8	8,5	8,6
Ammonium	mg/l NH4	< 0,03	< 0,03	< 0,03	< 0,03	< 0,03
Nitraat	mg/l NO3	12,2	11,3	13,7	14,8	12,9
Silicaat	mg/l Si	1,6	2,6	3,2	2,1	2,0
IJzer	µg/l Fe	< 5	< 5	< 5	< 5	< 5
Aluminium	µg/l Al	< 10	< 10	< 10	< 10	< 10
Fluoride	mg/l F	0,33	0,36	0,31	0,30	0,29
Kleurintens. Pt/Co-schaal	mg/l Pt	< 1	< 1	1	1	< 1
Som trihalomethanen	µg/l	8	2	< 1	< 1	< 1
Bacteriën van de coligroep	KVD/100 ml	< 1	< 1	< 1	< 1	< 1
Escherichia coli	KVD/100 ml	< 1	< 1	< 1	< 1	< 1
Enterococcen	KVD/100 ml	< 1	< 1	< 1	< 1	< 1
Clostridium perfringens (incl. sporen)	KVD/100 ml	< 1	< 1	< 1	< 1	< 1