BTO 2005.041

July 2005

Nanofiltration membrane fouling by Natural Organic Matter.

Focus on calcium effects

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11.1511.081

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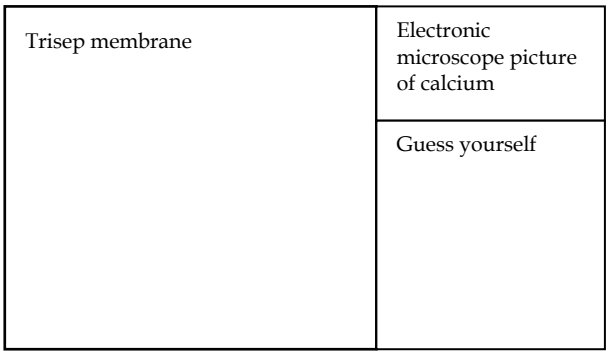
Preface

I would like to thank my two training supervisors Emile Cornelissen and Wolter Siegers for their help, their advice and for their availability. I would like to thank the following people for their assistance in completing the work : Ton Van Dam for his technical help on the MTA, Danny Harmsen for the work on the Spannenburg pilot and Théo Vermolen for the laboratory access and his help. I am also grateful to the Kiwa water treatment team for their help, their warm reception, the pleasant work atmosphere and efforts they made to speak English. And I want to add a special thank for Arne Verliefde and Benoit Teychéne for the nice atmosphere in our office.

Front cover picture:



Summary

Membrane applications are growing rapidly in drinking water and wastewater treatment. Membranes technologies can be competitive in term of efficiency and economics for water treatment compared to other technologies such as ion exchange, activated carbon, etc. However fouling is a major obstacle for the efficient use of membrane technology. The aim of this study is to investigate the fouling of nanofiltration membranes by natural organic matter (NOM) and more particularly the influence of calcium cations on membrane fouling by NOM.

The first part of this study was to prove the occurrence of calcium-NOM complexes in solution and measure if the complex was present. Two techniques were used to determine the part of calcium which is complexed by NOM and the free calcium ion in solution. The first technique was using an anionic exchange resin to remove the calcium NOM complex from the solution and measure the amount of removed complex. Waters from Weesperkaspel and Spannenburg were used. The second technique used a calcium specific electrode to measure the free calcium and the difference with total calcium, in order to determine the amount of complexed calcium. Spannenburg water was used for this experiment.

Two experiments were performed to study membrane fouling with water from Spannenburg. First at laboratory scale, a Membrane Test Apparatus (MTA) was used to perform some filtration experiments. The influence of the calcium concentration on the flux decline during the nanofiltration process was investigated. Secondly, with information from the Spannenburg water treatment pilot and a mass balance for each NOM constituent, we could determine which fraction of the NOM constitutes the deposit on the membrane surface.

With the ion exchange resin experiment, the calcium-NOM complex formation could be linked to the amount of calcium. A minimum calcium concentration (100 ppm) and a minimum DOC concentration (7.2 mgC/l) are required for calcium-NOM complex formation. The specific electrode experiment showed that both concentrations of calcium and NOM influence the complexation equilibrium. If only the calcium concentration increases from 0.7 and 90 mmol/l of calcium, nothing happens at 7.2 mgC/l DOC concentration. When both calcium and NOM concentrations exceed these values the percentage of complexed calcium increase quickly.

During membrane fouling experiments, the flux was affected by the calcium concentration as well. This fouling can be removed by SDS but not by acid and

alkaline cleaning. All membrane fouling experiments were not long enough to suffer from bio-fouling (shorter than 1 week). To prove the absence of scaling, acid cleaning of the membrane, membrane X-ray fluorescence analysis and calculation of the scalant concentration close to membrane surface were performed. Acid is known to remove scaling. In this case however the acid cleaning of the membrane did not provide any improvement of the flux, indicating that no scaling was present. The X-ray fluorescence analysis revealed the occurrence of calcium and silicium on the membrane surface. Calcium peaks could be related to possible calcium-NOM deposits, while small Si peaks could be due to result of Si in the feed water. The exact nature of the deposit, however, was not clear from X-ray fluuorescence. Filtration resluts in a concentration increase close to the membrane surface. The calculated β-factor which expresses this concentration increase, were between 1.02 and1.26. this indicated that the scalant concentrations close to the membrane were not high enough to cause scaling. If no bio-fouling and no scaling were found on the membrane, the flux decline can be ascribed to NOM fouling.

The calculation of the β-factor showed that the calcium and NOM concentration were increased enough (higher than DOC = 7.2 mgC/l & Ca^{2+} = 100 ppm) by concentration polarisation to obtain a calcium-NOM complex formation. Therefore during filtration process the membrane could be fouled by the calcium-NOM complex present on the membrane surface.

From mass balance over the Spannenburg pilot it was found that NOM fractions deposited on the membrane seem to be a function of the state of the membrane surface (charge, hydrophobicity, amount of fouling). Only the neutral deposit doesn't seem to be modify by the membrane state.

Calcium has an effect on the nanofiltration performance by enhancing the NOM fouling, more particularly with the calcium-NOM complex which is a function of the calcium concentration (in the range of 3.9 to 140 ppm) and NOM concentration (from 7.1 to 7.6 mgC/l).

Contents

1 Introduction

1.1 General introduction

Membrane applications are growing rapidly in drinking water and wastewater treatment. Membrane technology development has grown together with public demand for high water quality and strict regulations, and membranes are considered as a promising tool to provide better drinking water quality. Membrane technologies can be competitive in terms of efficiency and economics for water treatment. Moreover membrane processes can potentially simplify treatment processes by elimination of coagulation, flocculation and sedimentation processes. It can be considered as a substitute for conventional drinking water treatment. However fouling is a major obstacle for efficient use of membrane technology for treatment of natural waters. Fouling phenomena still represent a limitation for membrane processes. Membrane fouling can be subdivised into particulate fouling (scaling), biofouling and organic fouling. It is the last type of fouling which is the topic of this work.

Natural Organic Matter (NOM) is abundant in natural waters and is one of the major fouling agents during membrane filtration of surface water. The efficiency of membrane processes for the production of drinking water is greatly depends on the adverse fouling effects of NOM present in waters. The membranes are severely fouled by these compounds in natural water and the permeability of a virgin membrane can be lost rapidly. NOM is the major cause for the build-up of a dense fouling layer on the membrane, which can lead to severe flux decline.

NOM represents a broad range of structurally complex compounds derived from the degradation of plants and micro organisms. Characterization of NOM is difficult because of the heterogeneous size, structure, and functional chemistry of its constituent compounds. Considering the variety of sources for NOM and the numerous transformations that can affect molecules in NOM, it is not surprising that NOM is an extremely complex mixture of organic molecules spanning a great range of molecular weights. In addition, NOM composition can vary widely between and within ecosystems. Consequently, the study of NOM is complicated by the complexity of the material.

Membrane filtration may offer an economically competitive process to treat drinking water, but fouling of the membrane surface is a serious problem that leads to unacceptable flux decline for economic operation. Fouling represents a serious constraint for employing membrane systems as a substitute for conventional treatment, because serious irreversible fouling implies a substantial loss of capacity for a membrane facility.

1.2 Aim of the study

The aim of this study is to investigate and to prove the fouling of nanofiltration membrane by NOM and more particularly the influence of calcium cations on membrane fouling by NOM. Using the MTA, NOM fouling will be studied with Spannenburg water before ozonation at different calcium concentrations. Moreover, the NOM ability to complex calcium will be investigated with water from Weesperkarspel and Spannenburg. The objective is to establish a correlation between the calcium concentration and the fouling layer.

1.3 Presentation of Kiwa

To optimize its services Kiwa´s activities have been divided into specific divisions. These divisions continually exchange know-how, but operate independently of each other in the market with a large degree of autonomy.

- Kiwa Certification and Inspection
- Kiwa Inspection
- Kiwa Research and Consultancy
- Kiwa Management Consultants
- Kiwa Water Research. This work has been carried out at Kiwa WR. Kiwa WR is the Dutch research and knowledge institute for water and associated ecological and environmental questions. Key aspects of the work of about 120 employees are innovation and knowledge transfer. The focus is the entire process of extraction, treatment, distribution and quality assessment of drinking water, industrial water and domestic water, with a focus on drinking water.

International co-operation

Kiwa co-operates intensively with universities and other research centers and has an extensive network of contacts at home and abroad. In the Netherlands, Kiwa co-operates with the universities of Delft, Wageningen, Eindhoven, Twente, Utrecht and Groningen, with the National Institute of Public Health and Environmental Protection and other authorities. Internationally, Kiwa has co-operation agreements within EWRI, the European platform of water research institutes. The purpose of EWRI is to co-ordinate the various research programs and to submit joint research proposals for funding by the EC. The EWRI-partners are: Le Cirsee (France), Anjou Recherche (France), WRc (UK); TZW (Germany); LNEC (Portugal) and SVW (Belgium). Co-operation agreements also exist with research centers outside Europe,

such as CRCWQT (Australia), WRC (South Africa) and AWWA Research Foundation (AWWARF, United States). The (inter) national network with universities and research centers is to be developed further. The aim is to make international knowledge and expertise more accessible to the BTO-participants, to make research more efficient and to establish a stronger position for international fund raising.

2 Theoretical part

2.1 Membrane processes

Membrane separation processes are based on the use of a membrane to accomplish a particular separation. The separation is achieved because the membrane has the ability to transport one component from the feed mixture more readily than any other component. Membranes are filters that are used to separate suspended or dissolved species in a fluid. This ability to discriminate between different components gives rise to the common description of membranes as a "semi-permeable barrier". And so, membrane separation may be applied to separate ions, molecules (both small and large), emulsions and particulates (either individually or as aggregates). Membrane can be porous or non porous, neutral or charged, symmetric or asymmetric and it can be natural or synthetic. The passage trough the membrane is possible when a driving force is applied on the feed water. Many driving forces exist such as pressure difference, concentration difference, electrically difference or temperature difference. A representation of membrane separation is given in Figure 1.

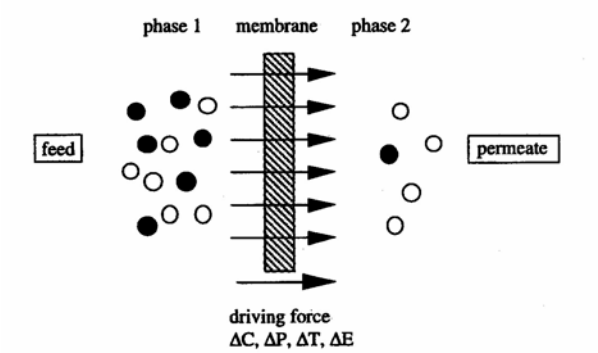


Figure 1, schematic representation of membrane separation

This work will focus on pressure driven membrane process.

In the field of pressure difference, four membrane processes exist such as:

1. microfiltration, (pore sizes from 10 to 0.05 µm) are used to retain suspensions and emulsions.
2. ultrafiltration, (pore sizes from 0.05 µm to 1 nm) is characterised by molecular weight cut-off, used to retain macromolecules and colloids.

Microfiltration and ultrafiltration membranes can both be considered as porous membranes and separation is based on sieve mechanism and size exclusion.

- nanofiltration, (characterised by salt retention with $MgSO_4$ or MWCO for "open" NF) retains divalent ions (Ca^{2+}, Mg^{2+}) and micro organism, NOM, etc.
- reverse osmosis, (characterised by salt retention with NaCl) retains almost all solutes

Nanofiltration and reverse osmosis are considered as dense nonporous membranes. The difference between these two membrane processes is that the structure of nanofiltration membranes network structure is more open. The separation is based on differences in solubility and/or diffusivity. They are used to retain low molecular weight solutes.

In order to apply membranes on a technical scale, large membrane areas are usually required. The smallest unit into which the membrane area is packed is called a membrane module. The module is the central part of a membrane installation. A number of module designs are possible and all are based on two types of membrane configuration: flat and tubular. Plate-and-frame and spiral-wound membrane involve flat membranes, whereas tubular, capillary and hollow fibre modules are based on tubular membrane configurations.

These modules can be operated in dead-end mode where the feed flow is perpendicular to the membrane surface or in cross-flow where the feed flow is parallel to the membrane surface.

80 to 90 % of the modules used in nanofiltration and reverse osmosis are spiral-wound cross flow membrane module. This module is shown schematically in figure 2.

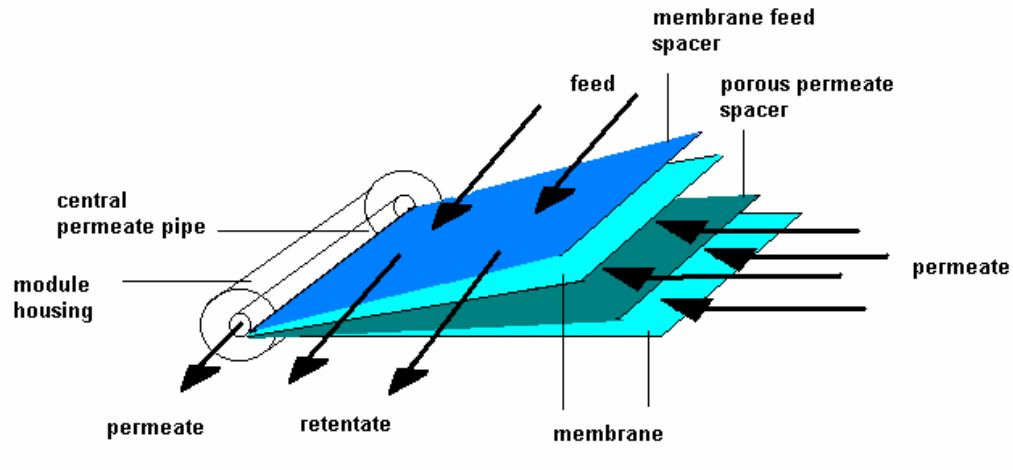


Figure 2, schematic drawing of a spiral-wound module

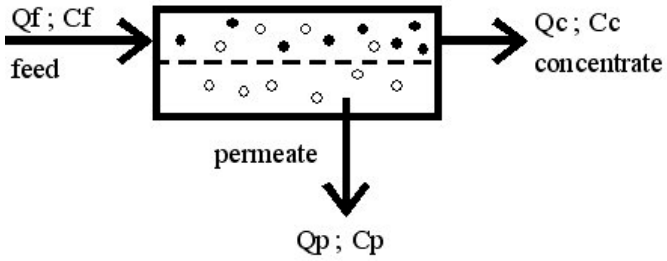


Figure 3, schematic drawing of a membrane system

The membrane process is schematically summarized in figure 3, including some parameters used on the following relationship:

- Mass balance for water flow:

$$Qf = Qp + Qc \qquad (1)$$

Where:

Qf = feed water flow rate (L/hr)

Qp = permeate flow rate (L/hr)

Qc = concentrate flow rate (L/hr)

- Mass balance for solute flux:

$$Qf\ Cf = Qp\ Cp + Qc\ Cc \qquad (2)$$

Where:

Cf = feed water solute concentration (mg/L)

Cp = permeate solute concentration (mg/L)

Cc = concentrate solute concentration (mg/L)

- Product Recovery rate:

$$S = \frac{Qp}{Qf} \qquad (3)$$

Where :

S = fraction of product water recovered from feed water

- Water flux:

$$J_w = K_w (\Delta P - \Delta\pi) = \frac{Qp}{A} = \frac{1}{A}\frac{dV}{dt} \qquad (4)$$

Where:

J_w = water flux (L/ m^2.hr)

K_w = water mass transfer coefficient, (m/s.bar)

ΔP = transmembrane pressure differential, (bar)

$\Delta\pi$ = transmembrane osmotic pressure differential, (bar)

A = effective membrane area (m^2)

- Retention Rt:

$$Rt = 1 - \frac{Cp}{Cf} \qquad (5)$$

Where :

Rt = express the selectivity of a membrane for a given solute

- Salt passage (SP) :

$$SP = 1 - Rt \qquad (6)$$

Where:

SP = express the salt passage

- Water transfer coefficient

$$Kw = \frac{Qp}{\Delta P * A * 1.026\text{^}\left(T^0 - 25\right)} \qquad (7)$$

Where:

T° = temperature (in degrees)

During the filtration process, because the membrane retains the solutes to a certain extent, there will be an accumulation of retained molecules near the membrane surface. The retained solutes can accumulate at the membrane surface causing the concentration to increase. So a concentration profile has been established in the boundary layer, see the figure 4. In other words, concentration polarization is the

accumulation of solute at the membrane surface. In figure 4 a concentration profile near the membrane surface is shown.

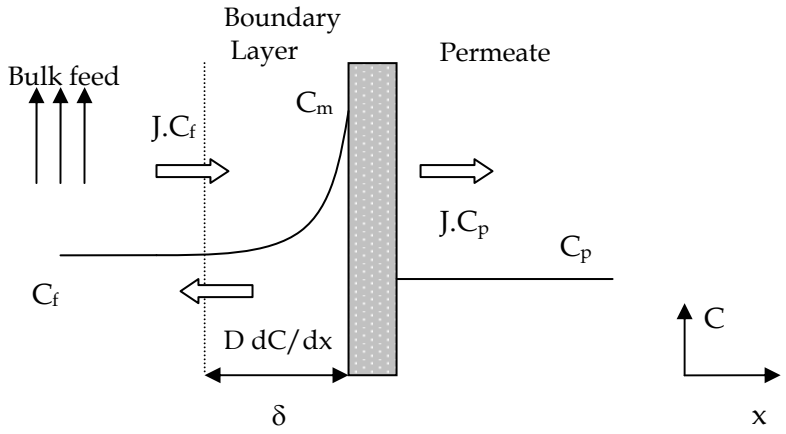


Figure 4, Concentration profile near the membrane surface

As membranes are selective barriers, some species accumulate at the membrane surface.

There is a back diffusion of the solute into the bulk stream (Ddc/dx). The concentration polarization can be calculated by assuming steady-state in cross-flow conditions:

$$J_w.C_f - D\frac{dC}{dx} = J_w.C_p = J_s \qquad (8)$$

Where :

J_s = solute flow (g/m²/s)

C_p = concentration of the permeate (g/L)

C_f = concentration of the feed solution (g/m³)

D = diffusion coefficient of the solute in water (m²/s)

The build up of solutes in front of the membrane surface is expressed as β-factor which can be calculated by equation (9). Solving equation over the laminary boundary layer with thickness gives equation :

$$\beta = \frac{C_m - C_p}{C_b - C_p} \cong \frac{C_m}{C_f} \equiv \exp\left(\frac{J_w}{k}\right) \qquad (9)$$

The mass transfer coefficient (k) can be determined by using empirical correlations :

$$Sh = \frac{k\ d_h}{D} = 0.065 \cdot \mathrm{Re}^{0.875} \cdot Sc^{0.25} \qquad (10)$$

The Sh relation for spiral wound modules is given by Schock & Miquel [1].

$$Sh = \frac{k\ d_h}{D} = 0.664 \cdot k_{dc}\ \mathrm{Re}^{0.5} \cdot Sc^{0.33} \left(\frac{2d_h}{l_m} \right)^{0.5} \qquad (11)$$

The Sh relation for flat sheet cell is given by Da Costa, Fane and Wiley [2].

Sh is the Sherwood number, it describes the effect of velocity versus the effect of diffusivity. k can be calculated from this equation. In Sherwood relation, Re is the Reynolds number and Sc the Schmidt number.

$$\text{Reynolds number : } \mathrm{Re} = \frac{\rho v d_h}{\eta} \qquad (12)$$

$$\text{Schmidt number : } Sc = \frac{\eta}{\rho D} \qquad (13)$$

Where :

ρ = density

ν = flow velocity

d_h = hydraulic diameter

η = dynamic viscosity

D = diffusion coefficient.

$$\text{Flow velocity : } \nu = \frac{Q_f}{hw\varepsilon} \qquad (14)$$

Where :

Q_f = feed flow (m^3/s)

h = high (m)

w = width (m)

ε = feed spacer porosity

Hydraulic diameter : $d_h = \frac{4hwl}{A}$ (15)

Where :

l = length (m)

A = effective membrane surface (m^2)

The equations 14 and 15 are only for flat sheet cells and are different for spiral wound modules.

Diffusion coefficient is necessary in (10), (11) and (13) and can be determined :

For organic molecules [3] : $D = 8.76*10^{-9} * M_w^{-0.48}$ (16)

Where :

M_w = molecular weight (g/mol)

For ionic compounds [4] : $D = 8.931*10^{-10} T \left(\frac{l_+^0 l_-^0}{\Lambda^0} \right) \left(\frac{z_+ + z_-}{z_+ z_-} \right)$ (17)

Where :

T = absolute temperature

l^0_+ = cationic conductance

l^0_- = anionic conductance

$\Lambda^0 = l^0_+ + l^0_-$

z_+ = valence of cation

z- = valence of anion

2.2 Natural Organic Matter (NOM)

Natural organic matter is ubiquitous in water sources throughout the world and can be described as a heterogeneous mixture of organic compounds of varying colour, structure and reactivity. NOM is formed from plant and animal tissues breakdown by chemical and biological processes. It is widely distributed over the earth's surface and occurs in almost all terrestrial and aquatic environments. NOM although harmless itself reacts with chlorine to form disinfection by-products. These by-products are mostly in the form of trihalomethanes, haloacetic acids and many other halogenated compounds.

NOM is constituted of both hydrophobic and hydrophilic components. Each of these components can be further separated into acids, bases and neutrals, each with a different chemical characteristics. The largest fraction of NOM in water is generally hydrophobic acids making up approximately 50% of the NOM and these can be described as the aquatic acids or humic substances composed of humic acids and fulvic acids. Little is known about the individual organics found in NOM although the structure of humic and fulvic acids have been studied intensevely and are very complex. A simplification of their structure can be made in by considering NOM as polymers with an aromatic ring representing the monomer and they contain acidic functional groups such as carboxylic acids. Carboxylic functional groups account for 60-90% of all functional groups. The figure 5 is showing an example of a possible natural organic matter structure.

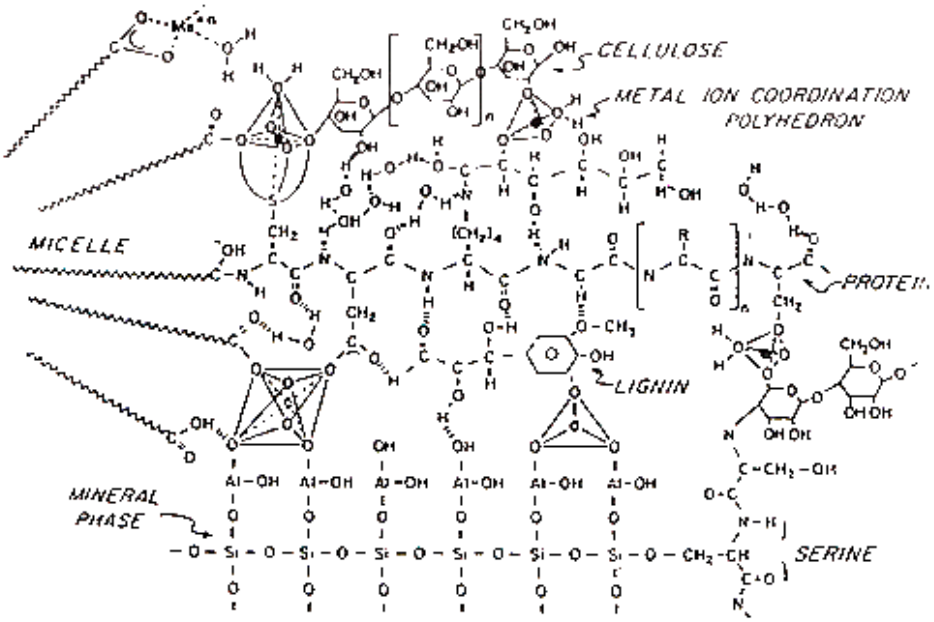


Figure 5, the structure of NOM shows the existence of H-bridges and aliphatic chains; presence of nitrogen groups and complexing sites; highly polyelectrolytic and aromatic nature; and the possibility of inter- or intra molecular aggregation [Buffle, 1988].

The potential sources of NOM are:

- Atmospheric deposition
- Forest canopy
- Forest floor pool of decaying litter and humus
- Soil organic matter
- Plant roots and fungi
- Wetland peat deposits
- Aquatic sediments
- Aquatic detritus
- Aquatic organism

The character of natural organic matter cannot be represented by just one parameter or a defined structural formula.

NOM is a precursor of haloforms and other toxic substances which occur as disinfection by-products after chlorination of drinking water. NOM is also forms complexes with heavy metals and pesticides which increase the persistence and bioaccumulation of these chemicals. During filtration process, fouling by NOM changes the rejection of cations and negatively charged low molecular weight acids [5].

2.3 Membrane fouling mechanisms

During a separation, the membrane performance can change considerably in time, and often typical flux decline on time behaviour may be observed. This behaviour is mainly due to fouling.

One of major problems in operation of membrane process is membrane fouling. Membrane fouling is referred to the flux decline caused by the accumulation of certain constituents in the feed water on the surface of the membrane or in membrane matrix.

According to the type of fouling materials, four categories of membrane fouling are generally recognized. They are: inorganic fouling, particle/colloids fouling, bio fouling and organic fouling.

Inorganic fouling/scaling is caused by accumulation of inorganic precipitates on the membrane surface. Precipitates are formed when the concentration of chemical species exceed their saturation concentrations.

Particulate/colloid fouling is caused by algae, bacteria or silts and clays which are into the size range of particle and colloids.

Bio fouling is a result of formation of a biofilm on membrane surfaces. Once bacteria attach to the membrane, they start to multiple and produce a viscous, slimy, hydrated gel layer.

Organic fouling is performed in membrane filtration with source water containing relatively high natural organic matters (NOM). Surface water generally contains higher NOM than ground water. For source water high in NOM, organic fouling is believed to be the most significant factor contributed to flux decline.

Membrane fouling is a complicate and complex phenomenon and typically results from several causes. Electrostatic and hydrophobic/hydrophilic interactions involve both membrane and fouling materials are recognized to have significant influence, especially for membrane fouling causes by natural organic matter (NOM) and microbial activities [6]. Electrostatic interactions occur between functional groups of membranes, fouling materials, and water primarily through dissociation, which strongly depend on the pH, ionic strength, and concentrations of multivalent cations in the solution. Hydrophobic/hydrophilic interactions exist between membranes and fouling materials and depend on the types and density of functional groups on both membranes surfaces and fouling materials, and solubility of molecules of fouling materials. As analytical techniques and knowledge of structural details of NOM progress, the structure-solubility correlations for synthetic compounds can be extended to natural organic matter with modifications to provide a rough assessment on the hydrophobic nature of NOM.

The phenomenon of fouling is very complex and difficult to describe, however four fouling mechanisms can be identified such as pore plugging, cake layer, internal fouling and adsorption.

Membrane fouling mechanisms are not only a function of NOM characteristics but also depend on membrane types and properties. The interactions between NOM and membrane surface influence the fouling phenomena. The role of membrane surface chemistry in NOM fouling is not clearly understood mainly because the chemistry of NOM is still largely unknown (A.R. Roudman *et al.* [8]).

The fouling process is controlled by the interactions between the foulant and the clean and fouled membranes surfaces Li et al. [9]. According to S. Hong *et al.* [11], generally, factors influencing NOM fouling can be classified as characteristics of NOM and membranes, hydrodynamic conditions and chemical composition of feed water. A fundamental understanding of these factors is essential for unravelling the mechanisms of NOM fouling and for developing efficient means for fouling control.

2.4 Influence of cations

The presence of cations has a fundamental effect on the molecular weight, shape and size of humic substances in solution. By high ionic strength the NOM molecule is neutralized and functional groups occurs. The large NOM molecules may reduce size by coiling and can pass more easily through the membrane. Multivalent ions, which are complexed or bound to humic substances, will be even more effective in the collapse or coiling of humic substances molecules than monovalent ions. The presence of calcium is found to lead to NOM-Ca complex formation and may lead to aggregation of organics [11].

Rong et al. [12] investigated the effects of Na^+ and Ca^{2+} on the apparent size distribution and removal efficiency of NOM by dead-end ultrafiltration. The effective size of the NOM was found to significantly reduce by increasing the Na^+ concentration. At much lower concentrations of Ca^{2+}, the size of the NOM was reduced as well, presumably by the mechanism attributed to Na^+. As the concentration of Ca^{2+} was further increased the NOM size increased more, due to aggregation or chelation of humic acid in the NOM due to Ca^{2+}. Ion interaction with NOM also had a significant impact on removal. For example, it is suggested that molecules of the humic matter tend to be linear at a low ionic strength (1 mmol.l-1 NaCl), whereas the structure was fully spherical at higher ionic strength (50 to 100 mmol.l-1) [12]. In addition, multivalent ions such Ca^{2+} and Mg^{2+} interact strongly with the humic substances, leading to the formation of stable complexes or aggregation brought about by the chelating effect of the divalent cations. There is an increase in both size and apparent molecular weight of the humic substances (Rong et al. [12]). The influence of the ionic strength and cations on the NOM configuration is illustrated in figure 6.

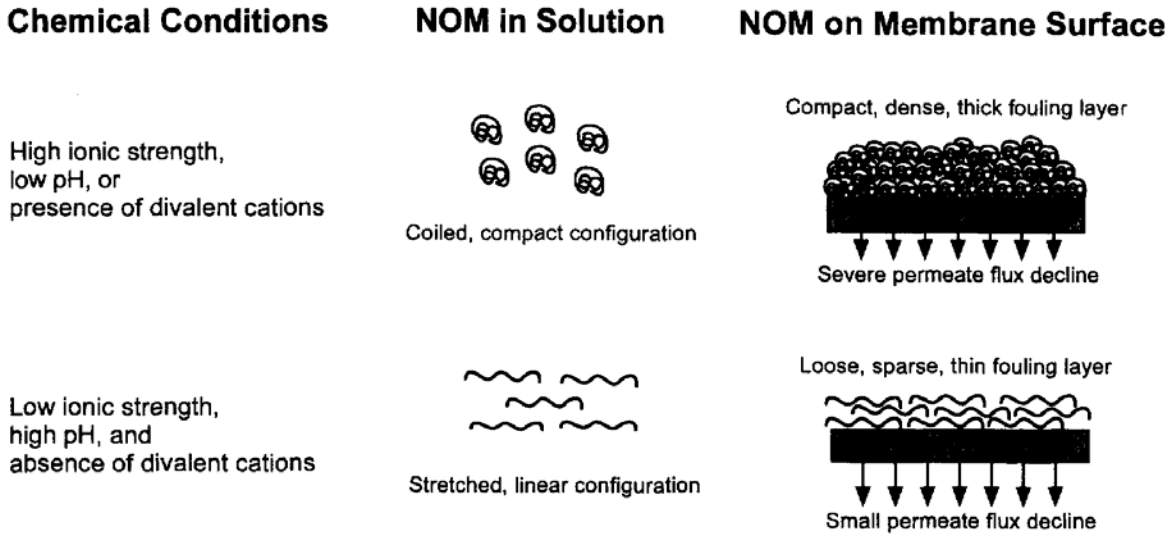


Figure 6, description of the effect of solution chemistry on the conformation of NOM and the effect on permeate flux [10]

According to Li et al. [9] the flux decline following the order of Ca^{2+} > Mg^{2+} > Na^{+} (cation concentration : 1mM), the strongest adhesion of foulant is caused by Ca^{2+} at same concentration. According to Hong et al. [10] membrane fouling increases with increasing electrolyte concentration and addition of divalent cations (Ca^{2+}). The figure 7 shows how the calcium can favorise the NOM deposition on the membrane.

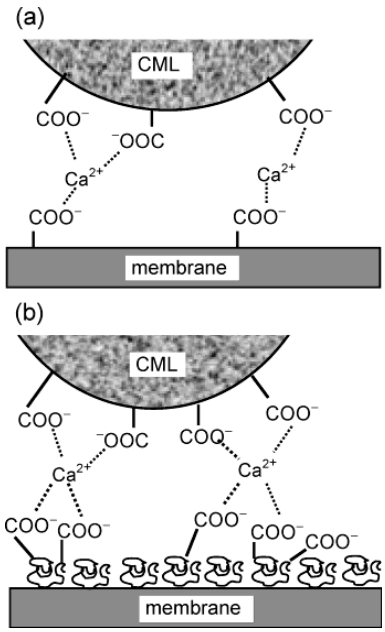


Figure 7, schematic illustration of the influence of Ca2+ on fouling, (a) with clean membrane, (b) with fouled membrane [9]

Calcium results in bridges between negatively charged NOM and the negatively charged membrane surface or NOM fouling the membrane. Consequently, a fouling layer can be formed on the membrane easier. To solve this problem, Hong et al. [10] used a strong chelating agent (EDTA) to destroy NOM-calcium complex bonds which causes fouling layer.

2.5 Fouling prevention

To prevent fouling, different approaches can be use, at different levels of the process.

- Feed water properties. The feed solution can be pre-treated by different methods: pH adjustment when the foulant solubility changes with pH, against scaling addition of complexing agents like EDTA, chlorination against bacteria or pre-filtration to limit particulate fouling.

- Membrane properties. A change of membrane properties can reduce fouling. The use of hydrophilic rather than hydrophobic membranes can help reducing

fouling. Charge membranes can also help especially in presence of charged compounds in the feed.

- Module and process conditions. Fouling can be reduced by increasing the mass transfer coefficient with high flow velocity. Also the use of various kinds of turbulence promoters will reduce fouling.

- Cleaning. Three cleaning methods can be distinguished: hydraulic cleaning, mechanical cleaning and chemical cleaning. Use water methods include back-flushing, alternate pressurising and depressurising and by changing the flow direction at a given frequency. Use mechanical action can only be applied in tubular systems using oversized sponge balls. Chemical cleaning is the most important method for reducing fouling. The chemicals, its concentration and the cleaning time are very important. Thus many chemicals can be used, the most important classes of chemicals are : acids (strong or weak), alkali (NaOH), detergents, enzymes, complexing agents (EDTA) and disinfectants (H_2O_2 and NaOCl)

3 Analytical techniques

3.1 DOC Labor analysis

The DOC Labor is located in Karlsruhe (Germany) and performs liquid chromatography analysis with organic carbon detection. With this technique the following informations are obtained:

Definitions:

- *TOC (Total OC):* Determined in the column bypass. slightly too low TOC-values are possible when samples are rich in particulate bound OC
- *DOC (Dissolved OC)*: As for TOC, but after filtration over a small 0,45µm filter
- *POC (Particulate OC):* Calculated as difference TOC - DOC
- *HOC (Hydrophobic OC):* Calculated as difference TOC - CDOC (CDOC= Chromatographic DOC"). CDOC is the OC value obtained by area integration of the total chromatogram. Therefore, all OC retained on the column is defined as „hydrophobic"
- *SUVA (SAC/DOC):* Additional parameter derived from DOC and SAC
- *SAC :* UV absorbance at 254 nm.

NATURAL ORGANIC MATTER (NOM)

Humics (HS): In LC-OCD measurements a tight definition exists for HS based on retention time, peak shape and SAC. Calibration on the basis of „Suwannee River"Standard IHSS-FA und IHSS-HA. In addition, statistical data are given, like molecular mass distribution (Mn) and aromaticity (SAC/OC).

Building Blocks (HS-Hydrolysates): The HS-fraction is overlain by broad shoulders. Shape, concentration and UV-activity varies. The shoulders represent HS produced from ultrasonification or mild oxidation. This suggests that the shoulders are sub-units („building blocks") of HS, molecular weights between 300-450 g/mol. Building Blocks are possibly created by weathering and oxidation of HS, and cannot be removed by flocculation processes.

LMW Organic-Acids: In this fraction all aliphatic low-molecular-mass organic acids co-elute due to an ion chromatographic effect. A small amount of HS may fall into this fraction and has to be substracted on the basis of SAC/OC rations.

LMW Neutrals: According to theory, only low-molecular weight weakly charged hydrophilic or slightly hydrophobic ("amphiphilic") compounds appear in this fraction, like alcohols, aldehydes, ketones, amino acids. The hydrophobic character

increases with retention time, e.g. pentanol at 120 min, octanol at 240 min. Compounds not eluting before 200 min are rated "hydrophobic" (HOC).

Polysaccharides ("EPS", including Amino Sugars, Polypeptides and Proteins): This fraction is very high in molecular weight (100.000 - 2 Mio. g/mol), are hydrophilic, and not UV-absorbing. Polysaccharides exist only in surface waters.

Inorganic Colloids (found only in UV-Chromatograms): Negatively charged inorganic polyelectrolytes, polyhydroxides and oxidhydrates of Fe, Al or Si are present and are detected by UV light-scattering (Raleigh-effect).

The amounts of each natural organic matter fractions are obtained by calculation with chromatogram which look like the figure 8.

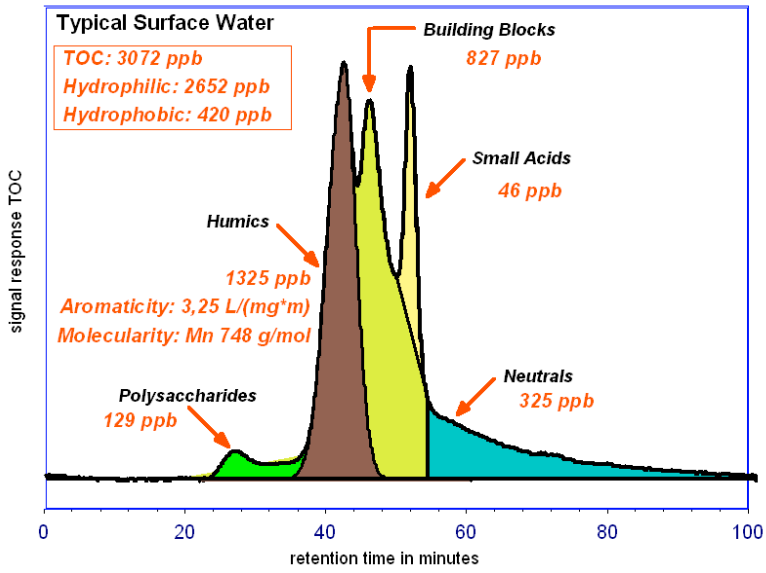


Figure 8, LC-OCD chromatogram

This technique was used in section Spannenburg mass balance. A picture of the DOC-Labor facilities is shown in appendix 1.

3.2 Kiwa lab

During all experiments, the Kiwa lab did calcium analysis, DOC and UV analysis. The specifications are shown in following table.

Table 1, analysis specifications

Parameter	Calcium	Total Organic Carbon	UV in E/m
Method	House method LAM-058, own method	Kiwa-house method LAM-041, own method	
Technique	Inductively Coupled Plasma – Mass Spectrometry (ICP/MS)	Infrared gas analysis	Spectrometry
Detection limit	0.05 mg Ca/l	0.2 mg C/l	0.3 E/m
Measurement uncertainty	5.6% (concentration level 10 mg Ca/l)	11.9% (concentration level 0.5 mg C/l)	3.0% (concentration level 12 E/m benzoate)
Storage	Plastic bottle, 5°C	Glass bottle, 5°C	Glass bottle, 5°C

3.3 X-ray fluorescence spectroscopy

The X-ray fluorescence is an elemental analysis, it works to analyse atoms which has atomic number higher than 8. X-ray excites the atoms and then to get back stable the atoms emit fluorescence radiation. The emited radiations have a frequency and an angle specific of one atom and are detected by cristal detectors. Consequently, we can identify the present elements.

The X-ray fluorescence analysis were performed in the European Membrane Institute (EMI) at the University of Twente in Enschede (Holland) with a Philips PW1480 X-ray spectrometer. The sample is a 4cm diameter membrane disc. Four different cristal detectors were used to analyse the presence of these elements : Ca, Cl, Cu, Fe, K, Mg, Mn, Na, P, S, Ti and Zn. One sample analysis requests one hour.

4 Calcium complex analysis

The aim of this part is to prove the existence of calcium-NOM complexes in solution and measure the presence of the complex. Two techniques were used to determine the part of calcium which is complexed with NOM and the free calcium ion in solution. The first technique is using anionic exchange resin to remove the calcium NOM complex from the solution and then measure the amount of removed complex. The second technique uses a calcium specific electrode to measure the free calcium and by difference with total calcium, determine the amount of complexed calcium.

4.1 Cationic exchange resin

During this experiment, the calcium NOM complexation has been studied with the use of ionic exchange resin. The resin acts to fix the organic matter, the including calcium complexed NOM. The idea is to determine the amount of calcium complexed with NOM because the calcium-NOM complexes are captured by the resin.

4.1.1 Materials

The first experiments were carried out with glass Schott bottles of 1L, magnetic stirring, anionic resin (amberlite IRA 958Cl) which fixes organic matter (more detail in list of chemical) and oven at 10°C.

The waters used came from Spannenburg groundwater and Weesperkarspel surface water and they were sampled before and after softening. The characteristics of these waters are shown in table 2.

Table 2, Source water characteristics

Component	Weesperkarspel		Spannenburg	
	Before ozone	After softening	Before ozone	After softening
PH	7,9	7,9	8,0	8,0
Conductivity (µS/cm)	550	500	670	510
Turbidity (FTU)	0.15	0.15	-	<0.2
Calcium (mg/l)	77	47	100	30
Magnesium (mg/l)	-	-	13	9,7
TOC (ppb)	5594	4861	7449	7222
DOC (ppb)	5433	4615	7215	6951
POC (ppb)	160	246	234	272
Polysaccharides (ppb)	76	76	9	11
Humics (ppb)	2258	1669	3053	2841
Building Blocks (ppb)	1765	1793	2336	2366
Organic acids (ppb)	51	89	139	113
Neutrals (ppb)	1103	811	1504	1317
HOC (ppb)	181	177	174	303
Aromaticity (l/(mg*m))	2,52	2,12	3,24	3,22
SUVA (l/(mg*m)	1,73	1,63	2,47	2,74

- : n/a

As can be observed in table 2, softening removes calcium ions. More calcium removal is found at Spannenburg, resulting also in a higher decrease in conductivity due to softening. The DOC values are higher before softening for both waters. By removing calcium by pellet softening, a small part of the DOC is removed. No significant difference in aromaticity and SUVA values have been found before and after softening. Weesperkarspel is lower in DOC, compared to Spannenburg. However the polysaccharides fraction is significant for Weesperkarspel. Spannenburg water is high in DOC but no significant fraction of polysaccharides could be detected. All other fractions of the DOC are higher for Spannenburg. Spannenburg water has a higher amount of calcium and magnesium.

4.1.2 Methods

The ion exchange experiments used waters shown in table 2. All glass bottles were rinsed with milliQ de-ionised water before use.

Different types of water were used for the ionic exchange experiment (see table 2). 1 L of water was introduced into a glass bottle (1 L). A specific amount of

respectively 150, 300, 600, 800 mg of anionic exchange resin was added. The different experimental conditions are shown in table 3. After wards the samples were put in an oven at 10°C and stirred at 350 rpm during two weeks. After two stirring weeks, the different waters are analysed by ICP-MS for calcium and DOC and UV at Kiwa lab.

The similar experiments were done with addition of calcium chloride as shown in table 3.

Table 3, Experimental conditions for calcium-NOM complex experiments

Water types	Resin weight (mg)	Calcium addition (mg)	Starting dates
Weesperkarspel before ozonation	0	0	21-03-2005
	150	0	
	300	0	
Weesperkarspel after softening	0	0	
	150	0	
	300	0	
Spannenburg before softening	0	0	
	150	0	
	300	0	
	0	0	13-04-2005
	600	0	
	800	0	
Spannenburg after softening	0	0	21-03-2005
	150	0	
	300	0	
	0	75	13-04-2005
	150	75	
	300	75	
	600	75	
	800	75	
	0	175	
	150	175	
	300	175	
	600	175	
	800	175	

4.1.3 Results and Discussion

The results from the performed experiments with Spannenburg and Weesperkarspel waters are shown the figure 9, 10 and 11.

The results of the ion exchange experiment for water from Weesperskarspel is given in figure 9. As a result of resin addition the DOC concentration decreases (over 2 weeks). The results for UV analysis are given in appendix 2. From the figure 9 we observe no decrease in calcium as a function of the resin addition. This indicates that no calcium-NOM complex formation occurs. If complex formation occurs, calcium concentration is expected to decrease together with the DOC.

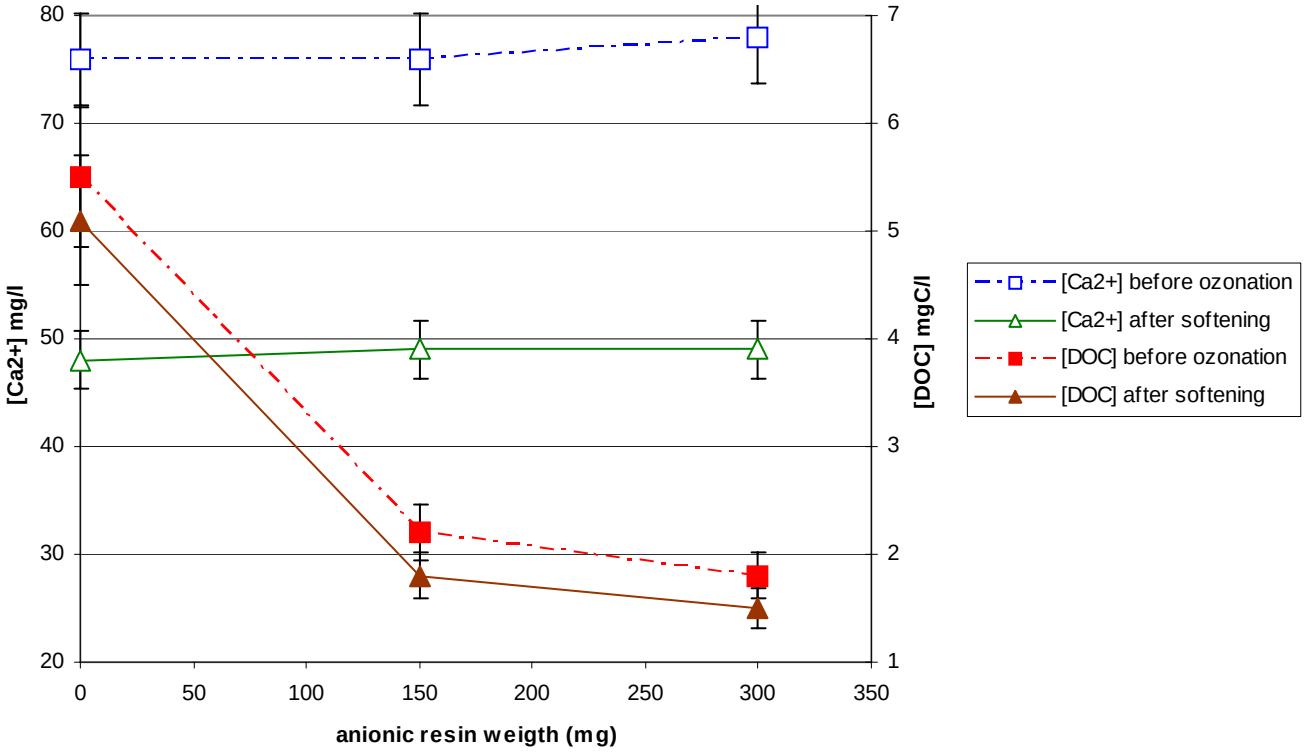


Figure 9, calcium and DOC variation function of the amount of resin with Weesperkarspel water

The figure 10 shows the results of the ionic exchange experiments for water from Spannenburg. As a result of resin addition the DOC concentration decreases (over 2 weeks). The results for UV analysis are given in appendix 2. From figure 10 we observe for the water after softening no decrease in calcium as a function of the resin addition. This indicates that no calcium-NOM complex formation occurs. Calcium concentration would be decreased together with the DOC. A decrease of calcium concentration occurs for Spannenburg water from before softening with addition of anionic resin. This indicates that due to calcium-NOM complex formation. Calcium is eliminated as function of anionic resin addition. To reproduce this result more anionic resin is added (600 and 800 mg). Increased amounts of anionic resin did not result in more reduction of calcium concentration. No explanation for this phenomenon could be found.

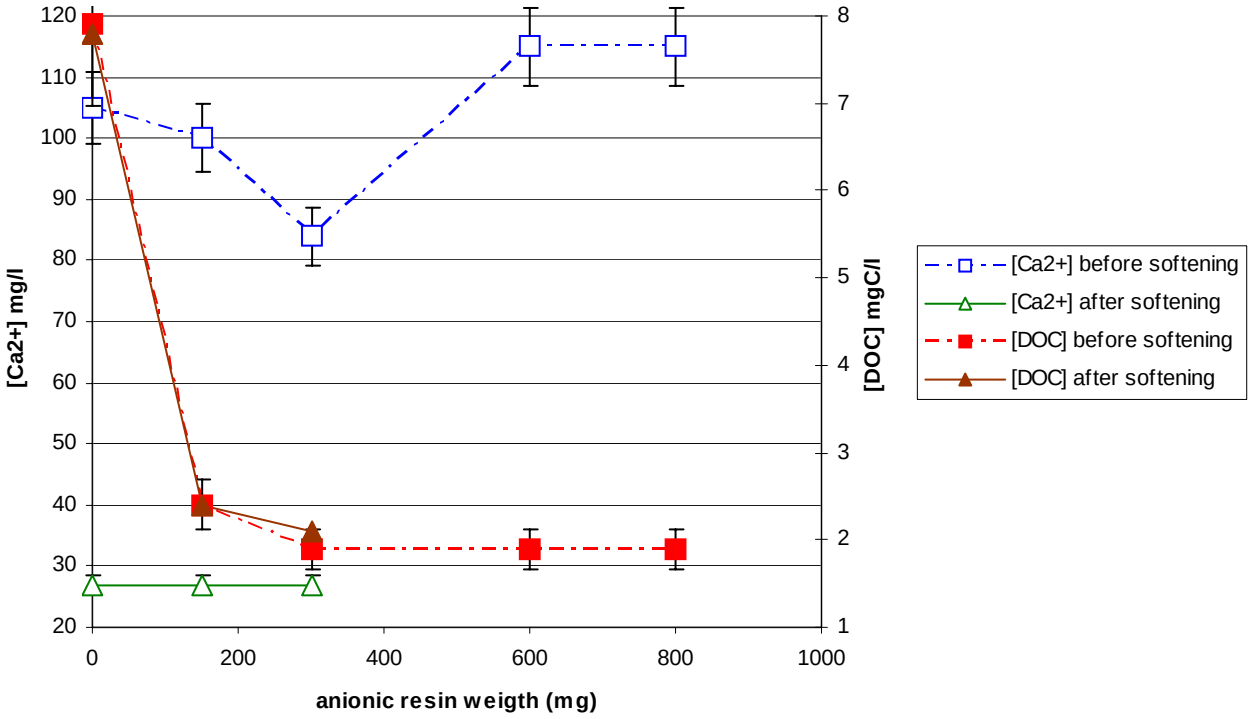


Figure 10, calcium and DOC variation function of the amount of resin with Spannenburg water

According to the results of the figure 10 for the Spannenburg water from before softening, the calcium-NOM complex formation could be linked to the amount of calcium. Therefore, some calcium was added (75 mg and 175mg, see table 3) in water coming from Spannenburg after softening. The results of ionic exchange experiments with calcium addition are shown in figure 11.

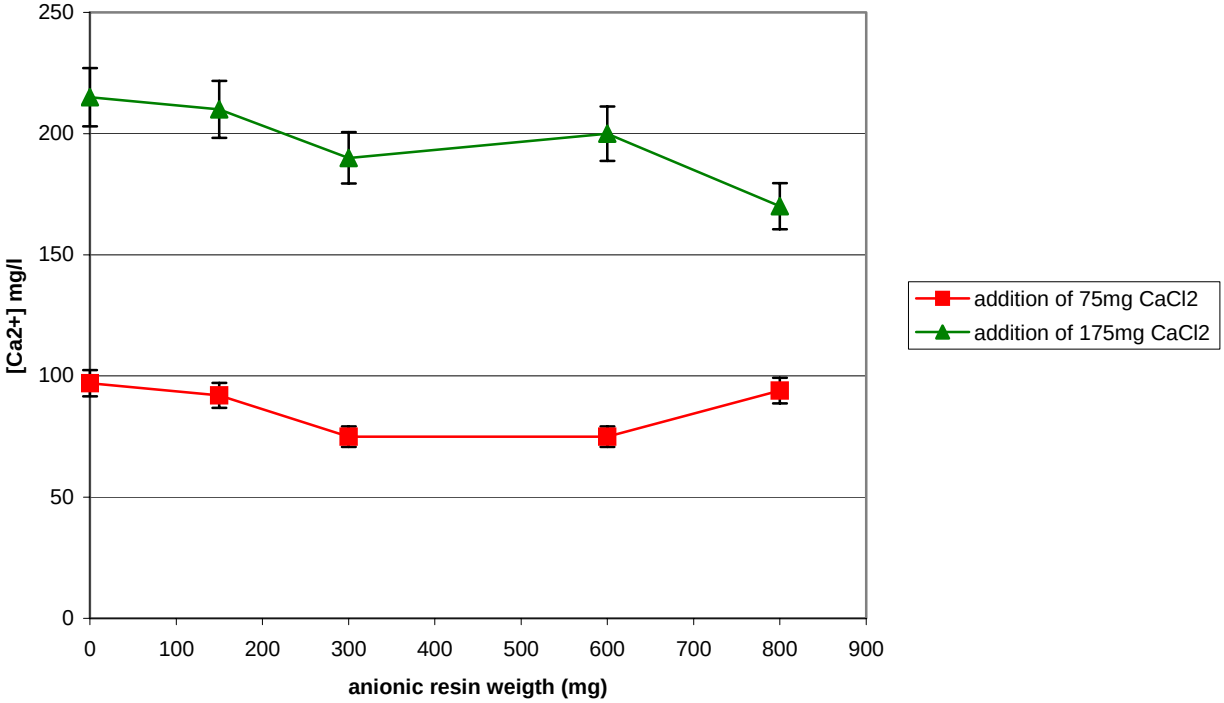


Figure 11, calcium evolution function of the amount of anionic resin for Spannenburg water before softening with calcium addition

The figure 11 shows that a decrease of calcium concentration occurs with addition of anionic resin for Spannenburg water after softening with addition of 175 mg Ca^{2+}. Calcium-NOM complex was formed. For Spannenburg water after softening with addition of 75 mg Ca^{2+}, the calcium concentration decreases with addition of anionic resin but for the highest anionic resin weigth the calcium concentration increases again. This result couldn't be explained.

According to these results a minimum calcium concentration and a minimum DOC concentration are requested for calcium-NOM complex formation. The calcium-NOM complex were observed for calcium concentration above 97 ppm and DOC concentration above 7.9 mgC/l. These results however have to be interpreted carefully because the effects of the resin on the NOM complexation abilities are unknown. The ionic exchange procedure to investigate the calcium-NOM complexation is not really effective.

4.2 Calcium specific electrode

The second technique used to determine the amount of complexed calcium by NOM in solution is the use of a calcium specific electrode. In solution, calcium consist of a free calcium cation fraction and calcium complexed by natural organic matter fraction. The calcium-NOM complex was determined with a calcium specific electrode technique. The electrode measured only the free calcium, while ICP-MS measured the total calcium and the fraction of complexed calcium was determined from the difference. In addition during the filtration process, concentration of components which don't go through the membrane increase close to the membrane surface. So due to this phenomenon the concentrations of NOM and calcium increase on the solution near the membrane surface during the filtration. During concentration polarization, the calcium-NOM complex formation could be forme easier since higher concentrations exist. So to study this phenomenon the solutions were concentrated to obtain complexation condition which is close to the membrane due to concentration polarization.

4.2.1 Materials and Methods

- Materials

This experiment was performed with :

- Orion 97-20 ionplus® calcium combination electrode
- pH/mV meter, Radiometer Copenhagen PHM85
- Rotavapor Heidolph WB 2000 with vacuum pump Edwards

The used waters came from Spannenburg, they were collected before (28th May 2005) and after (8th June 2005) softening. Their characteristics are shown in table 2.

- Calibration

Before each analysis serie the electrode has to be calibrate to obtain the most accurate result. The calibration curves are made up of five or eight points that depend on analysed samples. All standards were prepared with MilliQ water and one standard contains some calcium and also 40ppm of Mg and 20ppm of Na. Adding ions to the milliQ water standard is done to represent real ground water and minimise the the interference effects (the appendix 3 shows the influence of interference ions on the calibration curves). The interference is stronger at low calcium concentration. The

analysis is done with Orion 97-20 ionplus® linked to PHM85. All data is calculated using Microsoft Excel™ spreedsheet. Additional information about the calibration are in the appendix 3.

- Experiments, methods

Three types of experiments were performed with this electrode:

- The first one is the study of the Mg^{2+} and Na^{+} effects on the calibration curves
- The second one is the measure of the amount of calcium-NOM complex which is formed after concentration of the solution by evaporation. The aim of this concentration is to create the filtration condition close to the membrane surface
- The last one is to study the calcium-NOM complex if only the calcium concentration is increased by addition of calcium

➢ Mg^{2+} and Na^{+} effects on the curves

The curves were established with ten points, their concentrations are shown in appendix 3. The analytical conditions are shown in table 4. The calcium chloride, the magnesium sulphate and the sodium chloride used for standard solutions are described in section list of chemicals. All solutions were prepared with MilliQ water.

Table 4, analytical conditions

Curves	Mg concentration (ppm)	Na concentration (ppm)	Analytical dates
A	0	0	14-06-2005
B	0	0	15-06-2005
C	200	400	15-06-2005
D	200	400	16-06-2005
E	20	40	16-06-2005

➢ Evaporation experiments

Two water types were used for this experiment, Spannenburg water from before softening and from after softening. The compositions of the waters which were used for these experiments are shown in table 5. The analyses were done by the Kiwa lab.

Table 5, Spannenburg water compositions

Spannenburg waters	UV (E/m)	NPOC (mg C /L)	Calcium (mg/L)
After softening	20.0	7.1	28
Before softening	21.7	7.5	110

By evaporation different calcium and NOM concentrations will be obtained. Then the amount of calcium-NOM complex will be measured. The electrode measurements provided the free calcium concentrations and by difference with calcium total concentrations which were obtained by ICP-MS analysis, we were able to calculate the calcium fraction which is complexed by NOM in solution. The following equation was used for each sample tested:

$$\% \text{ Complexed Calcium} = [(C_i - C_x) / C_i] \times 100$$

where C_i is the total calcium concentration which is analysed by ICP-MS and C_x is the calcium concentration determined by electrode analysis. The electrode analysis concentrations were calculated using the calibration curves show in section II-1-2. The total calcium concentrations were calculated with concentration factors determined from ecaporation of the water and multiplied by the initial total calcium concentration measured by ICP-MS.

The two water types were concentrated by evaporation of water at 40°C with vacuum. The rotavapor Heidolph WB 2000 with vacuum pump Edwards was used. For each experiment, 400 mL of water was treated according to the following schedule which is presented in figure 12. All obtained samples were stored at 5°C and before analysis were put at ambient temperature.

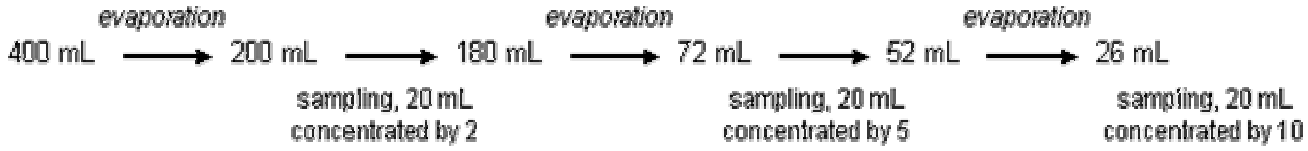


Figure 12, evaporation procedure

Three evaporation runs were done with the procedure and corresponding concnetration factor which is shown in figure 12. Two experiments were carried out with water before softening from Spannenburg. And one experiment was carried out with water after softening from Spannenburg. (see table 6)

Table 6, performed evaporation

Spannenburg water types	Sample name
Before softening	F
	G
After softening	H

➢ Calcium addition

This study was performed with two water types, Spannenburg water from before softening and from after softening. The compositions of the waters which were used for these experiments are shown in table 5.

In a 25mL flask, a small known volume of calcium solution (1 mol/L) was added and then the flask was filled with studied water. For each water type, ten flasks were prepared 24h before the electrode analysis. The final calcium concentrations are summed up in the table 7.

Table 7, calcium concentration in solution after calcium addition

Spannenburg waters	After softening	Before softening
Calcium concentration (mmol/L)	0.7	2.75
	2.90	4.95
	4.94	6.99
	7.94	9.99
	12.9	15.0
	22.9	25.0
	36.7	38.8
	52.7	54.8
	68.7	70.8
	84.7	86.8

4.2.2 Results and discussion

➢ Mg^{2+} and Na^{+} effects on the curves

The figure 13 is showing the curves which were obtained in different analytical conditions described in table 4.

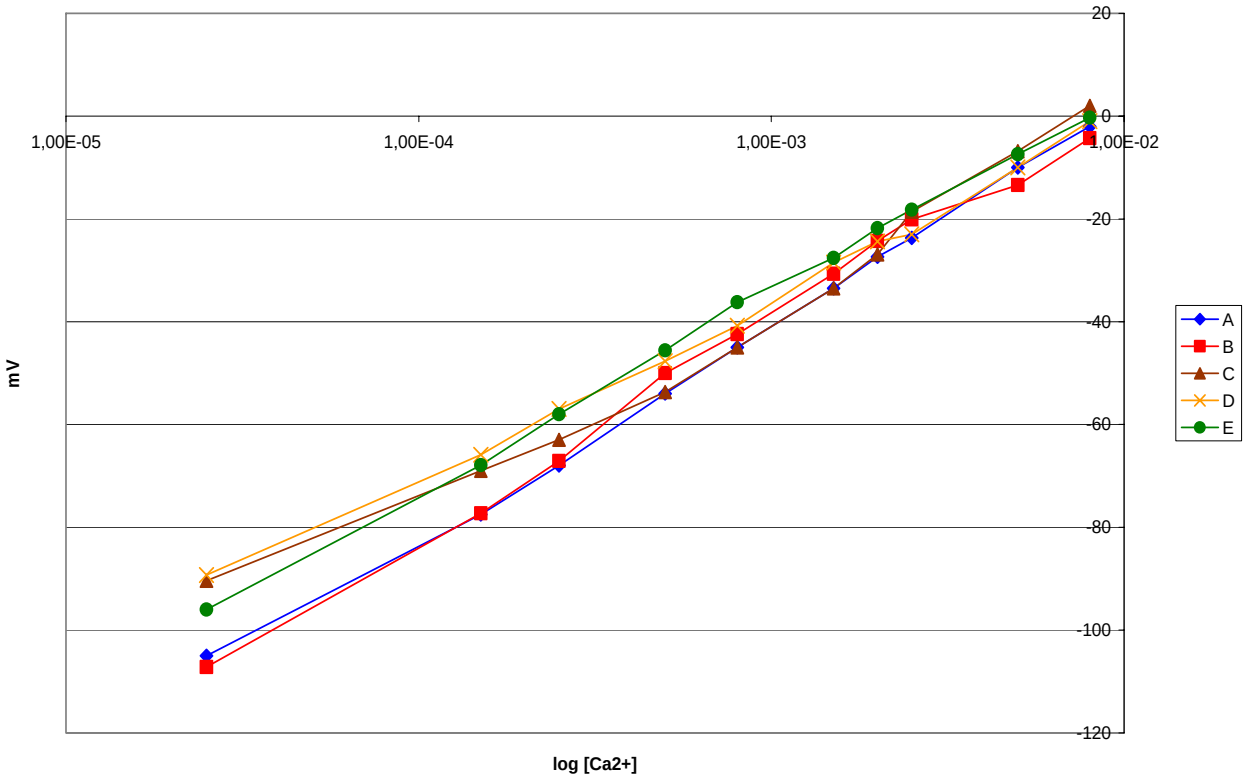


Figure 13, curve comparaison

At low concentrations of calcium (< 2.5 E-4 mol/l), the presence of sodium and magnesium produce three groups of curves, the first A and B, the second C and D and the third E. The slopes of the curves A and B (no Na and Mg) are 18 whereas for the curves C, D (high [Na] and [Mg]) and E (low [Na] and [Mg]) the slopes are 16, 15 and 17. The three lowest slopes are for solutions which contain sodium and magnesium. Moreover the R-square for solution without sodium and magnesium (A and B) are 0.9977 and 0.9941 and for solution which contain sodium and magnesium the R-square decrease to 0.9778 for solution C and D (high [Na] and [Mg]). However for solution E (low [Na] and [Mg]) the R-square is 0.9989. So the presence of sodium and magnesium

modifies the slope of the curves. The high concentration of sodium and magnesium (solution C and D) also disturbs the linearity, according to the R-squared values.

In Spannenburg water the sodium and magnesium concentrations are near 40 ppm and 20 ppm. For this reason, the calibration was done with curve looking like E for the following experiments.

➢ Evaporation experiments

The evaporation experiments were performed with Spannenburg water from before and after softening. The initial solutions did not present any complex between calcium and NOM because no difference was found between ICP-MS and calcium specific electrode calcium concentration results. This was due to a limited electrode accuracy. For each sample the total calcium concentration and the NOM concentration were calculated by a concentration factor. Further details on concentration factor are available in appendix 3. The obtained results are shown in figure 14.

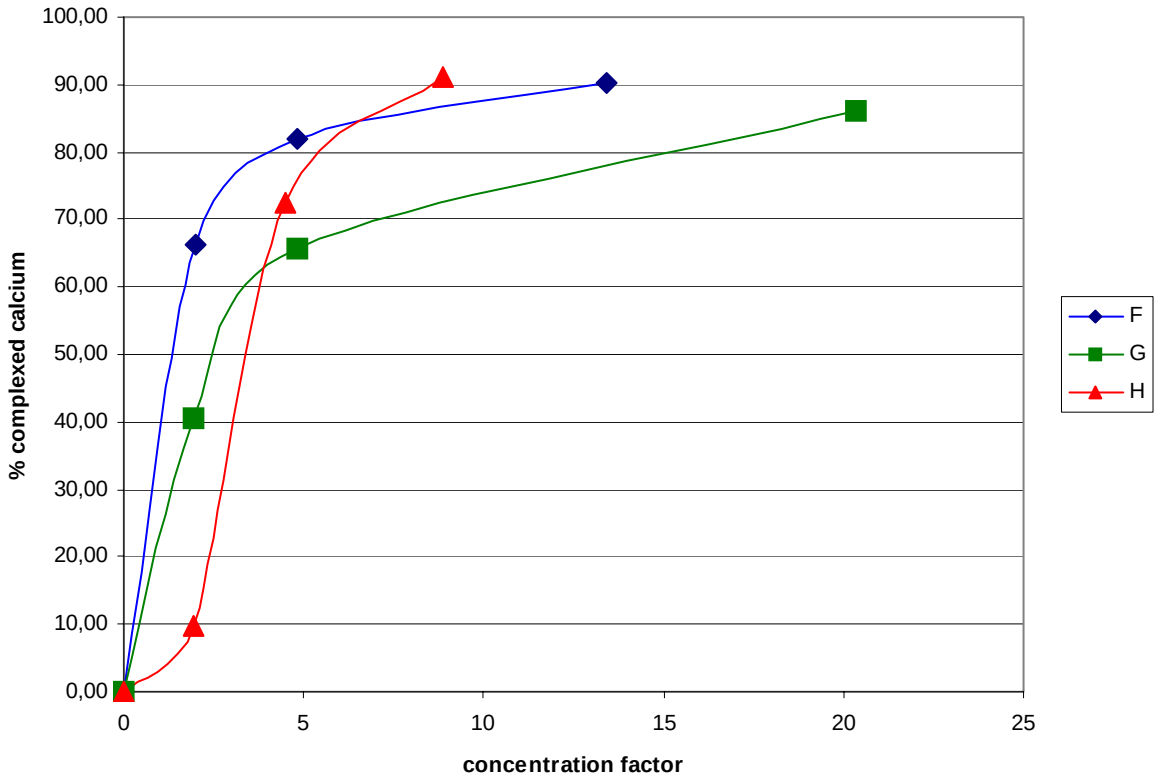


Figure 14, calcium-NOM complex according to the concentration factor

In the figure 14, the difference between the curves F and G shows the non reproducibility of the evaporation process. When the concentration is multiplied by

two by evaporation, we see three different amounts of complexed calcium, 10%, 40% and 65%. Here the difference between the three percentages is the calcium concentration, 10% is linked to 56 ppm of calcium and 40% and 65% are linked to respectively 210-220 ppm of calcium. In this case the calcium concentration is high enough to have an effect on the complexation. That confirms the observation of a calcium concentration threshold to obtain a calcium-NOM complex as was seen in section 4.1. In addition, even if the concentration factor get high like 20, the percentage of complexed calcium doesn't exceed 91%. When the concentrations get higher, the concentration effects on the complexation levelling-off which concentration factor is 5, the percentage of complexed calcium varied between 65 and 82% and when the initial concentrations are multiplied by 10 and more the NOM can't complex more than 90% of calcium which is present in solution whatever the real concentrations of NOM and calcium.

The figure 15 shows the percentage of complexed calcium function of the total calcium concentration in solution after evaporation.

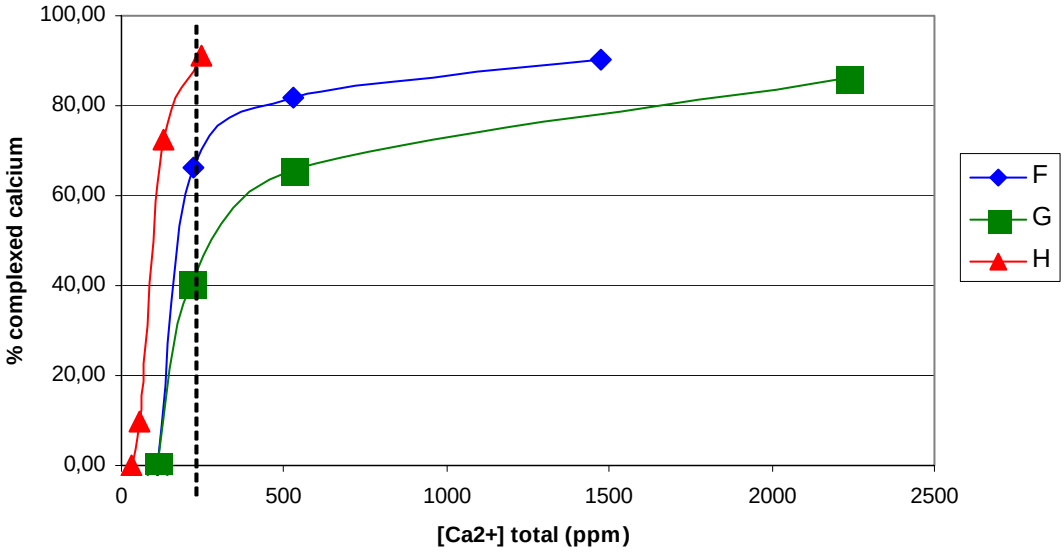


Figure 15, calcium-NOM complexation according to total calcium concentration

In the figure 15, the dotted line shows three points which have the same calcium concentration. The difference between them is the DOC concentration. 91% of complexed calcium is linked to 63 mgC/l and 66% and 41% of complexed calcium are linked to 15 mgC/l. The DOC concentration therefore affects also the amount of complexed calcium by NOM.

During the evaporation at 1.5-2 concentration factor, before the concentration get double, a yellow solid settled at the bottom of the balloon flask. The Ca-NOM complex or NOM get unsoluble.

In addition, the obtained results agree with study of Hong and Elimelech [10]. They investigated the calcium humic acid complexation with the similar technique using a synthetic solution composed of humic acid, $CaCl_2$ and NaCl in DI water. With natural water, we obtained the same curve trend than Hong and Elimelech [10].

The curve which represents the percentage of complexed calcium function of the DOC concentration is in appendix 3.

➢ Calcium addition

In order to only increase the calcium concentration, while maintaining a constant NOM concentration, calcium was added to Spannenburg water from before and after softening. The difference between the total calcium and the free calcium measured by the calcium specific electrode the amount of complexed calcium was determined. The curves obtained with this experiment are shown in figure 16, it presents the free calcium in solution function of the total calcium.

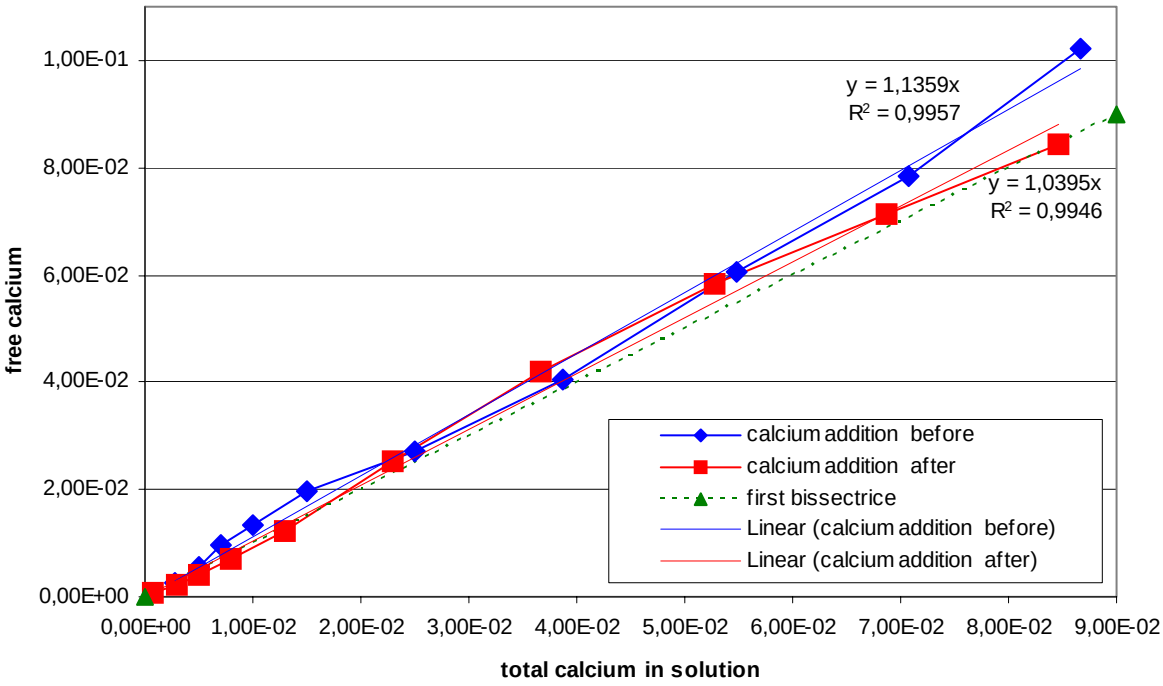


Figure 16, calcium addition effects

The figure 16 shows two linear curves higher than the first bissectrice. The first bissectrice is the curve obtained when total calcium is free in solution. That means the NOM does not complex the calcium because the total calcium is in free cation form in solution. If the calcium had been complexed, the amount of free calcium would have been lower than the total calcium and the curve would be under the first bissectrice and not linear, according to the previous result (see section 4.2.2 evaporation experiment).

According to these results, both concentrations of calcium and NOM influence the complexation equilibrium. There is a minimum calcium concentration and minimum NOM concentration to obtain a complexation. If only the calcium concentration increases at a low NOM concentration, nothing happens. When both calcium and NOM increase the percentage of complexed calcium increase rapidly at the beginning and levels off at higher calcium NOM concentration. The complexation curves that are presented in figure 15 and in appendix 3, can be useful to estimate the amount of complexed calcium by NOM in the boundary layer near the membrane surface where concentration polarisation occurs during filtration. This concentration polarisation has to be calculated, and is done in section 5.1.2.. In this way, the calcium-NOM complex behaviour could be linked to the membrane flux decline.

5 Membrane fouling experiments

Two experiments were performed to study the membrane fouling. The first one is with the Membrane Test Apparatus (MTA). MTA is used to perform some filtration experiments at a laboratory scale. In this part, the influence of the calcium concentration on the flux decline during the nanofiltration process is investigated. With this facilities four experiments have been performed with Spannenburg water at four different calcium concentrations. The second one used the informations from the Spannenburg water treatment pilot and the mass balance was performed for each NOM constituent. The aim of the second experiment was to determine which fraction of the NOM constitutes the deposit on the membrane surface.

5.1 Materials

Membrane

The membranes used in the SEPA cell came from a Trisep 4040 - TS80 - TSA spiral wound membrane elements (more information on Trisep membrane in appendix 4). This membrane is constituted of aromatic polyamide and it is frequently used by Dutch drinking water companies. For small-scale laboratory experiments, pieces of this membrane were cut and stored in 1% NaS_2O_5 solution at 5°C. The used membrane surface was 0.132 m^2 and its MWCO was 200 Da (Cornelissen et al. [7]).

Water used type

The water used for the experiments came from a Dutch drinking water supply company, Vitens N.V. which is located at Spannenburg in the north of the Holland. This ground water is treated as schematically shown in figure 17. Before experiments, the water was stored in jerricans (20L) at 5°C. The characteristiques of these waters are shown in table 2.

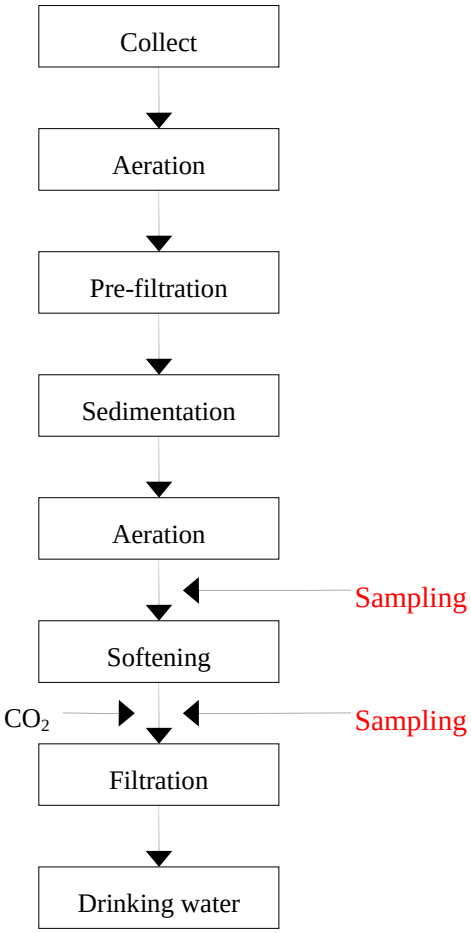


Figure 17, treatment process and collect points, Spannenburg water

The Spannenburg water compositions are shown in Table 2.

The experiments were performed with water from before and after softening in the treatment process as shown in figure 17.

5.2 Set-up

The fouling experiments were carried out with a flat sheet membrane test apparatus (MTA).

The MTA is composed of:

- a tank (volume 100l)
- a pump with a capacity of 600 l/h
- a cartridge filter, which avoid the particle effects, 0.45µm
- a security system for the pump, which stops the pump at 20 bars
- several flow meters (FI), with a precision between 1 and 2 %
- several pressure meters (PI), with a precision of 0.5%
- a cooling system
- a membrane cell called SEPA cell

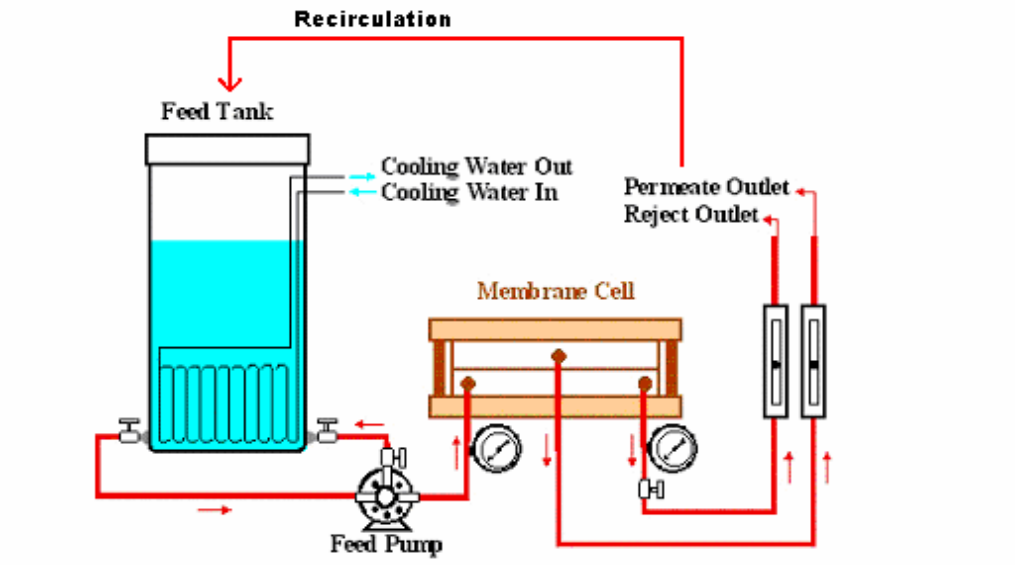


Figure 18, Schematic diagram of the experimental setup

SEPA cell

The membrane is put between the feed spacer and the permeate carrier in the SEPA cell. The maximum pressure and temperature allowed for the cell are 69 bars and 177°C respectively. It is made in stainless steel and the effective membrane area is 132 cm^2. More information is shown in appendix 5. During experiments, the pressure to close the SEPA cell was near 25 bars.

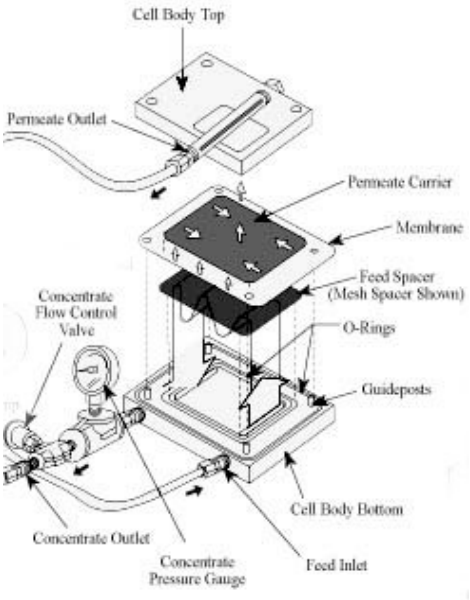


Figure 19, SEPA cell diagram and picture

5.3 Methods

5.3.1 Filtration

- **Membrane characterization and filtration experiments**

Each experiment was performed with a new piece of membrane. The membrane was characterized twice, one before the filtration experiment and one at the end of the filtration experiment. The characterization was done with a 1000 ppm $MgSO_4$ solution. The results obtained were used to determine water transfer coefficient (K_w), recovery (R), and rejection (Ri) of $MgSO_4$.

For the actual filtration experiment, 80L of feed water was used while the water temperature was kept constant at 20°C by a cooling system. The applied pressure for the experiment was 15 bar in order to induce a flux decline (possibly due to fouling). The feed flow was regulated at 27.2 L/h; the concentrate flow was always near to 26 L/h. Experiments were performed during 7 days. The NPOC, U.V. and calcium

concentration in the feed were analysed. Moreover, three times per day, the feed, concentrate and permeate flows, pHs and conductivities were measured.

- **Membrane cleaning experiment**

In order to get an indication of type of fouling, membrane cleaning experiments were carried out. Membrane cleaning with acids are known to remove scaling, while membrane cleaning with alkaline and detergents remove organic fouling. After the experiment with Spannenburg water before softening and calcium addition, cleaning experiments were carried out. The tank was filled with 40L of acid solution of HCl at pH 2. The membrane stayed in the Sepa cell and was cleaned during 1 hour. After the acid washing, the membrane was characterized again with $MgSO_4$. The tank was filled with alkaline solution of NaOH at pH 10 and the cleaning was done. Characterization was carried out. The cleanings were performed one after the other on the same membrane. Solutions were prepared with MilliQ water.

With a membrane that came from the Spannenburg pilot, the same procedure was carried out. The membrane used was from the surrounded membrane module in the appendix 11. However this time, first cleaning was done with nitric acid solution. And on a new piece of membrane, a cleaning with SDS solution at 10mmol/l was done. The solutions were prepared with tap water.

All cleaning experiments were done during one hour, the feed flow was 27.2 l/h and the feed pressure was 0.5 bar. 40l of cleaning solution at 20°C was used.

5.3.2 Analysis

Calcium, DOC and UV were analysed by Kiwa lab.

The fouled membrane obtained after the experiment with the Spannenburg water from before softening was analysed by X-ray fluorescence spectroscopy (XRF) to determine the presence of the following elements : Ca, Cl, Cu, Fe, K, Mg, Mn, Na, P, S, Ti and Zn. The similar analysis was performed with a virgin membrane.

5.4 Performed experiments

The experiments performed on the MTA are summed up in table 8 and table 9.

Table 8, filtration experiments performed on the MTA

Experiment	Water type	DOC (mgC/l)	Calcium (mg/l)	Starting date	Picking up date
1	Before softening with calcium addition	7.6	140	30th May 2005	27th May 2005
2	Before softening	7.5	110	11th May 2005	6th may 2005
3	After softening	7.1	28	26th April 2005	22nd April 2005
4	After softening with calcium removal	7.2	3.90	13th june 2005	8th June 2005

Table 9, cleaning experiments perfomed on the MTA

Used membrane	Cleaning solution	Cleaning date	Experiment
After fouling experiment 1	HCl, pH 2	7th June 2005	5
	NaOH, pH 10	8th June 2005	6
Spannenburg membrane	HCl, pH 2	22nd June 2005	7
	NaOH, pH 10	30th June 2005	8
	SDS, 10mmol/l	5th July 2005	9
	SDS, 10mmol/l, soaking 1 day at 20°C	6th July 2005	10

5.5 Results and Discussion

➢ Membrane filtration experiments

The MTA experiments were performed with Spannenburg water with respectively 140, 110, 28 and 3.9 ppm of calcium. In figure 20, flux curves are shown for MTA filtration experiments for the different types of water with different calcium concentration (details on flux in appendix 6). At lowest calcium concentration, the flux declined only a little and got constant after 20 hours. With the water after softening, the flux declined readily during the experiment. For the two highest calcium concentrations, the flux declined rapidly to 30% and 10% of the initial flux and then they kept stable at really low flux levels. The flux decline seems to be enhanced by calcium cation. That is interesting to note the highest calcium concentration didn't cause the lowest flux decline. The explanation given is that the NOM composition differs between experiments 1 and 2 since the samples were taken at different times. So

it seems that a optimal calcium concentration exist at which flux decline, due to fouling is at its maximum.

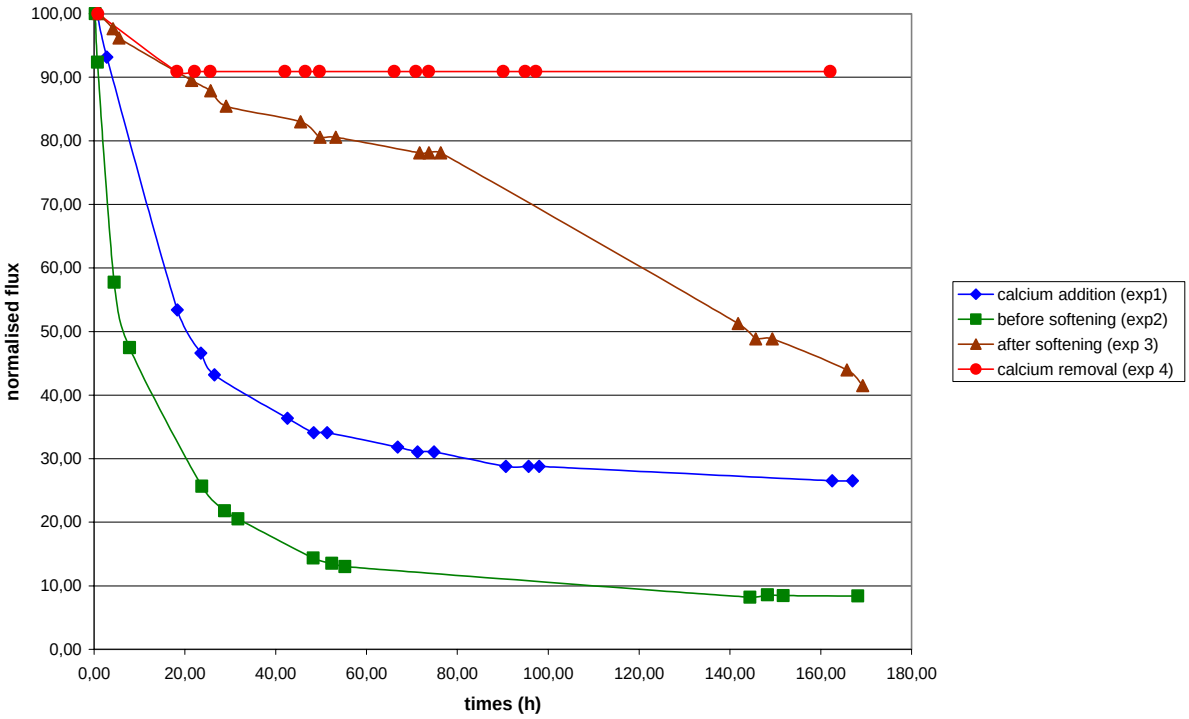


Figure 20, flux at different calcium concentrations

According to Rong et al [12] the presence of calcium has an effect on the NOM size and the ionic strenght which increase with the increasing of the calcium concentration, can cause a change in NOM molecule configurations (also according to Hong et al [10]). So that can result in NOM fouling of the membrane. (see section 2.4)

According to the results in section 4.2.2., in the initial solutions, no calcium-NOM complex was measured but close to the membrane surface, due to the concentration polarisation, the level of NOM and calcium were possibly high enough to form complex. During the nanofiltration process used for this experiment, because the membrane retains the solutes (fraction of calcium and NOM) to a certain extent, there will be an accumulation of retained compounds near the membrane surface. The retained compounds can accumulate at the membrane surface causing the concentration to increase. The concentration polarization is the accumulation of solute at the membrane surface. A factor obtained with the Sherwood relation can express the effects of the concentration polarisation on the solute concentrations for flat sheet cells (see chapter 2.1). It names β-factor. Thus the NOM concentration was multiplied by a β-factor of 1.6-1.76 and the calcium concentration by a β-factor near 1.20. These results were obtained with the Sherwood relation and the beta factors describe the increasing

of the concentration near the membrane surface. All details of the calculation are shown in appendix 7. Moreover, with shown results in section 4.2.2. and the curve of appendix 3 and 9, the Ca-NOM complexed amount has been estimated for each experiment. The calculated calcium and NOM concentrations close to the membrane surface and the complexed calcium percentage are shown in table 10.

For different experiments (with different water types) the DOC and the calcium concentrations at the membrane surface were calculated (given in table 10). The amount of calcium-NOM complex at these concentrations were determined with method described in section 4.2. The calcium and NOM concentrations show in table 10 are the initial concentration multiplied by the β-factor.

Table 10, concentration polarisation effects.

	Beginning			End, after 7 days		
	calculated		%	calculated		%
Experiment	**DOC (mgC/l)**	**Calcium (mg/l)**	**complexed calcium**	**DOC (mgC/l)**	**Calcium (mg/l)**	**complexed calcium**
1	12.23	162.72	50	8.62	145.7	4
2	13.16	131.38	at least 15	7.86	111.65	4
3	11.06	32.21	4	8.53	29.68	1
4	11.59	4.53	0	11.10	4.47	0

Thus for experiment 4 the complexed calcium amount is extremely low and the flux curve is constant and linear. For experiment 3 the flux declined and for the experiments 1 and 2, at the beginning, the complexed calcium amounts are between 15 and 50 % and the flux curve trends are different from experiments 3 and 4. Since the flux declined faster at the beginning. After seven days of experiment, all calcium-NOM percentages were all smaller than 5. Thus on the flux curves (1 and 2) , at the end, the flux was constant because no extra complex was formed and so no effective foulant which declines the flux, was present in solution.

As conclusion, the fouling can be due to the ionic strenght variation caused by calcium concentration variation or/and by the calcium-NOM complex which can modify the size [12], the form and the electronic properties of the NOM and therefore, the potentiel for NOM fouling as well [10]. So the calcium has an effect on the NOM fouling of membrane.

➢ Membrane cleaning experiments

In order to know the type of fouling, cleaning experiments were performed. Acid, alkaline and SDS solutions were used to identify if the flux decline was due to scaling or NOM fouling. The cleaning experiment was performed on a membrane from experiment 1 from MTA and on a membrane from the Spannenburg pilot plant.

About the cleaning experiments, the results are shown in the table 11 and 12.

Table 11, flux/pressure obtained by cleaning of the calcium addition fouling membrane

	Virgin membrane	Fouled membrane	After acidic cleaning (exp 5)	After alkaline cleaning (exp 6)
Flux/feed pressure ($l/h.m^2.bar$)	5.76	1.87	2.23	2.29

Due to the fouling, between the virgin membrane and the fouled membrane the flux is divided by 3 (5.76 get 1.87 $l/h.m^2.bar$). After cleaning less than 10% of the initial flux is obtained and improvement from fouled membrane is very small. The results in table 11 show that the cleaning by acid and base is not effective because respectively only 6 and 7% of the initial flux is regained so the cleaning cannot be considered efficient. The slight flux improvement can be ascribed both to removal of organic fouling and scaling. These results don't give a prove that NOM is the unique fouling type. However according to the beta factors for Ca^{2+} which are 1.25-1.26 (see appendix 7), the concentration close to the membrane does not increase enough to observe a deposit of scaling compound such as $CaCO_3$, $CaSO_4$ or CaC_2O_4. More information (Km, R, Rt, Ri) about this cleaning is available in appendix 10.

A X-ray fluorescence analysis of a fouled membrane surface and a virgin membrane surface were performed. This analysis informs about the kind of atoms which are on the membrane surface and then we can know if scaling is on the membrane. The results of the X-ray fluorescence analysis performed with a membrane from the experiment 2 are in table 12. The raw X-ray fluorescence data are in the appendix 8.

Table 12, X-ray analysis results

Element on virgin membrane	Ti, K, Cl, S, P, Na, Mn, Ca
Element on fouled membrane	Zn, Cu, Mn, Fe, Ti, Ca, K, Cl, S, P, Si, Mg
Element more present on fouled membrane	Si, Ca, Zn, Cu, Mn, Mg, Fe

The table 12 shows the presence of seven elements on the fouled membrane, Si, Ca, Zn, Cu, Mn, Mg and Fe. The feed water concentrations of copper, zinc, iron and manganese are too low to be responsible for scaling. Moreover the magnesium can be

from the $MgSO_4$ solution used for the membrane characterization. The concentrations of S and P are lower on fouled membrane so $CaSO_4$ and $CaPO_4$ scaling cannot be possible in this case. The calcium presence on the fouled membrane can be due to $CaCO_3$, CaC_2O_4 scaling and calcium-NOM complex fouling. According to X-ray laboratory, Si can be SiO_2 on the membrane.

Table 13, flux/pressure obtained by cleaning of the Spannenburg membrane

	Virgin membrane	Fouled membrane	After acidic cleaning (exp 7)	After basic cleaning (exp 8)	After SDS cleaning (exp 9)	After SDS soaking (exp 10)
Flux/feed pressure (l/h.m².bar)	5.88	4.66	4.24	4.62	5.76	5.76

This cleaning experiment was carried out with a fouled membrane from the Spannenburg pilot plant which worked on the Spannenburg water treatment plant. Cleaning experiments with HCl, NaOH and SDS were done on it.

In table 13, due to the fouling the flux is lower for the fouled membrane than for the virgin membrane. The acid and alkaline cleanings do not provide any improvement of the flux, only SDS cleaning presents an significant effect on the flux. As the previous results, the acidic and basic cleanings are not effective. After acidic cleaning the flux gets lower than after fouling possibly because of shrinkage of the membrane structure. It shows that no scaling is present. The flux decreasing can be due to the low solubilities of NOM in acid condition. Then the basic cleaning had to dissolve the NOM deposit but nothing happened and the flux is the same than after fouling. Only the SDS cleaned the membrane which regained its initial flux. There is 2% error between virgin membrane flux and after SDS cleaning flux. The results of SDS cleaning agree with Q. Li *et al* [9]. There is no additioned effect measured from soaking experiment with SDS.

The used membrane was from one of the first element of the pilot and the used water came from the ultrafiltration pilot. So there was no particulate fouling and the scaling probability was extremely low. In addition, the membrane didn't stay long enough in the pilot to suffer from bio-fouling and according to the membrane autopsy study, no bio-fouling was on it.

The calculated beta factors for potential scaling compounds such as as $CaCO_3$, $CaSO_4$ and CaC_2O_4 are for all one. According to the beta factor (β-factor ; 1), the pKs of these compounds and their concentrations, no scaling was able to foul the membrane. Concentrations, beta factors and pKs are available in appendix 11.

5.6 Spannenburg mass balance

The aim of this study is to investigate which fractions of the natural organic matter are responsible for the membrane fouling. A mass balance with comparaison of the feed water composition and the concentrate plus permeat water was done for each fraction. To obtain relevant variations this mass balance was performed directly with information from the water treatment pilot located to Spannenburg. The interest of this experiment performed with this pilot is working with a larger membrane surface than with MTA.

5.6.1 Materials and Methods

The mass balance was performed with information from the nanofiltration pilot located in Spannenburg. It is an online pilot which is working since 11th march 2004, and it is fed with water coming from an ultrafiltration unit.

The pilot is formed of 18 spiral-wound modules of 7.5 m^2, so the total membrane surface is 135 m^2. Trisep 4040-TS80-TSF membranes were used in this pilot, more information is available in appendix 4. The feed flow is between 3 and 3.20 m^3 per hour and the feed pressure is near 6 bars. The recovery is 75% and the water pH is 7.4. The scheme of this pilot is shown in appendix 12. Each hour, temperatures, flows and pressures are registered. Moreover, every months one sample from feed and permeate is picked up for DOC Labor analysis. For this experiment, in March (22.03.2005) and May (10.05.2005), the concentrate was also sampled.

The formulas used are:

$$Qf = Qc + Qp + \Delta_1 \quad (18)$$

$$Qf.Cf = Qc.Cc + Qp.Cp + \Delta_2 \quad (19)$$

Where:

Qf: feed flow

Qc: concentrate flow

Qp: permeate flow

Cf: feed concentration

Cc : concentrate concentration

Cp: permeate concentration

Δ_1 : flow balance variation

Δ_2: mass balance variation

The mass balance was done with these results: TOC, DOC, humics, building blocks, neutrals and acids. There is no polysaccharide in surface water.

5.6.2 Results and Discussion

The results of the flow variation and of the mass balance variation are shown in following tables 14, 15 and 16. The aim of this calculation is to know which fraction of the NOM is deposited on the nanofiltration membrane surface.

Table 14, Flow variation (m^3/h)

	Feed flow	**Concentrate flow**	**Permeate flow**	**Variation (Δ_1)**
22.03.2005	3.14	0.79	2.33	0.02
10.05.2005	3.23	0.80	2.40	0.03

The flow balance is balanced because the variation Δ_1 is due to the accuracies of the different flowmeters.

The table 15 and 16 are obtained by use of the formula 19. Δ_2 shows the mass of NOM fraction deposited on $1m^2$ of membrane during 1 hour. This amount of deposited NOM fraction is divided by Qf.Cf and multiplied by 100 to obtain the percentage of deposited NOM fraction on the membrane function of the total amount of this fraction in the feed water. Thus the "% on membrane " is the percentage of a fraction deposited on the membrane surface. At this result a coefficient was applied to know the percentage of deposited specific fraction function of the TOC. According to the deposited TOC, we can know the participation level of each specific fraction in the deposit, the specific fractions being DOC, humics, building blocks, neutrals and acids.

Table 15, Deposit on Spannenburg membrane, sample date: 22.03.2005

	Δ_2 ($mg/h/m^2$)	**accuracy**	**% on membrane**	**Relative % on membrane (related to TOC)**
TOC	1.92	± 0.31	1.1 ± 0.2	1.10
DOC	3.98	± 0.64	2.4 ± 0.4	2.28
Humics	1.83	± 0.09	2.7 ± 0.1	1.05
Building blocks	2.51	± 0.48	4.0 ± 0.8	1.43
Neutrals	1.12	± 0.18	3.6 ± 0.6	0.64
Acids	0.1	± 0.03	3.7 ± 1.1	0.05

As can be seen in table 15, nearly 1% of the total organic carbon fouls the membrane and 2.43% of the dissolved organic carbon fouls the membrane. Thus the

major part of the total organic carbon which fouls the membrane comes from the dissolved organic carbon and not from the particulate organic carbon. Then, each DOC fraction provides from 2.74% to 4.01% to foul the membrane. In addition, if the percentages of natural organic matter on the membrane are moderated by the amount of each fraction in the TOC, we can see that the most important fraction which fouls the membrane is the building blocks then the humics, the neutrals and the acids.

A similar analysis is done on 10.05.2005, the mass balance is done for each fraction using equation 19 and informations from Spannenburg water treatment pilot.

Table 16, Deposit on Spannenburg membrane, sample date: 10.05.2005

	Δ_2 (mg/h/m²)	accuracy	% on membrane	Relative % on membrane (related to TOC)
TOC	0.42	± 0.07	0.24 ± 0.04	0.24
DOC	1.65	± 0.26	1.0 ± 0.2	0.93
Humics	2.82	± 0.14	4.1 ± 0.2	1.59
Building blocks	0.18	± 0.03	0.27 ± 0.04	0.10
Neutrals	1.07	± 0.17	3.6 ± 0.6	0.60
Acids	0.61	± 0.19	18.3 ± 2.9	0.34

More details on the calculations are available in appendix 13.

In the table 16, 0.24% of the total organic carbon and nearly 1% of the dissolved organic carbon foul the membrane. In addition, each natural organic matter fractions provide from 0.27% to 18.3% to foul the membrane. And the most important foulant is the humics, followed by the neutrals, the acids and the building blocks.

Different results have been obtained from the mass balance experiments. Between the results shown in table 15 and in table 16, one third of membranes were changed in the Spannenburg pilot. Five membranes were changed on 31st March 2005 and one on 12th April 2005. So we cannot compare these two results. However, we can see an effect due to the new membranes. Thus, the comparison of the amount of organic carbon (TOC and DOC) which fouled the membranes, shows that the former membranes (table 15) which are already quite fouled, accepted easier some organic matter extra than the new membranes (table 16). The level of TOC fixed on the membrane was decreased with a factor by 4 with the new membranes. Moreover, the different NOM fractions (humics, building blocks, neutrals and acids) settled in different order in the two cases. Only the neutral deposit doesn't seem to be different for the two experiments, the same quantity of neutral stays on the membrane. At the same time, five times more of acids are deposed on the new membranes. The charge of the membrane which is little fouled, still favours the acid fixation. And when the membrane gets more fouled (table 15) the amount of acids on the membrane decreases. The behaviour of the humics is similar to the one of the acids but the humics

deposit on the membranes is only 1.5 time higher with new membranes (table 16). Contrary to the humics and acids behaviours, new membranes 15 times less of building blocks fouls them.

Thus, a new membrane which is still relatively hydrophobic and charge, seems to fixe more easily the acids and the humics fractions of natural organic matter, and a very few fraction of building blocks foul the membrane. With membranes which are eleven months old, the behaviour of the foulant is different. A low part of humics and acids foul the membranes and more building blocks stay on the membrane. Only the neutrals deposit do not seem to be influenced by the age and the state (hydrophobicity, charge) of the membranes. Thus more globally, less organic matter seems to foul the new membranes and more the membranes get old and fouled, more the organic matter can settle on the membranes.

6 Conclusion

The calcium effects on the NOM fouling has been investigated. By studying the calcium complexation by NOM and the influence of calcium on nanofiltration membrane fouling. In addition the fouling fractions of NOM were determined.

From the calcium-NOM complex experiments, the ion exchange experiment showed that no calcium-NOM complex formation occurred in Weesperskaspel water and for Spannenburg water. The calcium-NOM complex formation could however be linked to the amount of calcium. A minimum calcium concentration of 100 ppm and a minimum DOC concentration of 7.2 ppm are requested for calcium-NOM complex formation. In addition, the results of the ion exchange experiment have to be interpreted carefully because the effects of the resin on the NOM complexation abilities are unknown. The ion exchange procedure to investigate the calcium-NOM complexation is not really effective and reproducible.

The calcium specific electrode experiment confirmed the observation of a calcium concentration threshold of 60 ppm to obtain a calcium-NOM complex. The DOC concentration affects the amount of complexed calcium by NOM. From the evaporation experiments it was shown that the calcium-NOM complex or NOM get quickly unsoluble when their concentrations increase, with a concentration factor of 1.5. Thus both concentrations of calcium and NOM influence the complexation equilibrium. There is a minimum calcium concentration and minimum NOM concentration to obtain a complexation. If only the calcium concentration increases, nothing happens (at investigated concentrations). In addition, when both of them increase the percentage of complexed calcium increase quickly at the beginning and then more the concentrations get higher more the complexed calcium amount increases slowly.

During membrane fouling experiments, the flux was affected by the calcium concentration as well. This fouling can be removed by SDS but not by acid and alkaline cleaning. All membrane fouling experiments were not long enough to suffer from bio-fouling (shorter than 1 week). To prove the absence of scaling, acid cleaning of the membrane, membrane X-ray fluorescence analysis and calculation of the scalant concentration close to membrane surface were performed. Acid is known to remove scaling. In this case however the acid cleaning of the membrane did not provide any improvement of the flux, indicating that no scaling was present. The X-ray fluorescence analysis revealed the occurrence of calcium and silicium on the membrane surface. Calcium peaks could be related to possible calcium-NOM deposits,

while small Si peaks could be due to result of Si in the feed water. The exact nature of the deposit, however, was not clear from X-ray fluuorescence. Filtration resluts in a concentration increase close to the membrane surface. The calculated β-factor which expresses this concentration increase, were between 1.02 and1.26. this indicated that the scalant concentrations close to the membrane were not high enough to cause scaling. If no bio-fouling and no scaling were found on the membrane, the flux decline can be ascribed to NOM fouling.

The calculation of the β-factor showed that the calcium and NOM concentration were increased enough (higher than DOC = 7.2 mgC/l & Ca^{2+} = 100 ppm) by concentration polarisation to obtain a calcium-NOM complex formation. Therefore during filtration process the membrane could be fouled by the calcium-NOM complex present on the membrane surface.

From mass balance work over the Spannenburg pilot, the NOM fractions deposited on the membrane seem to be function of the state of the membrane surface (charge, hydrophobicity, amount of fouling). Only the neutral deposit doesn't seem to be modify by the membrane state.

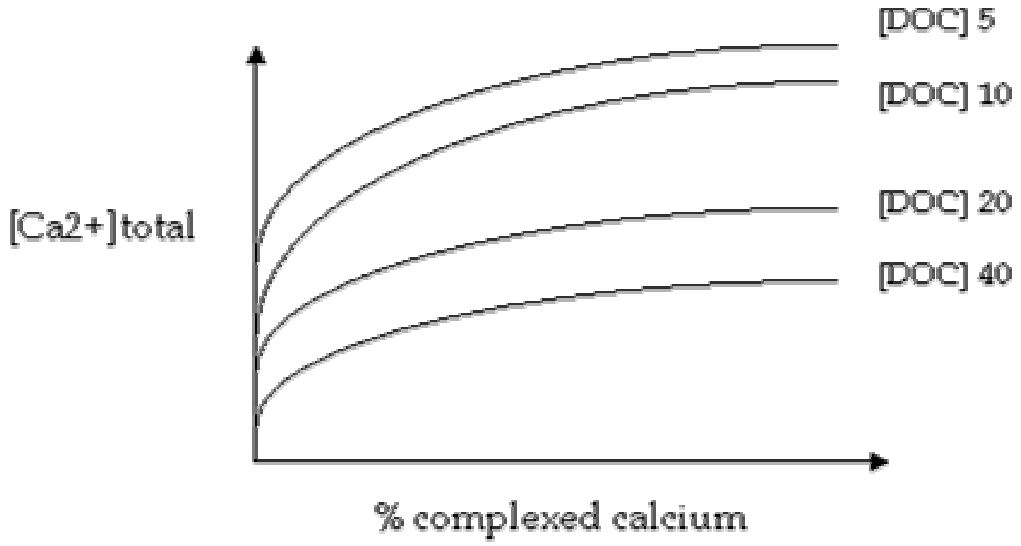
Thus the calcium has an effect on the nanofiltration performance by enhancing the NOM fouling more particularly with the calcium-NOM complex present on the membrane surface.

7 Recommandations

Several improvements need to be realised for further experiments:

- Electrode experiments

- To carry on the study of NOM complexation ability, the analyse of different water types will be interesting
- The evaporation method need to be improved to get more reproducible and to obtain some points extra for the complexation curves
- The total calcium concentration and the DOC concentration should be analysed by ICP-MS and DOC analysis for each solution which comes from evaporation
- Take care about the interference ions effects on the measurements
- To correlate the calcium concentration and the DOC concentration to the percentage of calcium-NOM complex a new method need to be developed. First step, the calcium will be removed from the solution. Then this solution will be concentrated by evaporation to obtain solutions of different NOM concentrations. Third step, for each concentrate some calcium addition will be done and each time the free calcium will be measured by electrode. Thus for a constant NOM concentration, the curve of the percentage of complexed calcium function of the total calcium will be obtained. So a figure looking like the following one could be established.



- MTA and cleaning experiments

- The MTA need to be managed to repair some leaks
- The effect of the velocity on the concentration polarization could be investigated
- By SEM-XPS analysis, the composition of the fouling layer can be measured
- SDS, EDTA, NaOH, etc solutions and mix of them could be tested to clean the membrane.
- The solution of the previous point and the ultra-sonic could be used for soaking the fouled membranes. Then the solutions would be sent to DOC Labor to determine the composition of the fouling layer.
- The soaking method doesn not modify the foulant molecules

LIST OF CHEMICALS

- Magnesium sulphate heptahydrate, Baker analyzed ; J.T. Baker Mallinckrodt Baker B.V., P.O. Box 1, 7400 AA Deventer Holland
- Calcium chloride dihydrate, Baker analyzed ; J.T. Baker Mallinckrodt Baker B.V., P.O. Box 1, 7400 AA Deventer Holland
- Amberlite IRA 958 Cl ; Laboratoire Chaunay, B.P. 48 Chaunay France
- Hydrochloric acid 36-38%, Baker analyzed ; J.T. Baker Mallinckrodt Baker B.V., P.O. Box 1, 7400 AA Deventer Holland
- Sodium hydroxide (pellet), Baker analyzed ; J.T. Baker Mallinckrodt Baker B.V., P.O. Box 1, 7400 AA Deventer Holland
- Sodium Chloride, Baker analyzed ; J.T. Baker Mallinckrodt Baker B.V., P.O. Box 1, 7400 AA Deventer Holland
- SDS Dodecylsulfate Na-salt, technical grad ; Serva, Brunschwig chemie Amsterdam Holland

LIST OF SYMBOLS and ABBREVIATIONS

Symbol	Name	Unit
A	Effective Membrane surface	m^2
β	Concentration polarization coefficient	-
C_c	Concentrate concentration	ppb
C_f	Feed concentration	ppb
C_p	Permeate concentration	ppb
D	Diffusion coefficient	m2/s
d_h	Hydraulic diameter	m
ΔP	Transmembrane pressure	bar
$\Delta\pi$	Osmotic pressure	bar
Δ_1	Flow balance variation	-
Δ_2	Mass balance variation	-
ε	Membrane porosity	-
h	Cell high	m
J_s	Solute flux	$g/m^2/s$
J_w	Water flux	$m^3/m^2/s$
k	Mass transfer coefficient	m/s
k_{dc}	Correction factor	-
K_w	Water transfert coefficient	m/s/bar
l^0_+	Cationic conductance	mhos/eq
l^0_-	Anionic conductance	mhos/eq
l	Cell length	m
l_m	Mesh size	m
M_w	Molecular weight	g/mol
η	Dynamic viscosity	Kg/m.s
ρ	Density	Kg/m^3
Q_c	Concentrate flux	m^3/s
Q_f	Feed flux	m^3/s
Q_p	Permeate flux	m^3/s
Re	Reynolds number	-
Ri	Rejection	%
Rt	Retention	-
S	Recovery	J/mol/K
Sc	Schmit' number	-
Sh	Sherwood number	-
T	Temperature	K
T^0	Temperature	^0C
v	Flow velocity	$m.s^{-1}$
w	Cell width	m
z-	Valence of anion	-
z_+	Valence of cation	-

Abbreviations

DOC	Dissolved organic carbon
EDTA	Ethylenediaminetetraacetic acid
HOC	Hydrophobic organic carbon
HS	Humic substances
LC-OCD	Liquid chromatography - organic carbon detection
LMW	Low molecular weigth
MTA	Membrane test apparatus
NOM	Natural organic matters
POC	Particulate organic carbon
SDS	Sodium dodecylsulfate
SEC	Size exclusion chromatography
SP	Salt passage
TOC	Total organic carbon

REFERENCES

[1] G. Schock & A. Miquel. *Mass transfer and pressure loss in spiral wound modules*. Desalination 64. **1987**, 339-352.

[2] A.R. Da Costa, A.G. Fane, D.E. Wiley. *Spacer characterization and pressure drop modelling in spacer-filled channels for ultrafiltration.* Journal of Membrane Science 87. **1994**, 79-98.

[3] B. Teychene. *Rejection properties of organic compounds by nanofiltration membrane*. Kiwa Nieuwegein (The Netherlands) **2005**.

[4] Perry & Chilton. *Chemical Engineers Handbook*, 5th edition

[5] A. Gorenflo, D. Velázquez-Padron, F.H. Frimmel. *Nanofiltration of a German groundwater of high hardness and NOM content: performance and costs.* Desalination 151. **2002**, 253-265.

[6] C. Liu, S. Caothien, J. Hayes. *Membrane Chemical Cleaning: from art to science.* Scientific andLaboratory Services,Pall Corporation, 25 Harbor Park Dr., Port Washington, NY 11050, USA

[7] E.R. Cornelissen, J. Verdouw, A.J. Gijsbertsen-Abrahamse, J.A.M.H. Hofman. *A nanofiltration retention model for trace contaminants in drinking water sources*. AMTA conference, San Antonio USA. **2004**.

[8] A. R. Roudman; F. A. DiGiano. *Surface energy of experimental and commercial nanofiltration membranes: effects of wetting and natural organic matter fouling*. Journal of Membrane Science 175. **2000**, 61-73.

[9] Q. Li, M. Elimelech. *Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms*. Environmental Science & Technology 38**. 2004**, 4683-4693.

[10] S. Hong; M. Elimelech. *Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes.* Journal of Membrane Science 132. **1997**, 159-181.

[11] F. Frimmel, F. Saravia, A. Gorenflo. *NOM removal from different raw waters by membrane filtration.* Water Science and Technology vol4 no4. **2004**, 165-174.

[12] W. Rong, A.G. Fane, W. Fook-Sin. *Influence of ionic composition on NOM size and removal by ultrafiltration.* Water Science and Technology vol4 no4. **2004**, 197-204.

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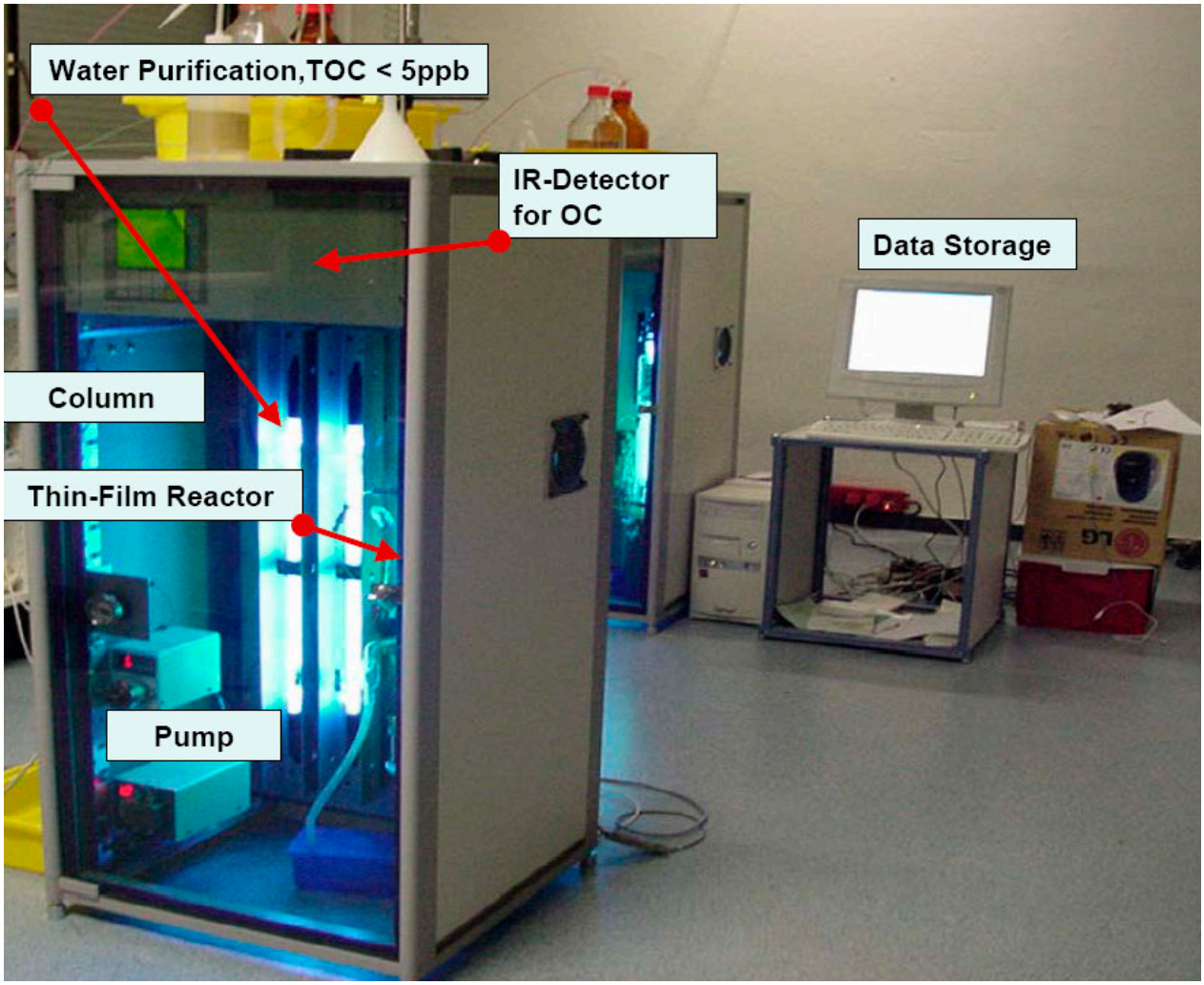
APPENDICES

1. Picture of the 3rd generation of DOC-Labor facilities



2. Cationic exchange resin experiments

Ionic exchange results with Weesperkarspel water

		Analytical results						% removal			Ratio	
Water types	Resin weight (mg)	UV (1/m)		NPOC (mgC/l)		Ca (mg/l)		UV	NPOC	Ca	Ca/NPOC	NPOC/g.resin
Before ozone	0	15	±0.5	5,5	±0.7	76	±4.3	0,00	0,00	0,00	13,82	
	150	2,7	±0.1	2,2	±0.3	76	±4.3	82,00	60,00	0,00		0,022
	300	2,1	±0.1	1,8	±0.2	78	±4.4	86,00	67,27	0,00		0,012
After pellet softening	0	8,8	±0.1	5,1	±0.6	48	±2.7	0,00	0,00	0,00	9,41	
	150	1,5	±0.0	1,8	±0.2	49	±2.7	82,95	64,71	0,00		0,022
	300	1,1	±0.0	1,5	±0.2	49	±2.7	87,50	70,59	0,00		0,012

Ionic exchange results with Spannenburg water

		Analytical results						% removal			Ratio	
Water types	Resin weight (mg)	UV (1/m)		NPOC (mgC/l)		Ca (mg/l)		UV	NPOC	Ca	Ca/NPOC	NPOC/g.resin
After pellet softening	0	20,9	±0.6	7,8	±0.9	27	±1.5	0,00	0,00	0,00	3,46	
	150	3,6	±0.1	2,4	±0.3	27	±1.5	82,78	69,23	0,00		0,036
	300	3	±0.1	2,1	±0.2	27	±1.5	85,65	73,08	0,00		0,019
Before pellet softening	0	21,5	±0.6	7,9	±0.9	105	±5.9	0,00	0,00	0,00	13,29	
	150	3	±0.1	2,4	±0.3	100	±5.6	86,05	69,62	4,76		0,037
	300	2,1	±0.1	1,9	±0.2	84	±4.7	90,23	75,95	20,00		0,020
	0					115	±6.4			0,00		
	600			1,9	±0.2	115	±6.4			0,00		
	800			1,9	±0.2	115	±6.4			0,00		

Water types	Resin weight (mg)	Ca concentration (mg/l)		% Ca removal
After pellet softening with calcium addition (75 mg)	0	97	±5.4	0,0
	150	92	±5.2	5,2
	300	75	±4.2	22,7
	600	75	±4.2	22,7
	800	94	±5.3	3,1
After pellet softening with calcium addition (175 mg)	0	215	±12.0	0,0
	150	210	±11.8	2,3
	300	190	±10.6	11,6
	600	200	±11.2	7,0
	800	170	±9.5	20,9

3. Calcium specific electrode experiments

- Calibration of the calcium specific electrode

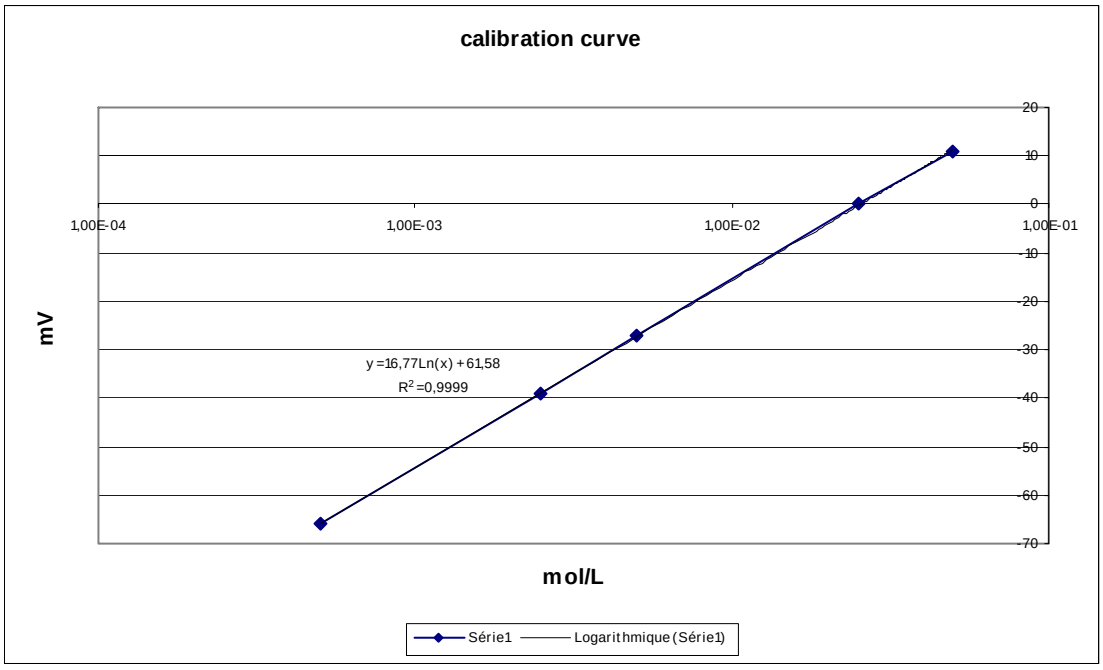
Milivoltage data for each calibration is used to produce the best line of regression line of y = a.ln(x) + b, from which the milivoltage values are converted into calcium concentrations. One new calibration curve was done before each sample series. The concentrations used to analyse samples are shown in following table.

Standard concentration (mol/L) for calcium electrode analysis

Concentration (mol/L)	Calibration with 5 points	Calibration with 8 points
2,50E-04		X
5,00E-04	X	X
2,50E-03	X	X
5,00E-03	X	X
2,50E-02	X	X
5,00E-02	X	X
1,00E-01		X
1,00E+00		X

As an example, calibration curves are similar to the following one.

Calibration curve for calcium electrode analysis



➢ Mg^{2+} and Na^{+} effects on the curves

Concentrations of the ten studied solutions

	Sol1	*Sol2*	*Sol3*	*Sol4*	*Sol5*
Concentration (mol/L)	2,50E-05	1,50E-04	2,50E-04	5,00E-04	8,00E-04
	Sol6	*Sol7*	*Sol8*	*Sol9*	*Sol10*
Concentration (mol/L)	1,50E-03	2,00E-03	2,50E-03	5,00E-03	8,00E-03

Values of the different curves

Concentration (mol/L)	Measured voltage (mV)				
	A	B	C	D	E
2,50E-05	-105	-107,2	-90,4	-89,3	-96
1,50E-04	-77,5	-77,3	-69	-65,9	-67,9
2,50E-04	-68	-67,1	-63	-57	-58
5,00E-04	-54	-50	-53,7	-47,7	-45,6
8,00E-04	-45	-42,4	-45	-40,8	-36,2
1,00E-03	-40	-37	-42,5	-34,8	-34,5
1,50E-03	-33,5	-30,7	-33,5	-28,5	-27,6
2,00E-03	-27,4	-24,3	-26,9	-24,4	-21,8
2,50E-03	-23,7	-20,1	-18,6	-23	-18,2
5,00E-03	-10	-13,4	-6,8	-10	-7,4
8,00E-03	-2	-4,3	2	-1	-0,3

A: curve, 14/06/2005
B: curve, 15/06/2005
C: curve, 15/06/2005 with addition of NaCl 400 ppm and $MgSO_4$ 200 ppm
D: curve, 16/06/2005 with addition of NaCl 400 ppm and $MgSO_4$ 200 ppm
E: curve, 16/06/2005 with addition of NaCl 40 ppm and $MgSO_4$ 20 ppm

➢ Evaporation experiments

1st concentration water before softening, 1st measurement

Calibration curve

Concentration (mol/L)	Measure (mV)
5,00E-04	-52,2
2,50E-03	-26,4
5,00E-03	-16
2,50E-02	10,7
5,00E-02	22,7

y = 16,229Ln(x) + 70,772
R2 = 0,9997

Calculation of percentage of complexed calcium by NOM

Evaporat	Free calcium measurement			pH	Concentration factor	Total calcium (ppm)	Total NPOC (mgC/L)	% Ca^{2+} complexed
	Measure (mV)	Concentration (mol/L)	Concentration (ppm)					
1	-31,3	1,86E-03	74,2	7,17	2	220	15	66,26
2	-27,2	2,39E-03	95,6	7,46	4,8	528	36	81,90
3	-20,6	3,59E-03	143,5	7,2	13,4	1474	100,5	90,26

1st concentration water before softening, 2nd concentration

Calibration curve

Concentration (mol/L)	Measure (mV)
5,00E-04	-66
2,50E-03	-39
5,00E-03	-27
2,50E-02	0
5,00E-02	11

y = 16,77Ln(x) + 61,58
R2 = 0,9999

Calculation of percentage of complexed calcium by NOM

Evaporat	Free calcium measurement			pH	Concentration factor	Total calcium (ppm)	Total NPOC (mgC/L)	% Ca^{2+} complexed
	Measure (mV)	Concentration (mol/L)	Concentration (ppm)					
1	-42	2,08E-03	83,1	7,17	2	220	15	62,22
2	-40	2,34E-03	93,6	7,46	4,8	528	36	82,27
3	-33	3,55E-03	142,1	7,2	13,4	1470	100,5	90,36

2nd concentration water before softening

Calibration curve

Concentration (mol/L)	Measure (mV)
5,00E-04	-66
2,50E-03	-39
5,00E-03	-27
2,50E-02	0
5,00E-02	11

y = 16,77Ln(x) + 61,58
R2 = 0,9999

Calculation of percentage of complexed calcium by NOM

Evaporat	Free calcium measurement			pH	Concentration factor	Total calcium (ppm)	Total NPOC (mgC/L)	% Ca^{2+} complexed
	Measure (mV)	Concentration (mol/L)	Concentration (ppm)					
1	-35	3,15E-03	126,2	7,17	1,93	212	14,5	40,58
2	-29	4,51E-03	180,4	7,46	4,8	528	36	65,83
3	-20	7,71E-03	308,6	7,2	20,35	2239	152,6	86,21

concentration water after softening

Calibration curve

Concentration (mol/L)	Measure (mV)
2,50E-04	-94
5,00E-04	-81
2,50E-03	-55
5,00E-03	-41
2,50E-02	-10
5,00E-02	3
1,00E-01	19
1,00E+00	69

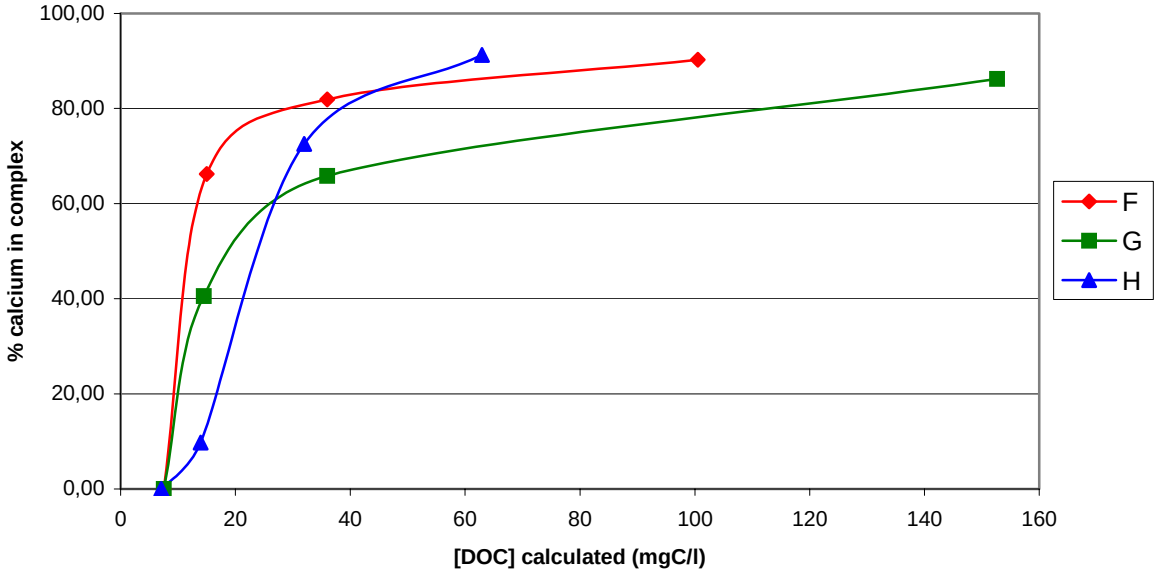
y = 19,449Ln(x) + 64,19

R2 = 0,9968

Calculation of percentage of complexed calcium by NOM

Evaporat	Free calcium measurement			pH	Concentration factor	Total calcium (ppm)	Total NPOC (mgC/L)	% Ca^{2+} complexed
	Measure (mV)	Concentration (mol/L)	Concentration (ppm)					
1	-66	1,24E-03	49,5	7,17	1,96	54,9	13,9	9,74
2	-73	8,64E-04	34,6	7,46	4,5	126,0	32,0	72,57
3	-82	5,44E-04	21,8	7,2	8,86	248,1	62,9	91,23

Calcium-NOM complexation according to DOC concentration



➢ Calcium addition

For these experiments two calibration curves were required.

Calibration curves

First calibration		Second calibration	
Concentration (mol/L)	Measure (mV)	Concentration (mol/L)	Measure (mV)
		2,50E-04	-94
5,00E-04	-66	5,00E-04	-81
2,50E-03	-39	2,50E-03	-55
5,00E-03	-27	5,00E-03	-41
2,50E-02	0	2,50E-02	-10
5,00E-02	11	5,00E-02	3
		1,00E-01	19
		1,00E+00	69
y = 16,77Ln(x) + 61,58 R2 = 0,9999		y = 19,449Ln(x) + 64,19 R2 = 0,9968	

Results of calcium specific electrode

Calcium addition in water before softening			Calcium addition in water after softening		
Total calcium concentration (mol/L)	Potential (mV)	Measured calcium concentration (mol/L)	Total calcium concentration (mol/L)	Potential (mV)	Measured calcium concentration (mol/L)
2,75E-03	-38,5	2,56E-03	7,00E-04	-55,7	9,18E-04
4,95E-03	-25,8	5,46E-03	2,90E-03	-40,8	2,23E-03
6,99E-03	-16,4	9,56E-03	4,94E-03	-31,2	3,96E-03
9,99E-03	-10,8	1,34E-02	7,94E-03	-21,8	6,93E-03
1,50E-02	-4,3	1,97E-02	1,29E-02	-12,1	1,24E-02
2,50E-02	1,1	2,71E-02	2,29E-02	0	2,54E-02
3,88E-02	1,9	4,07E-02	3,67E-02	2,5	4,19E-02
5,48E-02	9,7	6,07E-02	5,27E-02	8,9	5,83E-02

4. Trisep membrane informations

TRISEP corporation membrane

Model : 4040-TS80-TSF

Permeate flow : 2,000 m3/day

Average salt rejection : 99.00 %

Minimum salt rejection : 97.00 %

Membrane type : ANM aromatic polyamide

Configuration : spiral wound, fiberglass outer wrap

Active membrane area : 7.5 m2

Recommended applied pressure : 3 – 14 bar

Maximum applied pressure : 41 bar

Recommended operating temperature : 2 - 45°C

Feed water pH range : 4 – 11

Chlorine tolerance : <0.1 ppm

Maximum feed flow : 4.5 m3/h

Maximum turbidity : 1NTU

Element weight : 7 kg

Length : 1.016 m

Module diameter : 0.102 m

Permeate tube diameter : 0.91 cm

5. Sepa cell characteristics

parameter	**symbol**	**value**	**unit**
width of the cell	b	0,035	m
length of the cell	l	0,146	m
high of the feed side	h	0,001	m
total membrane surface	$A_{tot,SEPA}$	0,027	m^2
active membrane surface	$A_{eff,SEPA}$	0,0132	m^2
length of the feed channel	l_v	0,082	m
width of the feed channel	b_v	0,005	m
thickness of permeat spacer	$d_{sp,SEPA}$	$0,35 . 10^{-3}$	m
high of the feed spacer	h_{vs}	$0,75 . 10^{-3}$	m
porosity of the feed spacer	ε_{vs}	0,91	-
length of the concentrate channel	l_k	$82,20 . 10^{-3}$	m
width of the concentrate channel	b_k	$4,35 . 10^{-3}$	m

6. Raw data from the MTA experiments

Spannenburg, experiment 1

Water before softening with calcium addition

Date	hour	time (h)	volume (L)	temp. (C)	Pf (bar)	Pc (bar)	Qf (l/h)	Qc (l/h)	Qp (l/h)	R	J (L/m²*h)	pHf	pHc	pHp	Gf (µS/cm)	Gc (µS/cm)	Gp (µS/cm)
30/mai	14:40	0,67	80	20,5	15,02	15	27,2	26	1,32	4,9%	100,0	7,903	7,937	6,770	906	938	106
30/mai	16:50	2,83	80	20,5	15,05	15,03	27,2	26	1,23	4,5%	93,1	7,987	7,979	6,793	892	934	78
31/mai	8:20	18,33	80	20,1	15,01	14,99	27,2	26	0,71	2,6%	53,4	7,904	7,915	6,742	837	854	40
31/mai	13:30	23,5	80	19,9	15,01	14,99	27,2	27	0,62	2,3%	46,6	7,910	7,920	6,730	816	833	40
31/mai	16:30	26,5	80	20,4	15,07	15,05	27,2	27,5	0,57	2,1%	43,2	7,725	7,725	6,434	801	811	32
1/juin	8:35	42,58	80	20,6	15,04	15,02	27,2	27,5	0,48	1,8%	36,3	7,487	7,477	6,080	797	816	30
1/juin	14:20	48,33	80	20,3	15,22	15,25	27,2	26	0,45	1,7%	34,1	7,401	7,450	6,049	796	793	29
1/juin	17:20	51,33	80	20,2	15,06	15,04	27,2	27,5	0,45	1,7%	34,1	7,390	7,423	6,160	762	798	33
2/juin	8:50	66,83	80	20,1	15,03	15,01	27,2	27,5	0,42	1,5%	31,8	7,340	7,350	6,040	746	754	28
2/juin	13:15	71,25	80	20,1	15,04	15,02	27,2	27,5	0,41	1,5%	31,0	7,360	7,347	5,920	741	750	28
2/juin	16:50	74,83	80	20,1	15,05	15,03	27,2	27,5	0,41	1,5%	31,0	7,330	7,336	5,910	729	749	28
3/juin	8:40	90,67	80	19,7	15,02	15	27,2	27,5	0,38	1,4%	28,8	7,320	7,365	5,900	711	720	26
3/juin	13:40	95,67	80	20	15,08	15,06	27,2	27,5	0,38	1,4%	28,8	7,324	7,360	6,200	707	716	29
03-juin	16:00	98	80	20,2	15,10	15,08	27,2	27,5	0,38	1,4%	28,8	7,344	7,350	6,400	705	711	27
06-juin	08:30	162,5	80	19,7	15,07	15,05	27,2	27,5	0,35	1,3%	26,5	7,600	7,585	6,606	666	673	25
06-juin	13:00	167	80	20,1	15,04	15,02	27,2	27,5	0,35	1,3%	26,5	7,574	7,607	6,530	661	670	24

Spannenburg, experiment 2

Water before softening

Date	hour	time (h)	volume (L)	temp. (C)	Pf (bar)	Pc (bar)	Qf (l/h)	Qc (l/h)	Qp (l/h)	R	J (L/m²*h)	pHf	pHc	pHp	Gf (µS/cm)	Gc (µS/cm)	Gp (µS/cm)
11/mai	9:00	0,25	80	19,9	15,02	15	27,2	26,5	1,56	5,7%	118,1	8,387	8,385	7,460	650	666	57
11/mai	9:30	0,75	80	19,8	15,04	15,02	27,2	26	1,44	5,3%	109,0	8,413	8,405	8,326	621	630	381
11/mai	13:10	4,42	80	20,1	15,02	15	27,2	26,5	0,90	3,3%	68,2	8,460	8,390	8,300	610	619	298
11/mai	16:35	7,83	80	20,3	15,03	15,01	27,2	26,5	0,74	2,7%	56,0	8,400	8,398	8,292	600	606	285
12/mai	8:30	23,75	80	20,3	15,05	15,03	27,2	27	0,40	1,5%	30,3	8,369	8,390	8,296	555	565	234
12/mai	13:30	28,75	80	20,4	15,02	15	27,2	27	0,34	1,3%	25,7	8,350	8,346	8,324	548	556	217
12/mai	16:25	31,67	80	20,6	15,04	15,02	27,2	27,5	0,32	1,2%	24,2	8,340	8,341	8,204	545	550	207
13/mai	9:00	48,25	80	20,1	15,06	15,04	27,2	25	0,22	0,8%	17,0	8,384	8,380	8,208	520	524	162
13/mai	13:06	52,35	80	19,8	14,98	14,96	27,2	27	0,21	0,8%	16,0	8,378	8,389	8,124	507	514	142
13/mai	16:00	55,25	80	20,5	15,02	15	27,2	27	0,20	0,7%	15,4	8,376	8,391	8,343	501	508	143
17/mai	9:10	144,42	80	20,7	15,06	15,04	27,2	27,5	0,13	0,5%	9,7	8,544	8,556	8,256	425	413	61
17/mai	13:00	148,25	80	20,1	15,03	15,01	27,2	28	0,13	0,5%	10,1	8,558	8,557	8,229	411	413	56
17/mai	16:30	151,75	80	20,2	15,03	15,03	27,2	27,5	0,13	0,5%	10,0	8,528	8,521	7,919	411	410	55
18-mai	08:55	168,17	80	20,4	15,04	15,02	27,2	27,5	0,13	0,5%	9,9	8,552	8,572	7,900	402	406	47

Spannenburg, experiment 3

Water after softening

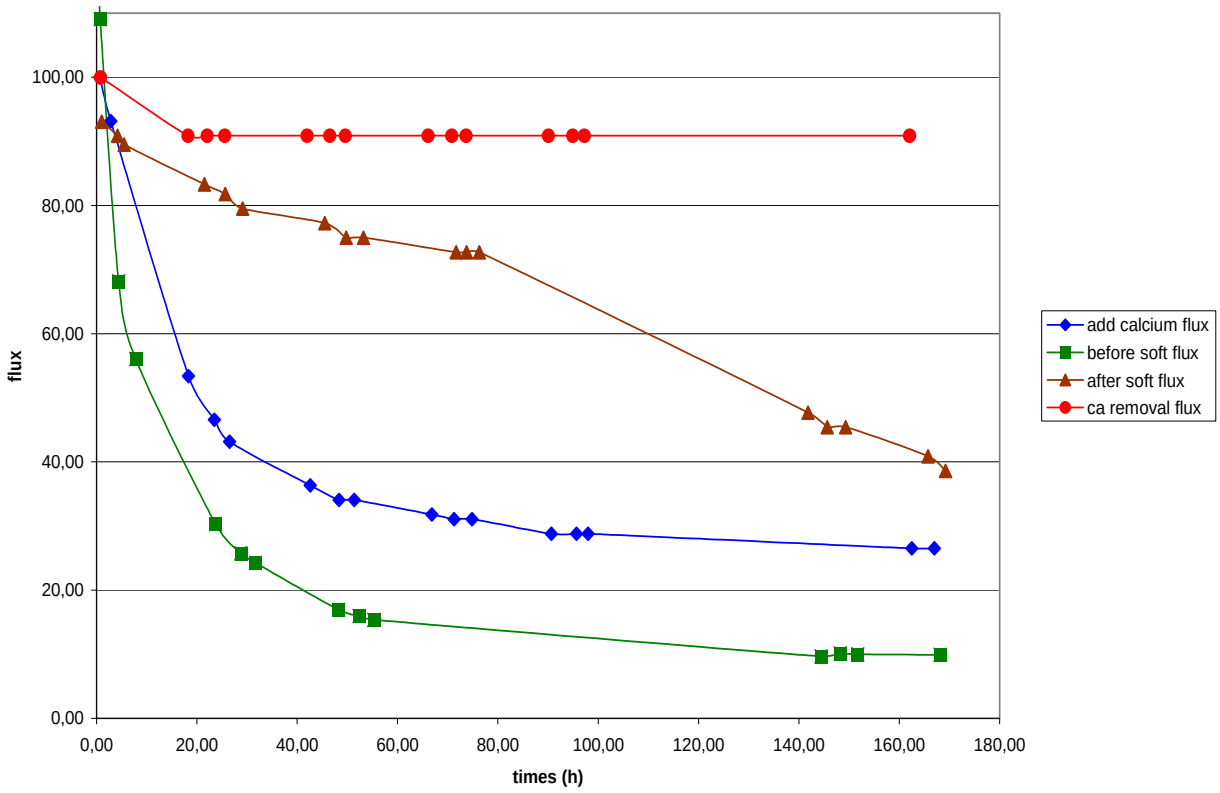
date	hour	times (h)	volume (L)	temp. (C)	Pf (bar)	Pc (bar)	Qf (l/h)	Qc (l/h)	Qp (l/h)	R	J (L/m²*h)	pHf	pHc	pHp	Gf (µS/cm)	Gc (µS/cm)	Gp (µS/cm)
26/avr	12:30	1,00	80	19,9	15,02	15	27,2	26	1,23	4,5%	93,1	8,605	8,653	8,146	503	522	58
26/avr	15:41	4,18	80	20,6	15,04	15,02	27,2	26	1,20	4,4%	90,9	8,602	8,711	8,530	508	533	37
26/avr	17:00	5,50	80	19,7	15,02	15	27,2	26	1,18	4,3%	89,5	8,665	8,730	9,251	508	522	36,5
27/avr	9:00	21,50	80	19,9	15,02	15	27,2	26,5	1,10	4,0%	83,3	8,860	8,878	9,915	506	519	29,3
27/avr	13:10	25,67	80	19,7	15,04	15,02	27,2	26,5	1,08	4,0%	81,8	8,888	8,896	9,929	504	524	27,1
27/avr	16:36	29,10	80	19,7	15,03	15,01	27,2	26,5	1,05	3,9%	79,5	8,886	8,885	9,840	504	523	28
28/avr	9:00	45,50	80	20,1	15,05	15,03	27,2	26,5	1,02	3,8%	77,2	8,888	8,895	9,875	504	519	24,4
28/avr	13:15	49,75	80	19,9	15,07	15,05	27,2	26,5	0,99	3,6%	75,0	8,855	8,820	9,530	496	519	24
28/avr	16:43	53,22	80	19,7	15,06	15,04	27,2	26,5	0,99	3,6%	75,0	8,788	8,830	9,190	498	518	23
29/avr	11:10	71,67	80	19,9	15,03	15,01	27,2	26,5	0,96	3,5%	72,7	8,800	8,810	8,795	502	520	23
29/avr	13:15	73,75	80	19,8	15,07	15,05	27,2	26,5	0,96	3,5%	72,7	8,804	8,800	8,850	505	523	23,1
29/avr	15:50	76,33	80	20,2	15,02	15	27,2	26,5	0,96	3,5%	72,7	8,832	8,795	8,600	504	517	22,2
2/mai	9:20	141,83	80	20,6	15,03	15,01	27,2	26,5	0,63	2,3%	47,7	8,950	8,960	9,050	500	506	20
2/mai	13:10	145,67	80	19,9	15,06	15,04	27,2	26,5	0,60	2,2%	45,4	8,980	8,987	9,200	496	507	20
2/mai	16:50	149,33	80	20,5	15,06	15,04	27,2	26,5	0,60	2,2%	45,4	8,997	8,975	9,2	503	505	19,4
3/mai	9:15	165,75	80	20,4	15,02	15	27,2	26,5	0,54	2,0%	40,9	8,985	8,99	9,305	503	510	20
3/mai	12:45	169,25	80	20	15,05	15,03	27,2	26,5	0,51	1,9%	38,6	8,965	8,985	8,945	497	506	17,4

Spannenburg, experiment 4

Water after softening with calcium removal

Date	hour	time (h)	volume (L)	temp. (C)	Pf (bar)	Pc (bar)	Qf (l/h)	Qc (l/h)	Qp (l/h)	R	J (L/m²*h)	pHf	pHc	pHp	Gf (µS/cm)	Gc (µS/cm)	Gp (µS/cm)
13/juin	15:35	0,83	80	19,6	15,04	15,02	27,2	26,5	1,32	4,9%	100,0	7,700	7,670	7,200	614	638	53
14/juin	9:00	18,25	80	19,9	15,01	14,99	27,2	26,5	1,20	4,4%	90,9	7,900	7,890	7,900	613	640	23
14/juin	12:50	22,08	80	20,4	15,03	15,01	27,2	26,5	1,20	4,4%	90,9	7,900	7,910	7,870	615	636	19,8
14/juin	16:20	25,58	80	19,8	15,04	15,02	27,2	26,5	1,20	4,4%	90,9	7,950	7,945	7,880	610	638	18,7
15/juin	8:45	42,00	80	20	15,01	14,99	27,2	27	1,20	4,4%	90,9	7,908	7,900	8,024	616	640	17,2
15/juin	13:15	46,50	80	20,6	15,04	15,02	27,2	27,5	1,20	4,4%	90,9	8,032	7,963	8,001	611	633	16,9
15/juin	16:22	49,62	80	20,3	15,22	15,25	27,2	26,5	1,20	4,4%	90,9	7,930	7,941	8,016	614	629	20,4
16/juin	8:50	66,08	80	20,2	15,06	15,04	27,2	26,5	1,20	4,4%	90,9	7,930	7,910	7,740	611	634	16,4
16/juin	13:35	70,83	80	20,1	15,03	15,01	27,2	26,5	1,20	4,4%	90,9	7,937	7,950	7,820	612	632	16
16/juin	16:25	73,67	80	20,1	15,04	15,02	27,2	26,5	1,20	4,4%	90,9	7,920	7,900	7,840	611	634	19,4
17/juin	8:50	90,08	80	20,1	15,05	15,03	27,2	26,5	1,20	4,4%	90,9	7,960	7,960	7,870	609	636	17,2
17/juin	13:40	94,92	80	19,7	15,02	15	27,2	26,5	1,20	4,4%	90,9	7,961	7,962	7,860	593	632	16,4
17/juin	16:00	97,25	80	20	15,08	15,06	27,2	26,5	1,20	4,4%	90,9	7,962	7,910	7,950	609	633	16,7
20-juin	8:50	162,08	80	20,2	15,10	15,08	27,2	26,5	1,20	4,4%	90,9	7,953	7,900	7,680	607	638	27,1

Curve of the non normalized flux



7. Determination of the beta factor (β) with the Sepa cell.

Used equations :

$$\beta = \frac{C_m - C_p}{C_b - C_p} \cong \frac{C_m}{C_f} \equiv \exp\left(\frac{J_w}{k_m}\right)$$

$$Sh = \frac{k_m d_h}{D} = 0.664 \cdot k_{dc}\,\mathrm{Re}^{0.5} \cdot Sc^{0.33}\left(\frac{2d_h}{l_m}\right)^{0.5}$$

$$\mathrm{Re} = \frac{\rho v d_h}{\eta}$$

$$Sc = \frac{\eta}{\rho D}$$

$$v = \frac{Q_f}{hw\varepsilon}$$

$$d_h = \frac{4hwl}{A_m}$$

$$D = 8.76 * 10^{-9} * M_w^{-0.48}$$

$$k_{dc} = 1.654(d_f/h)^{-0.039}\,\varepsilon^{0.75}\,(\sin\theta/2)^{0.086}$$

h	1,00E-03	m
w	3,50E-02	m
ε	0,91	
Q_f	7,6E-06	m^3/s
l	1,46E-01	m
l_m	2.5E-3	m
A_m	1,40E-02	m^2
ρ	9,98E+02	kg/m^3
η	1,00E-03	kg/m.s
M_w *humic*	1,00E+03	g/mol
M_w *building blocks*	4,00E+02	g/mol
J_w	variable	$m^3/s.m^2$
θ	95	°
T	298	K
$D\ Ca^{2+}$	1.58E-9	m^2/s

In the case of the Sepa cell in the MTA, the following results were obtained :

v = 2.37E-01 $m.s^{-1}$

d_h = 1.46E-03

D_{humics} = 3.18E-10

$D_{building\ blocks}$ = 4.94E-10

Re = 346

Sc_{humics} = 3150

$Sc_{building\ blocks}$ = 2030

Sc_{Ca2+} = 633

The Sh value can be determined and then for each flux the beta factor values.

Sh_{humics} = 289

$Sh_{building\ blocks}$ = 250

Sh_{Ca2+} = 170

$k_{m\ humics}$ = 6.30E-05

$k_{m\ building\ blocks}$ = 5.45E-05

$k_{m\ Ca2+}$ = 1.85E-04

Beta factor and concentration for water with calcium addition

		Beta factor β						Concentration on membrane surface	
Times (h)	Flux (l/m².h)	humics	building blocks	CaC_2O_4	$CaCO_3$	$CaSO_4$	Ca^{2+}	DOC (mgC/l)	Ca^{2+} (ppm)
0,67	99,96	1,55	1,67	1,25	1,26	1,25	1,16	12,23	162,72
2,83	93,15	1,51	1,61	1,23	1,24	1,23	1,15	11,84	161,06
18,33	53,39	1,27	1,31	1,13	1,13	1,12	1,08	9,80	151,71
23,50	46,57	1,23	1,27	1,11	1,11	1,11	1,07	9,49	150,16
26,50	43,17	1,21	1,25	1,10	1,10	1,10	1,07	9,33	149,39
42,58	36,35	1,17	1,20	1,09	1,09	1,08	1,06	9,03	147,87
48,33	34,08	1,16	1,19	1,08	1,08	1,08	1,05	8,94	147,37
51,33	34,08	1,16	1,19	1,08	1,08	1,08	1,05	8,94	147,37
66,83	31,81	1,15	1,18	1,07	1,08	1,07	1,05	8,84	146,86
71,25	31,05	1,15	1,17	1,07	1,07	1,07	1,05	8,81	146,70
74,83	31,05	1,15	1,17	1,07	1,07	1,07	1,05	8,81	146,70
90,67	28,78	1,14	1,16	1,07	1,07	1,07	1,04	8,72	146,19
95,67	28,78	1,14	1,16	1,07	1,07	1,07	1,04	8,72	146,19
98,00	28,78	1,14	1,16	1,07	1,07	1,07	1,04	8,72	146,19
162,50	26,51	1,12	1,14	1,06	1,06	1,06	1,04	8,62	145,70
167,00	26,51	1,12	1,14	1,06	1,06	1,06	1,04	8,62	145,70

Beta factor and concentration for water before softening

		Beta factor β						Concentration on membrane surface	
Times (h)	Flux (l/m².h)	humics	building blocks	CaC_2O_4	$CaCO_3$	$CaSO_4$	Ca^{2+}	DOC (mgC/l)	Ca^{2+} (ppm)
0,25	118,06	1,68	1,83	1,31	1,31	1,30	1,19	13,16	131,38
0,75	109,05	1,62	1,74	1,28	1,28	1,27	1,18	12,61	129,61
4,42	68,16	1,35	1,42	1,17	1,17	1,16	1,11	10,37	121,88
7,83	56,04	1,28	1,33	1,13	1,14	1,13	1,09	9,79	119,68
23,75	30,29	1,14	1,17	1,07	1,07	1,07	1,05	8,66	115,13
28,75	25,75	1,12	1,14	1,06	1,06	1,06	1,04	8,48	114,34
31,67	24,23	1,11	1,13	1,06	1,06	1,05	1,04	8,42	114,08
48,25	16,96	1,08	1,09	1,04	1,04	1,04	1,03	8,13	112,84
52,35	15,98	1,07	1,08	1,04	1,04	1,04	1,02	8,09	112,68
55,25	15,37	1,07	1,08	1,04	1,04	1,03	1,02	8,07	112,57
144,42	9,69	1,04	1,05	1,02	1,02	1,02	1,01	7,85	111,62
148,25	10,15	1,05	1,05	1,02	1,02	1,02	1,02	7,87	111,69
151,75	10,00	1,05	1,05	1,02	1,02	1,02	1,02	7,87	111,67
168,17	9,92	1,04	1,05	1,02	1,02	1,02	1,02	7,86	111,65

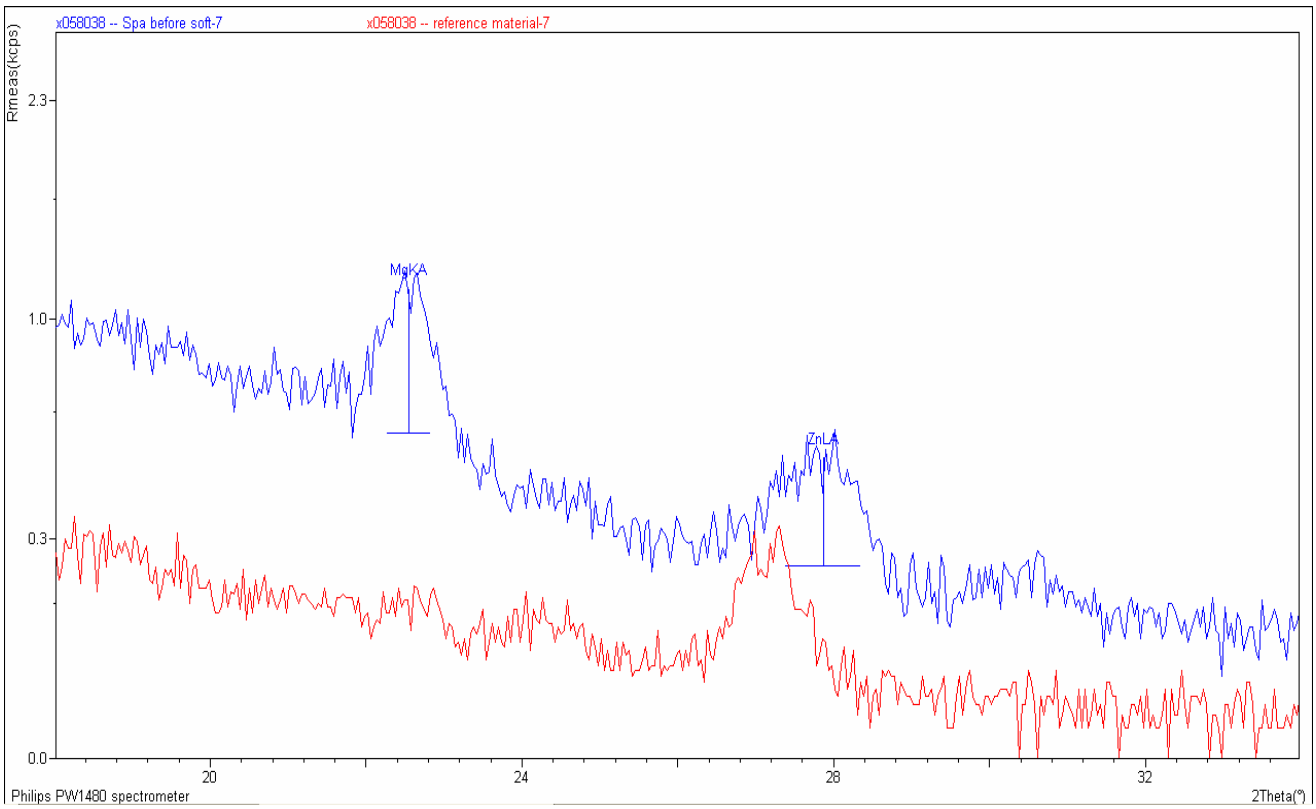
Beta factor and concentration for water before softening

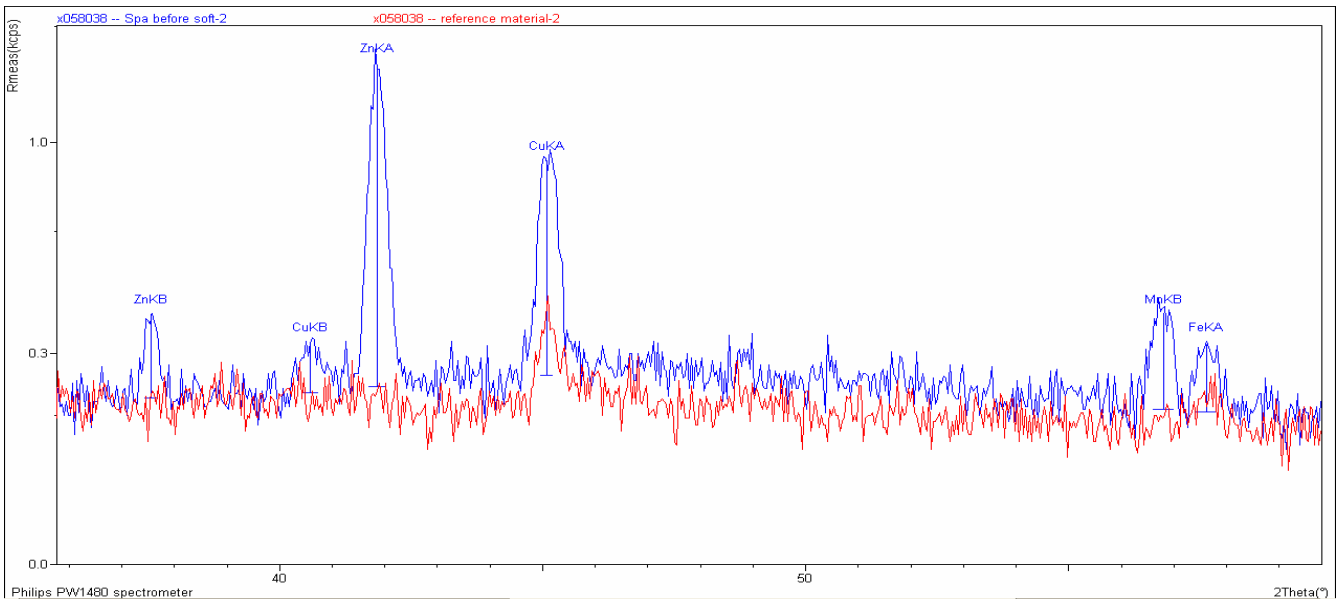
		Beta factor β						Concentration on membrane surface	
Times (h)	Flux (l/m².h)	humics	building blocks	CaC_2O_4	$CaCO_3$	$CaSO_4$	Ca^{2+}	DOC (mgC/l)	Ca^{2+} (ppm)
1,00	93,07	1,51	1,61	1,23	1,24	1,23	1,15	11,06	32,21
4,18	90,87	1,49	1,59	1,23	1,23	1,22	1,15	10,94	32,10
5,50	89,51	1,48	1,58	1,22	1,23	1,22	1,14	10,87	32,04
21,50	83,30	1,44	1,53	1,21	1,21	1,20	1,13	10,56	31,74
25,67	81,79	1,43	1,52	1,20	1,20	1,20	1,13	10,48	31,67
29,10	79,52	1,42	1,50	1,20	1,20	1,19	1,13	10,37	31,56
45,50	77,24	1,41	1,48	1,19	1,19	1,18	1,12	10,26	31,45
49,75	74,97	1,39	1,47	1,18	1,19	1,18	1,12	10,15	31,34
53,22	74,97	1,39	1,47	1,18	1,19	1,18	1,12	10,15	31,34
71,67	72,70	1,38	1,45	1,18	1,18	1,17	1,12	10,04	31,24
73,75	72,70	1,38	1,45	1,18	1,18	1,17	1,12	10,04	31,24
76,33	72,70	1,38	1,45	1,18	1,18	1,17	1,12	10,04	31,24
141,83	47,71	1,23	1,28	1,11	1,11	1,11	1,07	8,91	30,08
145,67	45,44	1,22	1,26	1,11	1,11	1,10	1,07	8,81	29,98
149,33	45,44	1,22	1,26	1,11	1,11	1,10	1,07	8,81	29,98
165,75	40,89	1,20	1,23	1,10	1,10	1,09	1,06	8,63	29,78
169,25	38,62	1,19	1,22	1,09	1,09	1,09	1,06	8,53	29,68

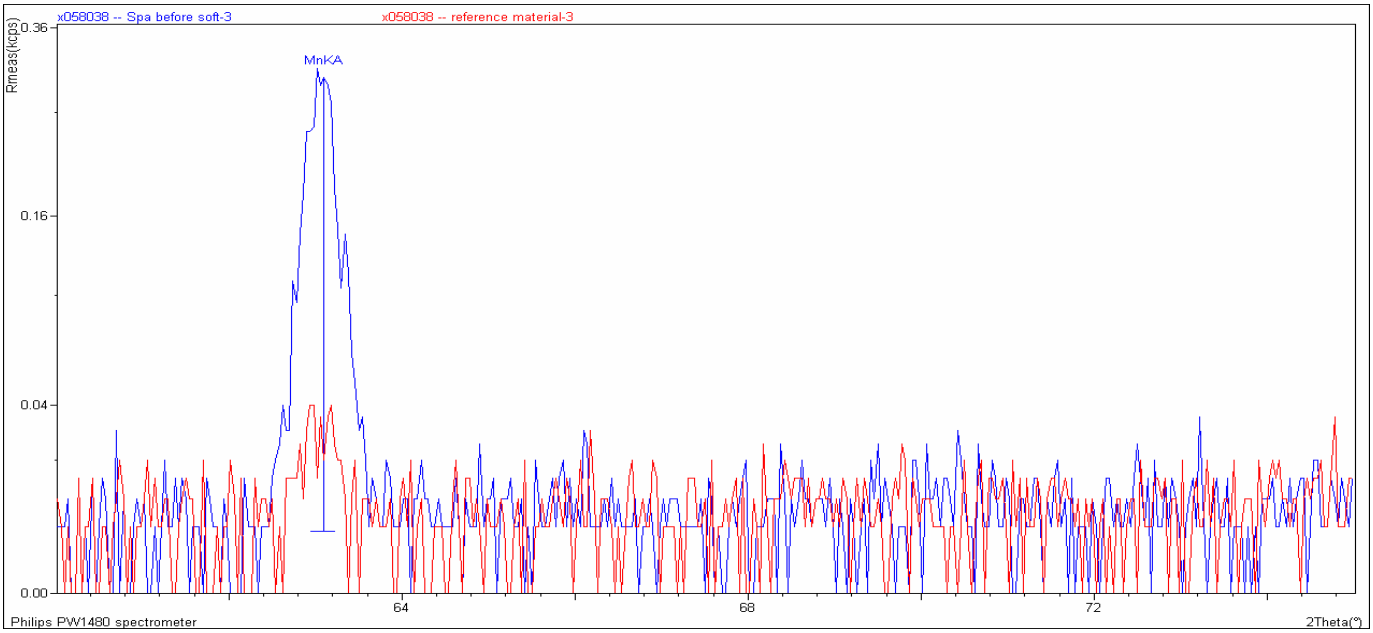
Beta factor and concentration for water with calcium removal

		Beta factor β						Concentration on membrane surface	
Times (h)	Flux (l/m².h)	humics	building blocks	CaC_2O_4	$CaCO_3$	$CaSO_4$	Ca^{2+}	DOC (mgC/l)	Ca^{2+} (ppm)
0,83	99,96	1,55	1,67	1,25	1,26	1,25	1,16	11,59	4,53
18,25	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
22,08	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
25,58	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
42,00	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
46,50	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
49,62	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
66,08	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
70,83	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
73,67	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
90,08	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
94,92	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
97,25	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47
162,08	90,87	1,49	1,59	1,23	1,23	1,22	1,15	11,10	4,47

8. raw data of the X-ray fluorescence analysis



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x058038 -- reference material-3
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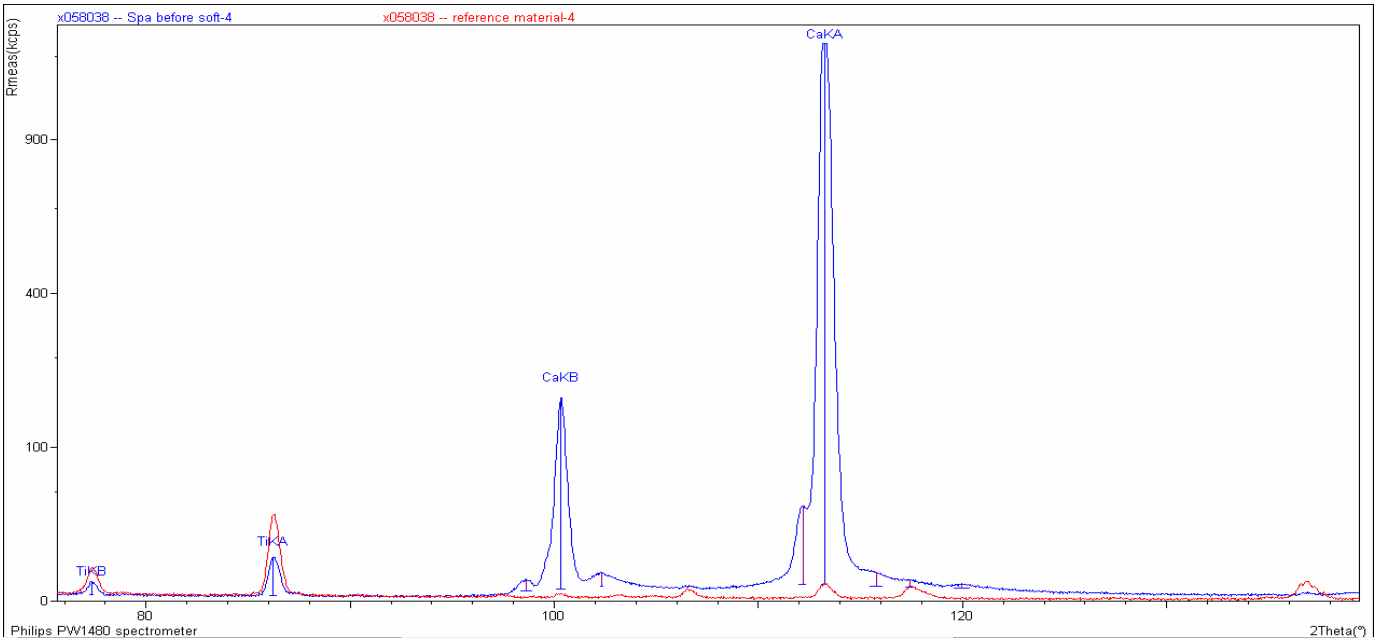
0.16
0.04
0.00
MnKA
64
68
72
Philips PW1480 spectrometer
2Theta(°)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x058038 -- reference material-4
Rmeas(kcps)
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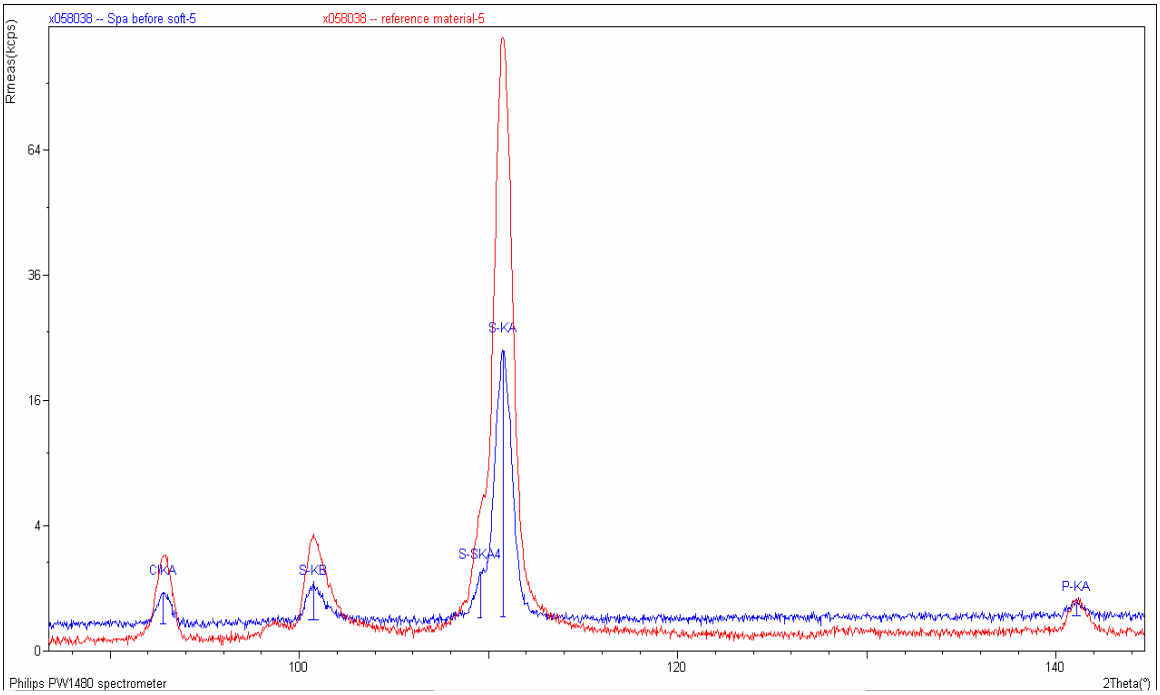
400
100
0
CaKA
CaKB
TiKA
TiKB
80
100
120
Philips PW1480 spectrometer
2Theta(°)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Rmeas(kcps)
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16
4
0
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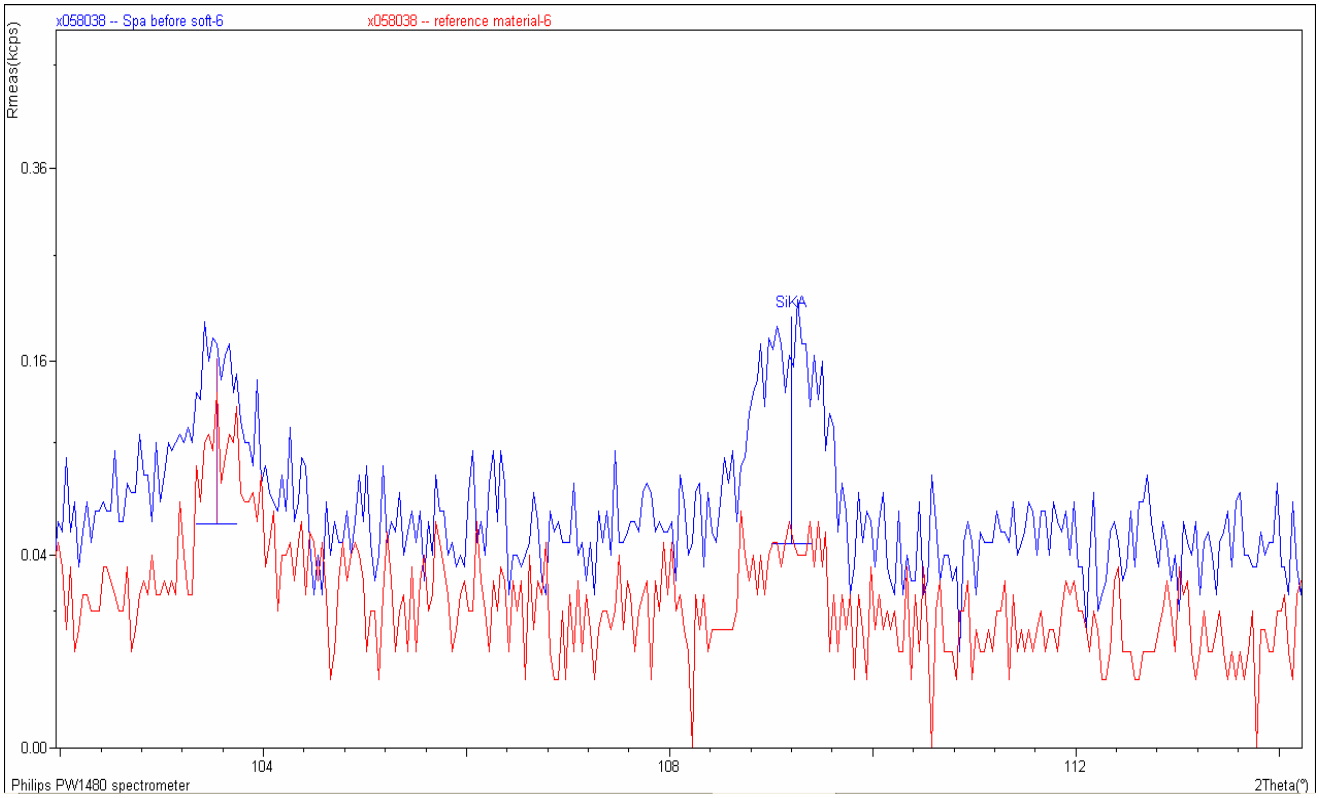
ClKA
S-KB
S-SKA4
P-KA
100
120
140
Philips PW1480 spectrometer
2Theta(°)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x058038 -- reference material-6
Rmeas(kcps)
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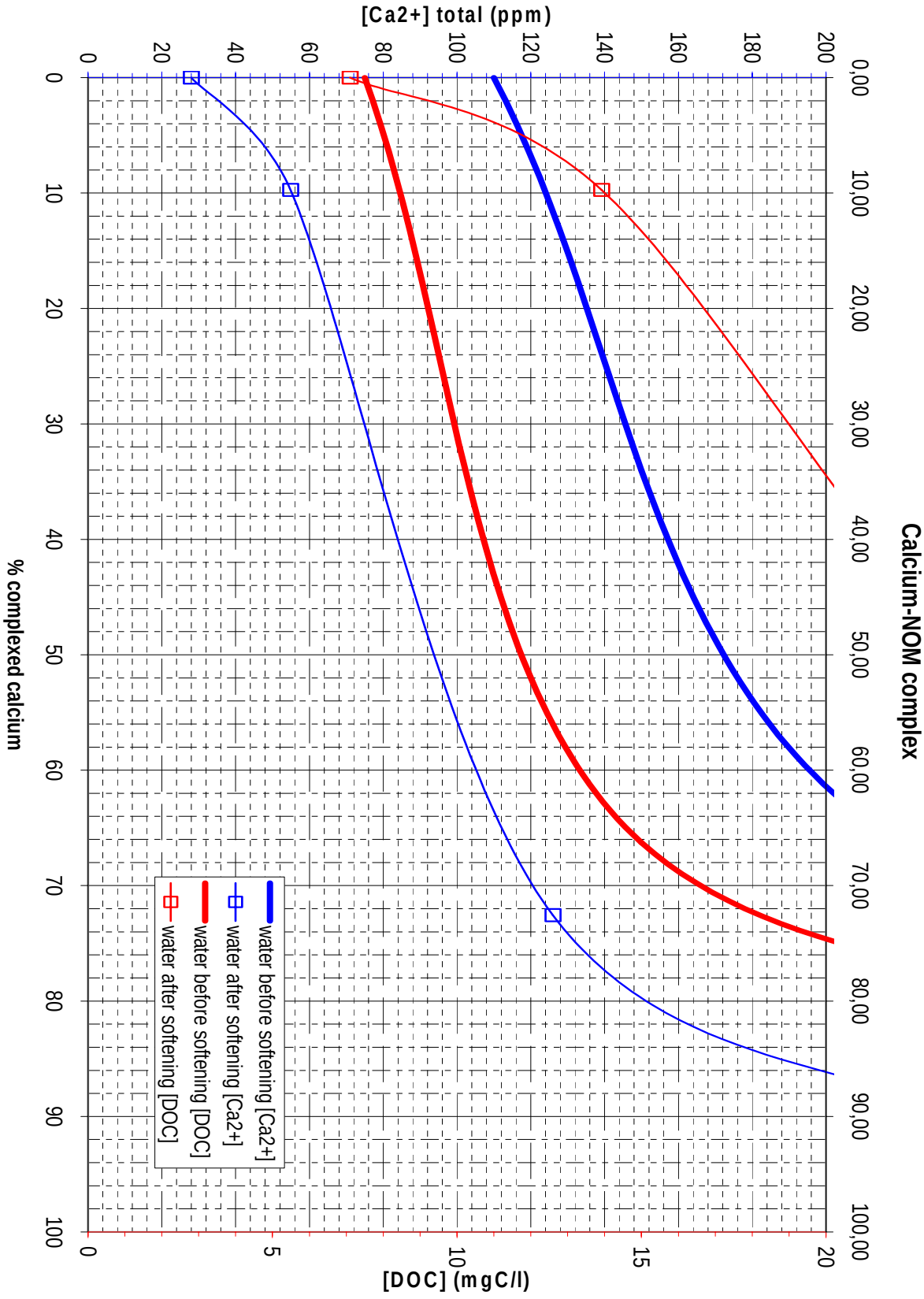
0.04
0.00
SiKA
104
108
112
Philips PW1480 spectrometer
2Theta(°)

9. Calcium-NOM complex curve



With these curves we can estimate the percentage of complexed calcium.

- The bold curves are for calcium concentration between 110 and 200 ppm.
- The thin curves are for calcium concentration between 28 and 80 ppm.
- The red curves show the % complexed calcium as function of DOC concentration
- The blue curves show the % complexed calcium as function of total calcium concentration
- Couple of curves (thin red and blue or bold red and blue) has to be considered to evaluate the percentage of complexed calcium

For example:

- The calcium concentration is 140 ppm so use blod curves
- At 140 ppm of calcium, the percentage of complexed calcium is 24%, according to the blue bold curve
- According to the red bold curve, to obtain 24%, the amount of DOC has to be 9.6 mgC/l at least
- If the DOC concentration is less than 9.6 mgC/l, the percentage of complexed calcium provided by the red bold curve will be considered
- This example would be the same with the thin curves, for calcium concentration between 28 and 80 ppm.

10. Details on the cleaning results

Results obtained by cleaning of the calcium addition fouling membrane

	calcium addition			
	beginning	After fouling	after acid washing	after caustic washing
J_w (L/h.m^2)	14,39	4,67	5,58	5,73
J_w/2,5 (L/h.m^2.bar)	5,76	1,87	2,23	2,29
Kw (m/s.bar)	1,82E-06	5,92E-07	7,08E-07	7,19E-07
R (%)	0,7	0,23	0,27	0,28
Rt (%)	94,38	93,9	91,92	92,34
Ri (%)	5,62	6,1	8,08	7,66

Results obtained by cleaning of the Spannenburg membrane

	Supplier information	After fouling	After acid washing	After NaOH washing	After SDS washing	After SDS soaking
J_w (L/h.m^2)	44,6	11,66	10,6	11,55	14,39	14,39
J_w/2,5 (L/h.m^2.bar)	5,88	4,66	4,24	4,62	5,76	5,76
Kw (m/s.bar)		1,51E-06	1,33E-06	1,43E-06	1,77E-06	1,81E-06
R (%)		0,58	0,51	0,56	0,7	0,7
Rt (%)		89,66	84,08	83,7	88,45	80,17
Ri (%)		10,34	15,92	16,3	11,55	19,83

11. Trisep TS 80 4040 Spannenburg experiments

- Determination of the beta factor (β) with Trisep TS80

Used equations :

$$\beta = \frac{C_m - C_p}{C_b - C_p} \cong \frac{C_m}{C_f} \equiv \exp\left(\frac{J_w}{k_m}\right)$$

$$Sh = \frac{k_m d_h}{D} = 0.065 \cdot \mathrm{Re}^{0.875} \cdot Sc^{0.25}$$

$$\mathrm{Re} = \frac{\rho v d_h}{\eta}$$

$$Sc = \frac{\eta}{\rho D}$$

$$v = \frac{Q_f}{L h_{sp} \varepsilon}$$

$$d_h = \frac{4\varepsilon}{\frac{2}{h_{sp}} + (1-\varepsilon) S_{v,sp}}$$

$$D = 8.76 * 10^{-9} * M_w^{-0.48}$$

$$D = 8.931 * 10^{-10} T \left(\frac{l_+^0 l_-^0}{\Lambda^0}\right)\left(\frac{z_+ + z_-}{z_+ z_-}\right)$$

$k_{dc} = 1.654(d_f/h)^{-0.039}\ \varepsilon^{0.75}\ (\sin\theta/2)^{0.086}$

L	7,50E-01	m
w	9,70E-01	m
h_{sp}	6.6E-4	M
ε	0,91	
Q_f	8,6E-04	m^3/s
l	1,46E-01	m
l_m	2.5E-3	m
A_m	7,5	m^2
ρ	9,98E+02	kg/m^3
η	1,00E-03	kg/m.s
M_w *humic*	1,00E+03	g/mol
M_w *building blocks*	4,00E+02	g/mol
J_w	4.79E-06	$m^3/s.m^2$
θ	95	°
T	298	K
$D\ Ca^{2+}$	1.58E-9	m^2/s
S	1.18E-5	m

In the case of the Trisep membrane in Spannenburg pilot, the following results were obtained :

v = 1.91E-01 $m.s^{-1}$
d_h = 8.90E-04

D_{humics} = 3.18E-10
$D_{building\ blocks}$ = 4.94E-10
D_{CaCO3} = 8.52E-10
D_{CaSO4} = 9.00E-10
D_{CaC2O4} = 8.64E-10

Re = 170
Sc_{humics} = 3150
$Sc_{building\ blocks}$ = 2030
Sc_{Ca2+} = 633
Sc_{CaCO3} = 1180
Sc_{CaSO4} = 1110
Sc_{CaC2O4} = 1160

The Sh value can be determined and then for each flux the beta factor values.
Sh_{humics} = 326
$Sh_{building\ blocks}$ = 292
Sh_{Ca2+} = 260
Sh_{CaCO3} = 255
Sh_{CaSO4} = 252
Sh_{CaC2O4} = 254

$k_{m\ humics}$ = 1.17E-04
$k_{m\ building\ blocks}$ = 1.62E-04
$k_{m\ Ca2+}$ = 2.31E-04
$k_{m\ CaCO3}$ = 2.44E-04
$k_{m\ CaSO4}$ = 2.54E-04
$k_{m\ CaC2O4}$ = 2.47E-04

β_{humics} = 1.04
$\beta_{building\ blocks}$ = 1.03
β_{Ca2+} = 1
β_{CaCO3} = 1
β_{CaSO4} = 1
β_{CaC2O4} = 1

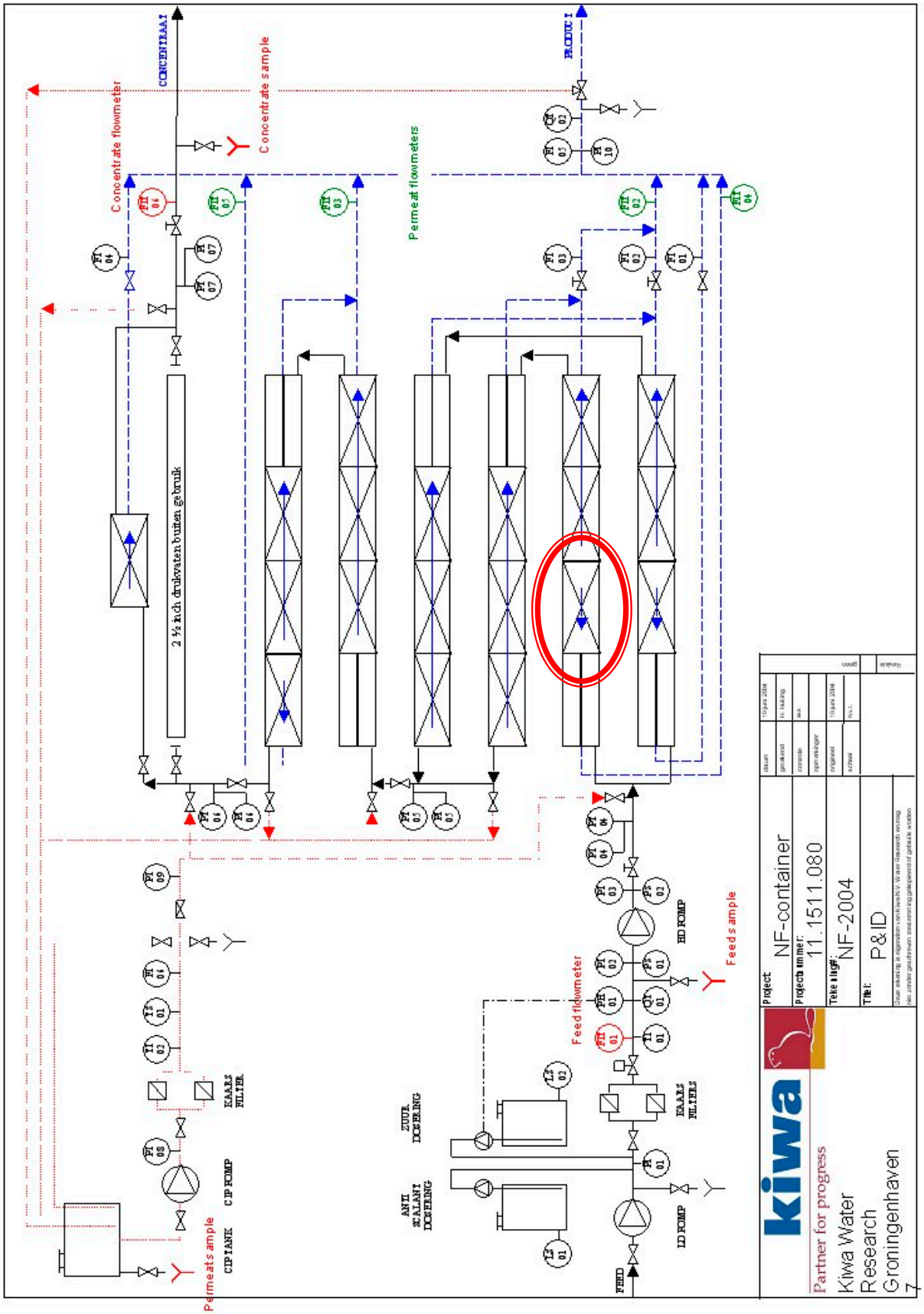
- pKs of potential scalant

	pKs
Calcium carbonate	19.12
Calcium sulfate	9.55
Calcium oxalate	19.87

- Water composition

Analyse	Concentration (ppm)
Fe2+	0.01
Na^+	74
K^+	2.3
Ca^{2+}	32
Mg^{2+}	10
NO^{3-}	12
SiO_4^{2-}	15
SO_4^{2-}	2.5
HCO^{3-}	286
Cl^-	30
CO_3^{2-}	1
COD	30

12.Scheme of Spannenburg pilot



13. Mass balance calculation details

- Sample date 22.03.2005

Feed pressure : 5.88 bar

Recovery : 74.8

Results coming from DOC Labor	Concentration (ppb)		
	Feed	Concentrate	Permeate
TOC	7523	29352	75
DOC	7059	27170	70
Humics	2875	11114	Nn
Building Blocks	2688	10202	18
Neutrals	1329	5044	16
Acids	112	414	5

$Qf=Qc+Qp+\Delta_1$

	Flow (m3/h)	accuracy
Feed	3.14	±0.005
Concentrate	0.79	±0.005
Permeate	2.33	±0.005
Δ_1	0.02	±0.015

$Qf.Cf=Qc.Cc+Qp.Cp+\Delta_2$

	Qf.Cf (mg/h)	Qc.Cc+Qp.Cp (mg/h)	Δ_2 (mg/h/m²)	accuracy	% on membrane	Relative % on membrane
TOC	23 622.22	23 363.13	1.92	±0.31	1.10	1.10
DOC	22 165.26	21 627.68	3.98	±0.64	2.43	2.28
Humics	9 027.5	8 780.06	1.83	±0.09	2.74	1.05
Building Blocks	8 440.32	8 101.59	2.51	±0.48	4.01	1.43
Neutrals	4 173.06	4 022.10	1.12	±0.18	3.62	0.64
Acids	351.68	338.73	0.1	±0.03	3.68	0.05

To obtain the relative % on the membrane, the % on the membrane is multiplied by a coefficient. This coefficient is calculated by the division of the Qf.Cf of each fraction by the Qf.Cf of the TOC.

- Sample date 10.05.2005

Feed pressure : 5.84 bar

Recovery : 75.2

Results coming from DOC Labor	Concentration (ppb)		
	Feed	Concentrate	Permeate
TOC	7437	29 797	53
DOC	7050	28 027	53
Humics	2864	11 087	0
Building Blocks	2778	11 150	12
Neutrals	1254	4 858	8
Acids	140	450	4

$Qf=Qc+Qp+\Delta_1$

	Flow (m3/h)	accuracy
Feed	3.23	±0.005
Concentrate	0.8	±0.005
Permeate	2.40	±0.005
Δ_1	0.03	±0.015

$Qf.Cf=Qc.Cc+Qp.Cp+\Delta_2$

	Qf.Cf (mg/h)	Qc.Cc+Qp.Cp (mg/h)	Δ_2 (mg/h/m²)	accuracy	% on membrane	Relative % on membrane
TOC	24 021.51	23 964.69	0.42	±0.07	0.24	0.24
DOC	22 771.50	22 548.69	1.65	±0.26	0.98	0.93
Humics	9 250.72	8 869.60	2.82	±0.14	4.12	1.59
Building Blocks	8 972.94	8 948.78	0.18	±0.03	0.27	0.1
Neutrals	4 050.42	3 905.58	1.07	±0.17	3.58	0.6
Acids	452.20	369.59	0.61	±0.19	18.3	0.34

To obtain the relative % on the membrane, the % on the membrane is multiplied by a coefficient. This coefficient is calculated by the division of the Qf.Cf of each fraction by the Qf.Cf of the TOC.