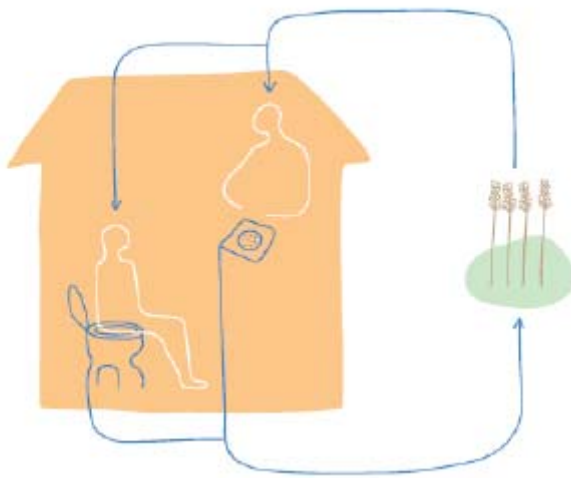# CHALMERS

Black Water Recycling at Skogaberg

VSEP Reverse Osmosis Membrane Pilot Tests

Master's Thesis in the International Master's Programme Applied Environmental Measurement Techniques

MARIE-CATHERINE COQUIN

Department of Civil and Environmental Engineering
Water Environment Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2005
Master's Thesis 2005:97

Black Water Recycling at Skogaberg
VSEP Reverse Osmosis Membrane Pilot Tests

Master's thesis 2005:97

Department of Civil and Environmental Engineering
Water Environment Technology
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone: +46(0)31-772 1000

Abstract

Separate pipelines for grey and black water have been installed in 130 houses in the new Skogaberg neighbourhood in the City of Gothenburg (Sweden). Black water is a mixture of waste water from toilets and food left-over while grey water is water from the dish-washer and the showers. The goal is to treat the less contaminated black water separately so as to recover nutrients like phosphorus, potassium, ammonium and nitrogen for agricultural use. The city has built a pilot waste water treatment plant in order to study different treatment techniques for black water.

As a continuation of the Laboratory-mode tests (L-mode) carried out in April 2005, Pilot-mode (P-mode) tests were performed to study the concentration of black water by Vibratory Shear Enhanced Reverse Osmosis (VSEP- RO). VSEP provides a higher shear rate at the surface of the membranes compared to conventional reverse osmosis processes, through the constant vibration of the unit. Besides it is possible to operate at relatively low pressures from 8 to 25 bars. The main difference between laboratory mode tests and pilot tests is that the pilot unit is composed of 38 membranes instead of one.

Three batch tests were carried out in which 500 litres of black water were concentrated at different operating conditions: for batch I acid was dosed until reaching a pH of 6, for batch II antiscalant was dosed at 10 ppm and for batch III there was no dose at all. The objective of the study was to evaluate the change in black water chemistry during concentration, to assess fouling occurrence, to determine the best conditions to control it and to recover the maximal amount of nutrients. Moreover a comparison was made between the results of the L-mode and the P-mode.

It was found that fouling has a similar effect on the three batches performed on the P-mode: dramatic permeate flow decrease (>60% decrease in two hours) after achieving a concentration factor of approximately 4. Besides, both organic and inorganic fouling were found. Batch I had the highest percentage of nutrient recovery (>70% for nitrogen) and the lowest amount of precipitation. The comparison between L-mode and P-mode showed that in the L-mode more nutrients were recovered because of a higher membrane rejection. Fouling affected the L-mode permeate flow in a smoother way compared to the P-mode probably because mainly organic fouling was found in the L-mode whilst both inorganic and organic fouling affected the P-mode.

Key-words:
VSEP, reverse osmosis, black water concentration, precipitation, nutrient recovery, fouling, permeate flow, laboratory mode, pilot mode, membrane rejection.

Acknowledgements

This work could not have been completed without the help of all the Skogaberg project team members. I would like to thank all of them for their support.

I would like to thank in particular Mark de Blois and Britt-Marie Wilén for their assistance during the writing of this report; Anne Tuisku and Carl-Henrik Hansson for their help with all the practical matters and technical problems at the pilot plant. Moreover, I wish to express my gratitude to, Pascal Karlsson for his efforts to make the work easier at Skogaberg.

I must also say that this work could not have been initiated without the help of Magdalena Svanström.

Last but not least, I would like to thank Hervé Boileau for all the efforts he has made to encourage the students from ESIGEC to go abroad.

Table of contents

Index of figures

Index of tables

Abbreviations

COD: Chemical Oxygen demand

eq/l: equivalent per litre

g/pd: gram per person and per day

IE: Inhabitant Equivalent

L-mode: laboratory mode

l/s: litres per second

meq/l: milliequivalent per litre

mg/l: milligram per litre

ml/min: millilitre per minute

NA: not available

NM: not measured

Ntot: Total Nitrogen

P-mode: pilot mode

Ptot: Total phosphorus

RO: Reverse Osmosis

SS: Suspended Solids

TOC: Total Organic Carbon

VSEP: Vibratory Shear Enhanced Process

1. <u>Introduction</u>

The use of sewage sludge on arable land must follow very specific requirements in Europe (Directive 86/278/EEC) so as to avoid pollution by e.g. heavy metals. Even if the Government encourages the recycling of sewage sludge, especially to recover phosphorus, the Swedish Farmer's association (LFR) does not accept to use it [1].

Consequently, the City of Gothenburg decided to invest in a project in which the nutrient rich and less polluted "biowaste" or "biosewage" was going to be collected separately and several alternatives to wastewater treatment were going to be evaluated with the final goal of producing an economically valuable product: a fertilizer for agricultural use.

In order to achieve that, together with a real estate company Egnahem Bolaget, the City built a neighbourhood equipped with a separating system for black and grey water as well as a pilot wastewater treatment plant. The idea was to isolate black water, which contains a lot of important nutrients that can be used in agriculture, from the pollutants that grey water can bring (e.g. heavy metals). It would then be recovered in a special waste water treatment in which it would be filtrated, concentrated, probably digested or oxidized in order to end up with a fertilizer [2].

The Recycling Board of the City of Gothenburg is responsible of the project. A team composed of consultants and students carries it out and Pascal Karlsson, project manager from the Recycling Board is the leader. Today the project is at a stage in which it has already been decided which technologies should be studied. One of them is the concentration of black water by Vibratory Shear Enhanced Process Reverse Osmosis (VSEP RO) membranes. This report presents the study carried out by a Pilot-mode (P-mode) unit of VSEP RO composed of 38 membranes.

This study is a preliminary study of the P-mode configuration of the VSEP RO. The goals are to study the evolution of the chemistry of black water during a concentration process so as to determine the possible nutrient recovery and estimate the amount of precipitation. Moreover, the analysis of fouling is carried out: fouling occurrence, type and cleaning procedures. In addition to that, as these tests is the continuation of a previous study of black water concentration carried out in the laboratory configuration (L-mode) of the VSEP RO unit composed of only one membrane, the comparison between the performances of the P-mode unit and the ones of the L-mode unit will be carried out. Therefore three batch tests will be performed at different operating conditions: a first one dosed with acid, a second one dosed with antiscalant and a third one not dosed at all.

The present report is divided into three main chapters. Firstly the background of the project is given as well as the theoretical aspects of the black water chemistry. In a third chapter, the materials used and the methodology followed to carry out, to analyze and to study the batch tests are described. In a fourth chapter the results made from the experiments are given and explained. In the fifth chapter the conclusions are given. Finally, some recommendations for future studies are given in chapter six.

2.   <u>Background</u>

2.1. <u>Skogaberg Project Background</u>

From a global point of view, the main objective of the Skogaberg Project is to recover as many nutrients as possible from household waste water in order to recycle them for agricultural use. All this should be done of course without bringing any pollutants to the land or the river. That's why a source separating system was installed in a new neighbourhood of Gothenburg (Sweden), Skogaberg. There, the real estate company Egnahem Bolaget built 110 houses and 17 apartments equipped with a separating system for black and grey water[1]. Moreover, the houses have a two-sink system that allows the recovery of food-leftovers separately from the dish-wash waste water [2].

Black water is made up of waste water from toilets and kitchen sinks [2]. It is collected in a separate piping system in order to avoid the mixing with grey water which contains heavy metals and cleaning agents. The recycling of black water appears to be very interesting since it doesn't carry high amounts of pollutants. Therefore, it can be concentrated and used as a fertilizer: nutrients (e.g. phosphorus, nitrogen, potassium and sulphur) from faeces, urine, and food-leftover can be recovered for agricultural use. Still, hygenisation and stabilisation are needed before spreading on agricultural land so a preliminary anaerobic digestion ought to be used for that.

The main responsible of the project is the Recycling Board of the City of Gothenburg. Its role is to follow the financial aspects of the project and to take care of external investigation commissions. In addition to that, the Board is responsible for all the field work of the project and its practical matters: building, pilot plant operation and some municipal administrative issues [2]. The Board is also constantly in contact with Swedish universities so as to engage students to collaborate in the project.

2.2. <u>Black water characteristics</u>

The black water from Skogaberg is drained off by gravity to the pilot waste water treatment plant [2]. The grey water is sent to Gryaab, the waste water treatment plant of Gothenburg, in order to be treated.

The pilot station receives everyday an approximate flow of 16 m³ (50 l/d) [3], which is automatically sent to the drum-screen. The description of the pilot plant is further detailed in chapter 3.

---

[1] Grey water corresponds to household washing waters.

The nutrients that can be recovered from black water are phosphorus, nitrogen, potassium, sulphur and some organic compounds. The general characteristics of black water from Skogaberg are presented on table 1.

Parameter	Production (g/pd)	Concentration (mg/l)
TS	105	2100
BOD7	37	740
Ntot	8.5	170
Ptot	1.1	22
K	2.6	52

Table 1: Characteristics of black water at Skogaberg [3]

The water composition has a diurnal variation since in the afternoon more food leftovers are thrown in the sink than in the morning. The comparison between morning and evening samples was made on August 2004 [4] and it was found that in the morning, black water contained generally more faeces, more urine, a higher alkalinity, a higher ammonium concentration and that they were oversaturated in calcium carbonate. However, afternoon samples had a higher TOC and COD due to higher suspended solid values (because of the food left-over).

Besides, because of its high organic and nutrient content, there are several processes going on in the black water [4]. If water is accumulated in pipes or tanks, parameters such as pH, alkalinity, ammonia, fatty acid and carbonate concentrations change. The study of the chemistry of black water is further detailed in paragraph 2.4 (Theoretical Background).

2.3. VSEP reverse osmosis membrane filtration

Membrane separation processes can be classified according to size range of the materials that are rejected by it (see figure 1). Reverse Osmosis is a pressure-driven separation technique like micro-, ultra- and nanofiltration, but it needs a higher pressure [5]. Typical feed pressure ranges of reverse osmosis processes are [5]:

- For brackish water applications: between 8 bars and 20 bars (low pressure) or between 24 bars to 41 bars (high pressure).
- For seawater applications: from 55 bars to 83 bars.
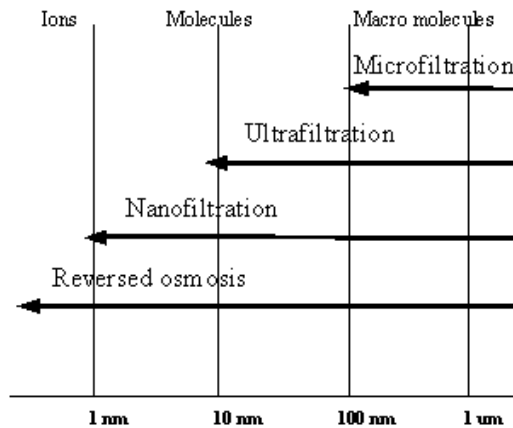
Figure 1: Classification of membrane filtration [6].

The applied pressure must be superior to the osmotic pressure of the effluent. Osmotic pressure is demonstrated by the following experiment (see figure 2): If a semi permeable membrane is placed between two compartments containing a low concentrated solution on one side (B) and a high concentrated one on the other (A), there will be water movement following the concentration gradient in order to achieve equilibrium [7]. The osmotic pressure is then represented by the height difference between t=0 and t=$t_{equilibrium}$ of the water in compartment (A). So, when reversed osmosis is carried out, transport is made against the concentration gradient in order to concentrate on one side of the membrane and have pure water on the other side.

Figure 2: Demonstration of Osmotic Pressure
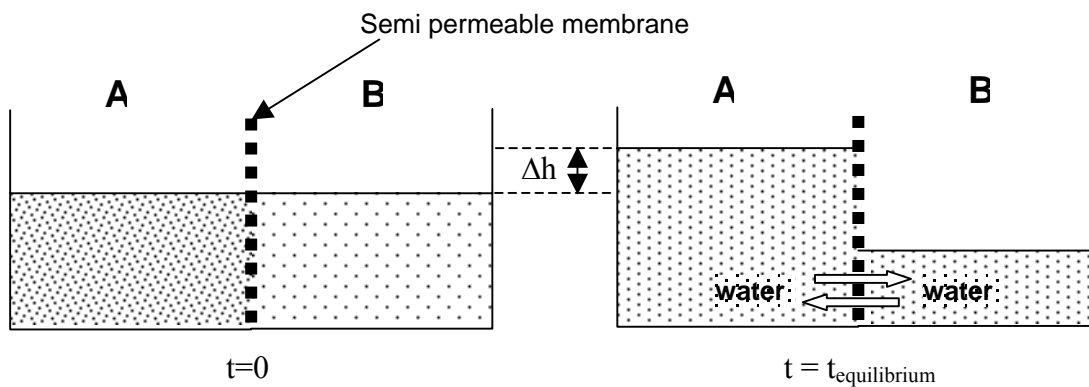
Some common applications of reverse osmosis in industry are pure water production, paint recovery from rinses, milk and juice concentration, among several others. It is possible to remove very small solutes (c.f. figure 1) like ions; the rejection coefficient is usually expressed as percentage of Na$^+$ rejected. However, even if this technique is widely used to purify water, it is not commonly used to treat household waste water mainly due to the rapid fouling of the membrane.

Fouling is a major problem since "it results in a continuous decline in membrane permeation rate […] and eventually blocking of flow channels" [8]. Increasing the shear rate on the membrane through cross-flow filtration can control this, but this needs high recirculation rates. Therefore high amounts of energy are needed and there is still formation of a fouling boundary layer [7]. Another technique that has been introduced to increase the shear rate is the Vibratory Shear Enhanced Process (VSEP) [7]. Vibration is created at the surface of the membrane, which results in the release of foulant from the membrane surface to the bulk. Other advantages are that no recirculation is needed and feeds with high viscosity can be filtered [7].

The system is composed of a membrane stack on the top sustained by a torsion string that is fixed to a seismic mass. The vibration is produced by an eccentric weight that will drive the rest of the equipment (see figure 3 and schematic in appendix 2). Typical vibration frequencies are around 50 Hz [7].
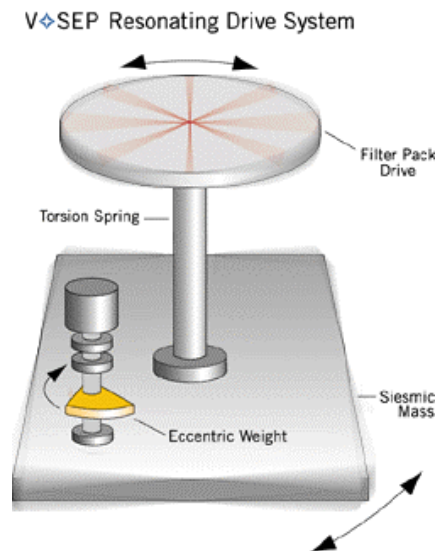
Figure 3: VSEP resonating drive system [7].

Some applications of this technique have shown to be very interesting [9-10]. For instance, in the pulp and paper industry, VSEP nanofiltration revealed good results regarding treatment of paper mill effluents [9]. High permeate fluxes were obtained even with high concentration factors. Another example of application is filtration of manure wastewater [10]. Different techniques of manure wastewater treatment were compared and VSEP RO membrane showed promising results in Korea. It was found that 99% of nutrients can be recovered and that permeate can be reused for animal drinking. Moreover, this technique can be utilized as a complement to biological treatment and even replace lagoons [10]. The features of VSEP have been studied in several areas like the ones mentioned above, but no records exist on household wastewater treatment. Therefore, the Skogaberg Project represents an innovative technique to treat black water.

2.4. Theoretical Background

2.4.1. Biologic degradation

In order to understand the evolution of the different parameters observed during a black water reverse osmosis test, it is necessary to explore the chemistry of it. Hence, it will be possible to predict which compound will precipitate or will be degraded during a batch test based on equilibrium equations and degradation rate conditions.

Black water is a mixture of urine, faeces and food leftover; therefore it is a source of nitrogen. Ammonification of organic nitrogen in urea produces ammonium and hydrocarbonates.

$$(NH_2)_2 - C = O + 3H_2O + CO_2 \rightarrow 2NH_4^+ + 2HCO_3^- \qquad \text{(i)}$$

$$(NH_2)_2 - C = O + 2H_2O \rightarrow NH_4^+ + NH_3 + HCO_3^- \qquad \text{(ii)}$$
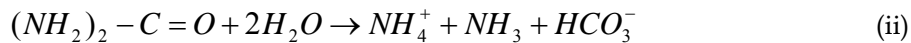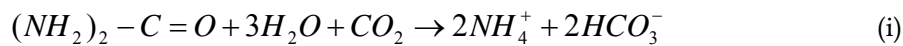
The reaction is catalyzed through the presence of *ureas* enzyme (present in faeces), which activity depends on water temperature and pH. Up to 60°C, the higher the temperature, the faster urea is degraded. The rate of degradation is higher at a pH value between seven and eight. Reactions (i) and (ii) are responsible for the pH increase up to a value of 9. When pH>9, degradation rates are much lower. As the reactions produce ammonium and carbonates, there is a direct relation between alkalinity and ammonification [4].

Moreover, there is another process that can influence the alkalinity due to carbonates of black water: acidification of organic compounds through anaerobic degradation (hydrolysis). Indeed, the hydrolysis of carbohydrates, fat and proteins to fatty acids and sugars (which can be further transformed into volatile fatty acids) will decrease pH and alkalinity due to carbon dioxide production. These reactions will lead for instance to the production of acetic acid or propionic acid, which will make pH and alkalinity go down (see equation iii).

$$CH_3COOH + HCO_3^- \rightarrow CH_3COO^- + CO_2 + H_2O \qquad \text{(iii)}$$
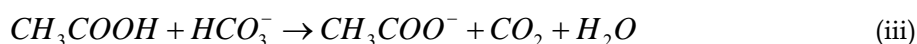
There can be two ways of acidification: hydrolysis of particulate organics or hydrolysis of dissolved organics. This latter has a higher degradation rate in a short period of time than the particulate organics. But the degradation rate is also dependant on the ratio of particulate to dissolved matter, so their influence on pH and alkalinity will vary in function of time and concentration and [4].

2.4.2. Chemical equilibrium

Black water has metals that, in combination with phosphates, carbonates and hydroxides, can be expected to precipitate during a concentration operation. The main metal salts that can precipitate in black water are calcium carbonate, calcium phosphate, and magnesium ammonium phosphate among others [4]. Therefore, the main equilibriums to be considered were selected regarding the general composition of black water. Their equilibrium equations are presented in appendix 1. Of course, as pH and temperature are changing during a batch test, this will influence the precipitation rate of the different compounds that ought to be formed.

The diagrams below (figures 4 and 5) show the predominance zones of ionic compounds present in black water. The pH of black water is usually between seven and eight [4]. These diagrams were drawn using the MEDUSA program [11], considering an aqueous solution containing only phosphates, carbonates, or sulphates. Consequently, it is possible to roughly visualize in which ionic form phosphates, carbonate and sulphates are present in black water. Of course, the amount of each compounds depend on the concentration of other compounds (e.g. calcium, magnesium) present in solution since other ionic complexes can be formed [12].
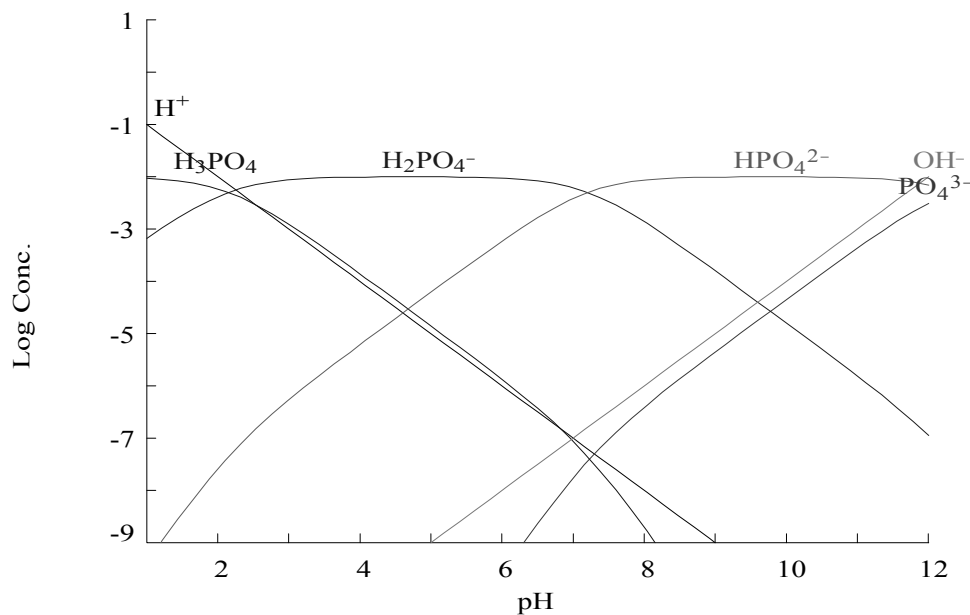
Figure 4: Evolution of the different ionic forms of phosphates in function of pH at a total phosphate concentration of 10 mM.
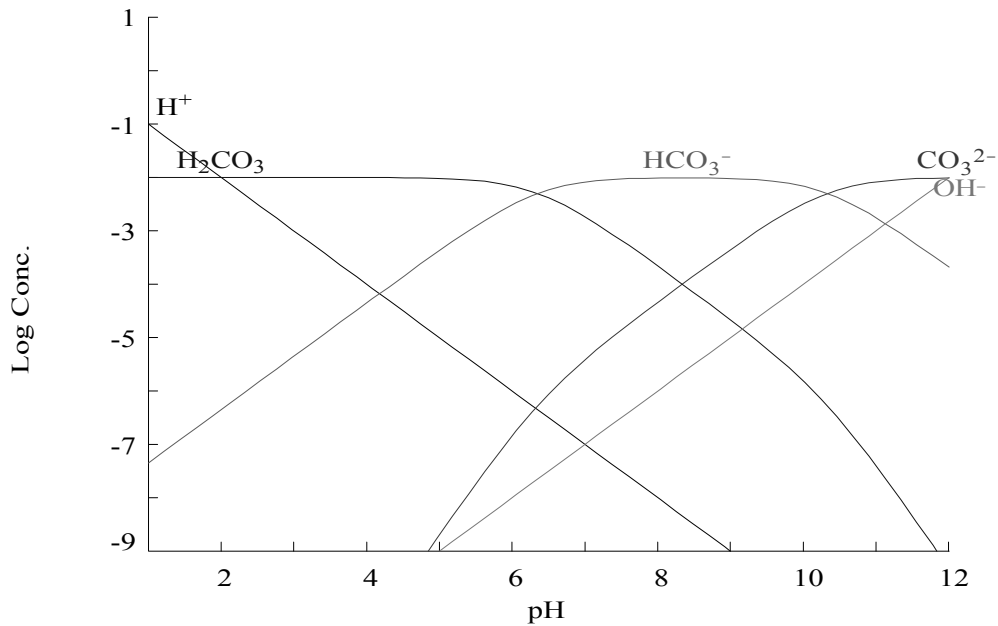
Figure 5: Evolution of the different ionic forms of carbonates in function of pH at a total carbonate concentration of 10 mM.
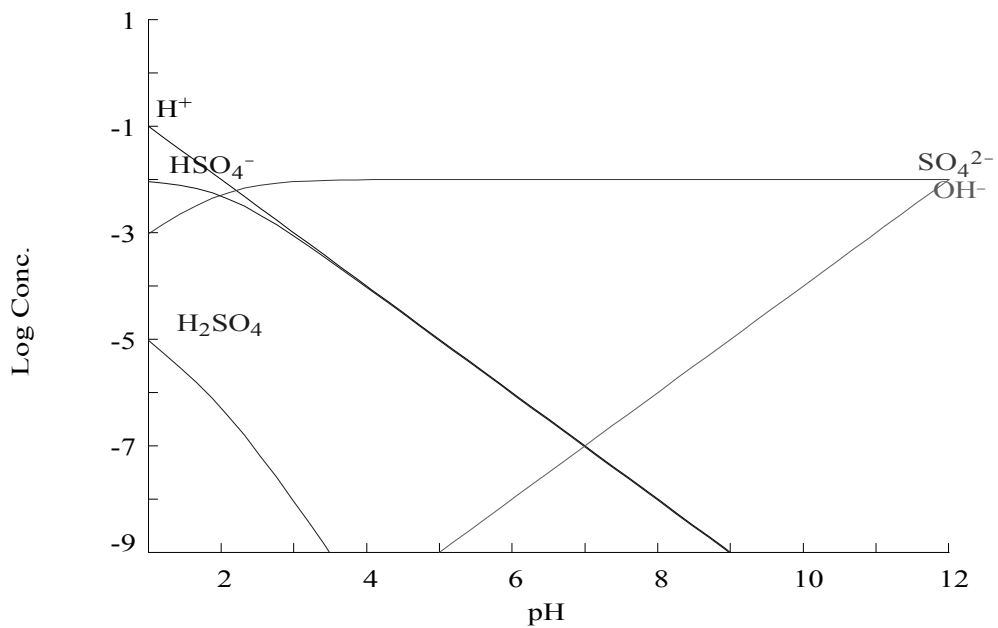
Figure 6: Evolution of the different ionic forms of sulphates in function of pH at a total sulphate concentration of 10 mM.

Evaporation of ammonia

Ammonia is one of the products of urea ammonification. Its equilibrium with ammonium (see equation iv) is influenced by pH and temperature. Vaporization of ammonia starts to be significant at pH values superior to eight. For instance, when pH=9 approximately 50% of ammonium is converted into ammonia. As ammonia has a very low solubility in water, it quickly diffuses into the surrounding air. The consequences of ammonia evaporation are acidification of the solution from which it was

produced and loss of alkalinity, as it is shown by equation (iv). However, if the pH of water is close or inferior to seven, the evaporation of ammonia is negligible. Therefore in order to control the loss of nitrogen through ammonia evaporation, the black water pH should be kept lower than eight [4].

$$NH_4^+ + H_2O \leftrightarrow NH_3(g) + H_3O^+ \qquad\qquad (iv)$$
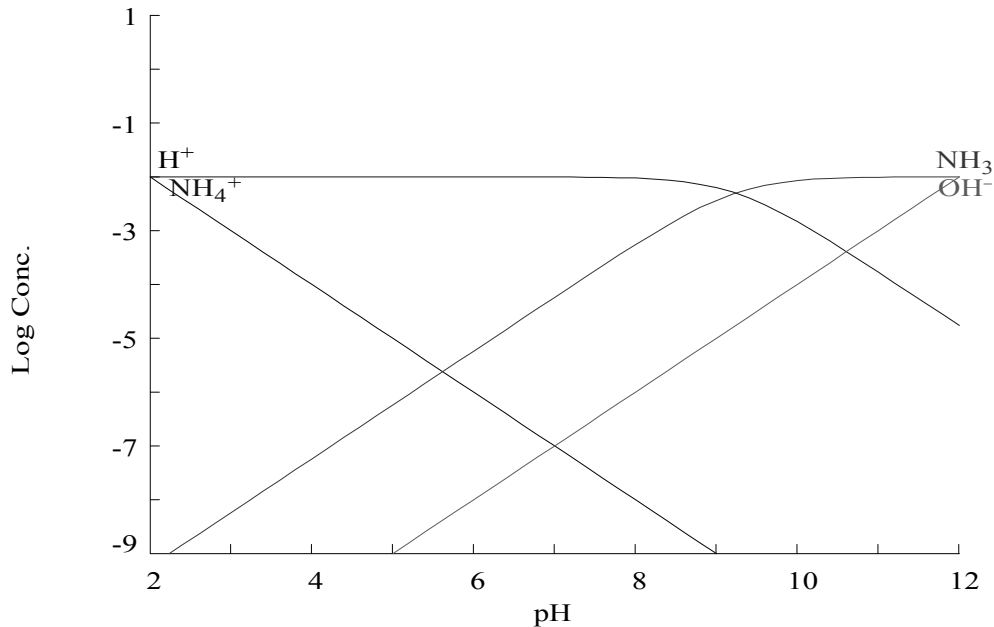
Figure 7: Evolution of ammonium and ammonia concentrations in function of pH at a total nitrogen concentration of 10 mM.

2.5. <u>Previous laboratory tests on LFC-1 RO membrane</u> [13]

Four batch tests were performed on the laboratory mode (L-mode) of the VSEP unit, but only three of them will be considered for this report:

- Batch I: acid dosed to initial pH=6
- Batch II: antiscalant dosed at 10 ppm.
- Batch III: no dosing at all

Figure 8 gives a general description of the L-mode test unit. The unit consists of a feed tank of 55 litres, which is filled with pre-filtrated (0.5 mm mesh screen) black water. A hydracell feed pump is placed before the VSEP unit in order to create pressure and cross-flow. The feed stream goes then through a filter unit, which is composed of a single Low Fouling Composite-1 (LFC-1) membrane from Hydranautics®. Once the water has gone through the membrane, the concentrate is recirculated into the feed tank and the permeate is released into the drain.
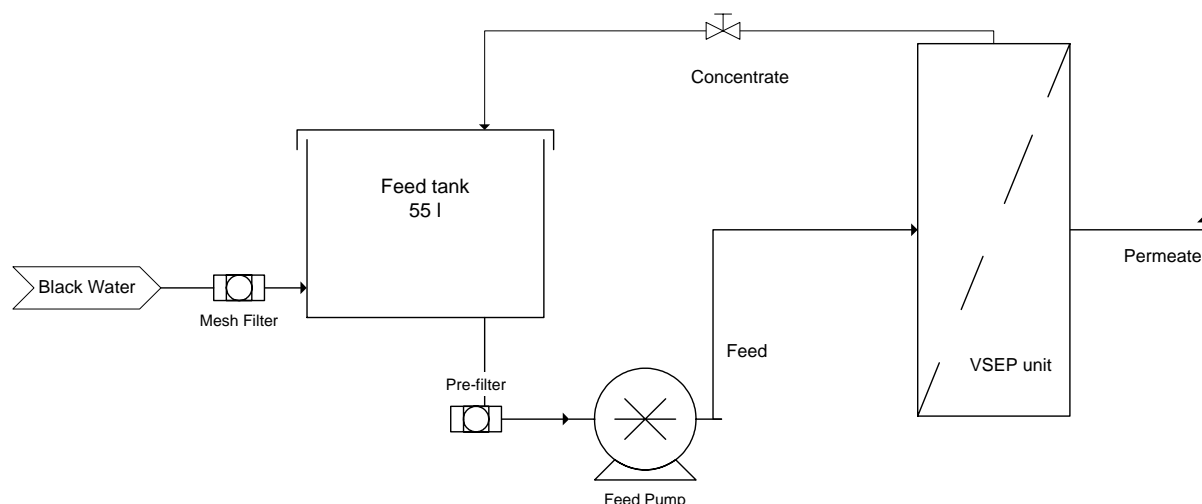
Figure 8: L-mode test unit general description

Water tests were carried out before and after each batch test to study the variation of permeate flow after a batch test compared to a clean membrane permeate flow. The operating pressures of the system during a batch test were between 12 bars at the beginning of the operation and 20 bars at the end of the concentration. Samples of feed, permeate and concentrate were taken at different degrees of concentration and analyzed. The type of samples and analyses carried out were the same as the ones done for the P-mode test and are therefore detailed later in the report.

Different washing procedures were carried out manually: the VSEP unit was taken apart and the membrane was cut into different parts in order to test several cleaning products.

The objectives of the tests performed on the L-mode were to carry out an overview study about the concentration of screened black water using a VSEP reverse osmosis membrane unit and to investigate the fouling potential of the membrane.

2.5.1. <u>Clean membrane permeate flow</u>

The laboratory membrane unit consisted of only one membrane. The clean membrane permeate flow obtained was of 23 ml/min at 11.5 bars and 20 °C. As the pilot stack is composed of 38 membranes, it is then expected to obtain a clean membrane permeate flow 38 times bigger than the one of the laboratory configuration. That would be approximately 880 ml/min at 11.5 bars and 20 °C. However, after the batch tests on L-mode, it was not possible to recover the initial permeate flow. The clean membrane permeate flow obtained after the three batch tests performed was of 21 ml/min. It was therefore concluded that the membrane had adapted to the operating conditions. So, if in the P-mode, clean membrane permeate flow cannot be recovered back to the initial one, it is expected to have a clean membrane permeate flow of approximately 800 ml/min. In that case it will be concluded that the membrane stack has adapted to the operating conditions.

<u>2.5.2. L-mode result overview</u>

Batch test characteristics

The three batch carried out had different operating conditions. Batch I was dosed with hydrochloric acid until reaching an initial pH of 6, batch II was dosed with antiscalant *flocon 260* at 10 ppm and batch III was not dosed at all. Fouling occurred in the same way for all three batches. At around 80% volume reduction, a high permeate flow decrease was observed. It was concluded that it was due to fouling. Moreover, different degrees of concentration were reached for each batch.

More details about the batch test characteristics are given later in the report since a comparison with the results from the pilot mode test is carried out.

Nutrient recovery

The recovery of NH_3 and N-tot was higher (> 90%) for acid and antiscalant dose compared to no dose test (~ 76%). In the case of phosphorus, the maximum recovery was achieved with antiscalant dose (82.6%), followed by acid dose (70%) and finally, the un-dosed batch recovery was 65%. For potassium, at least 85% was recovered in all tests.

Precipitation

The precipitation of insoluble metal salts was estimated to be significant after achieving 80% volume reduction (concentration degree of 5). Large differences of calcium, magnesium, phosphate and alkalinity concentrations were found between filtrated and un-filtrated samples. Therefore, the main insoluble salts that were estimated to have been formed were calcium phosphate, calcium carbonate and magnesium ammonium phosphate. No theoretical study of chemical equilibrium was carried out in order to predict the possible precipitates that could have been formed.

Cleaning and analysis of fouling

The cleaning analysis of the membrane indicated that the fouling was mainly organic. From the different detergents tested, the most effective ones were high pH NC2 and pure Ariel. More details about these detergents are found later in the report since they were used also during the P-mode tests. But in order to carry out these analyses it was necessary to install a new membrane before each batch test.

2.6. <u>Goals of the pilot tests on LFC-1 RO membrane</u>

The pilot VSEP RO pilot tests carried out at Skogaberg have several goals:

- ▪ To study the unit response in order to compare it to the performance of the L-mode equipment.

- To evaluate the fouling occurrence: type, amount and consequences.

- To determine the best operating condition to control fouling.

- To explore washing procedures.

- To evaluate the unit operation performance: nutrient recovery and permeate quality study

In order to achieve that, pilot tests will be carried out at the same conditions as the laboratory-mode. Three batch tests will be performed: one with acid dosing until reaching an initial pH of 6, one with antiscalant dosing at 10 ppm and a last one with no dosing at all.

It is expected to obtain results similar to the L-mode ones.

3. <u>Materials and Methods</u>

3.1. <u>Pilot plant description</u>

The following paragraph presents a brief description of the pilot plant, where membrane operations are carried out. The pilot plant is also described in figure 9. The water coming from the houses of the Skogaberg neighbourhood is pumped into the pilot plant through a grinder pump (1). Black water goes first through a pre-treatment consisting of a drum-screen with a cut off level of 0.6 mm (2). This system works batchwise. An approximate volume of 170 litres of black water has to be accumulated in the pump sump in order to start the grinding pump and the drum-screen. The flow of black water into the station is 2 l/s and the pump works every fifteen to twenty minutes. After treatment at the pilot plant, the water is sent back to the city sewage piping system in order to be treated at Rya wastewater treatment plant (Gryaab). Once black water has gone through the pre-treatment, it can be sent to the membrane unit (4). Water is first collected in a stirred tank of 600 litres (3). This tank is also used for pH adjustment or antiscalant addition if necessary. The tank has two pH-meters, a conductivity meter and a level tracer that measure on-line. The data is constantly recorded by a computer system.

The VSEP RO osmosis pilot unit is equipped with Low Fouling Composite 1 (LFC-1) membranes from Hydronautics® (see appendix 3). These membranes have a neutral surface charge and are hydrophilic. This combined with the fact that they have high rejection levels make them suitable to treat municipal wastewater. But, their use is limited to certain ranges of temperature and pH: temperature should not exceed 40°C and pH should be kept between 2.5 and 11.5 [14]. More detailed technical information about the membranes is presented in appendix 3. Then, permeate is sent to the sewer and the concentrate can either be recirculated or pumped to the drain. The establishment of cross-flow at the membrane surface is ensured by a feed pump (feed pump 2) of type Hydracell. So both cross-flow and vibration allow the control of concentration polarization. This system differs from the purge mode system since the feed is recirculated instead of being accumulated in the membrane stack and purged. The unit is also equipped with a washing system consisting of a 30-litre tank connected to the VSEP unit feed pump. Washing can be carried out automatically or manually.

During operation, it is possible to take samples automatically from the system. There are four sampling points: unscreened feed (5), feed from the tank (6), permeate (7) and concentrate (8).

Figure 9: Schematic of the Pilot Plant
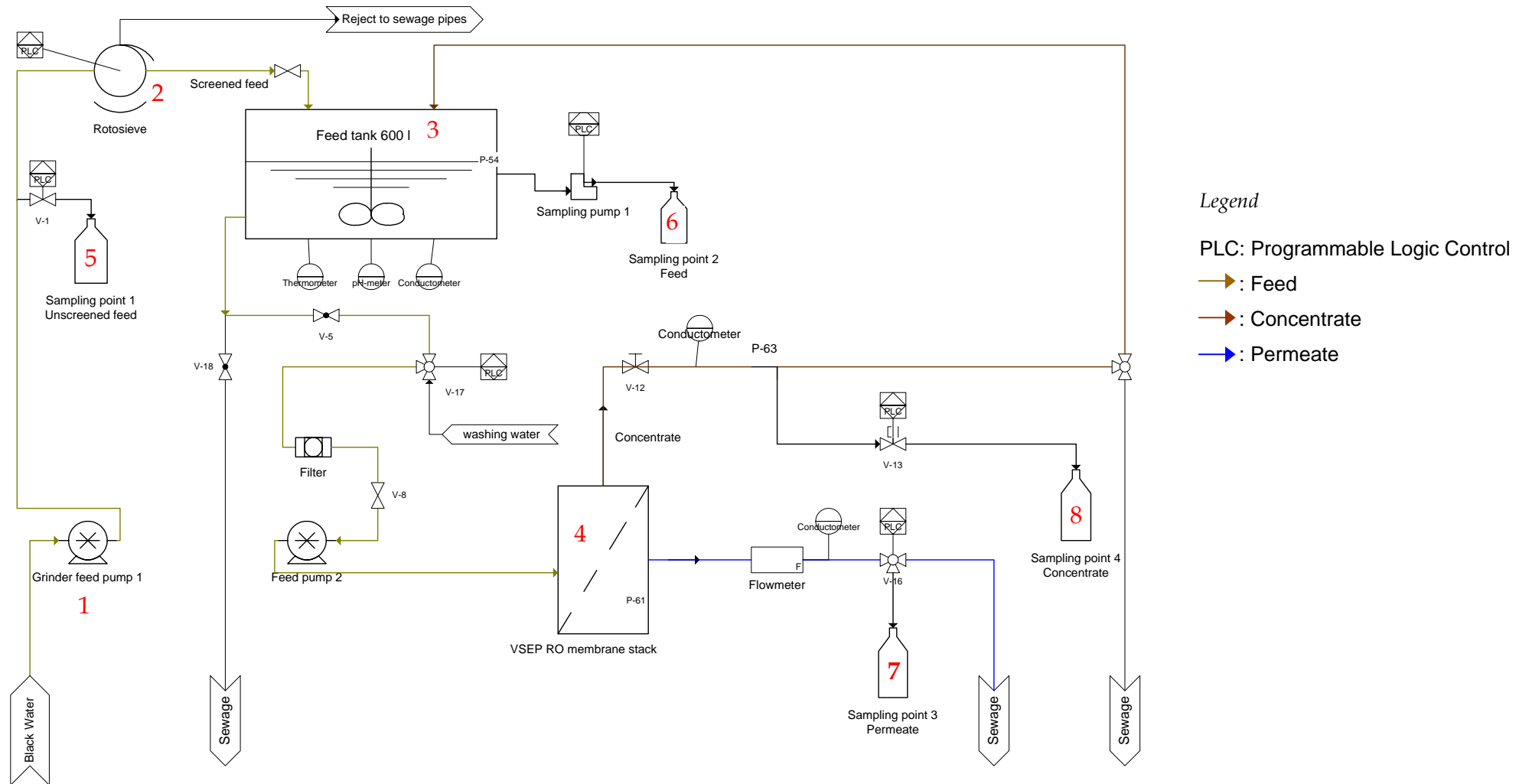
3.2. <u>Methodology</u>

A series of batch tests are carried out in order to compare the pilot membrane stack behaviour to the L-mode performances. These tests have the same characteristics as the ones performed in the L-mode:

- Batch I: acid dosing to have an initial feed pH of 6.
- Batch II: antiscalant dosing at 10 ppm.
- Batch III: no dosing at all.

All batch tests are started with an initial pressure of twelve bars, and then pressure is further increased during operation so as to compensate for osmotic pressure increase due to concentration raise. Pressure is increased manually during the operation. When carrying out a batch test, five main steps must be followed as shown in figure 10. Step number one is used to determine the reference permeate flow of a clean membrane. All other permeate flows obtained after steps three, five and eventually seven are then compared with the reference flow in order to determine if membrane surface has been lost. The dotted arrows mean that it might not be necessary to carry out the following step if the membrane capacity has been recovered. Once all steps are completed, a new batch test can be performed.

Step	Type	Applied pressure (bar)	Vibration amplitude (inches)	Vibrator Frequency (Hz)	Duration (hours)	Other characteristics
1	Water test	11.5	1/2	49	2	
2	Batch test	12 (initial)	1/2	49	12 - 14	Depending on which batch test is performed there is acid dosing until reaching a pH of 6 or antiscalant dosing at 10 ppm. Pressure is gradually increased to compensate for osmotic pressure raise. At end of operation, a pressure of 20 bars can be attainted.
3	Water test	11.5	1/2	49	2	
4	Cleaning procedure	3 - 4	1/2	49	0.3	Detergent: NC2 at 2% and at high pH (10.5-11)
5	Water test	11.5	1/2	49	2	
6	Acid Cleaning procedure	3 – 4	1/2	49	0.3	Detergent: NC4 at 4% and at low pH (2.5-3)
7	Water test	11.5	1/2	49	2	
8	Cleaning procedure	3 - 4	1/2	49	0.3	Detergent: Ariel Color at 4%, no pH adjust should be necessary (pH should be around 8)

Table 2: Description of the sequence of tests performed in a batch test series

Step   Step objective

Step	Step objective

1. Water test

✓ Clean membrane permeate flow (reference flow).

2. Batch test

Note: right after the batch test the unit is flushed with water during 10 minutes at a pressure of 12 bars in order to protect the unit from microbial growth.

3. Water test

✓ Fouled membrane permeate flow
✓ Membrane capacity decrease due to fouling

4. High pH cleaning procedure

✓ Organic fouling removal

5. Water test

✓ Permeate flow after first cleaning procedure determines if scaling has occurred

6. Acid cleaning procedure

✓ Inorganic fouling removal

7. Water test

✓ Permeate flow after second cleaning determines if there is still organic fouling

8. Final cleaning procedure

✓ Remaining organic fouling cleaning

Figure 10: Test procedure

Cleaning procedure

The same method for cleaning should be used after each batch test, in order to make the results comparable. Actually this is a very important step during the test series since it will determine the type of fouling that has taken place on the membrane surface.

If permeate flow is recovered after a basic cleaning procedure with NC2, then there was organic fouling and it could be removed with that washing procedure. This can be enough to recover the membrane capacity, but if not, there may be inorganic scaling. That's why, an acid cleaning follows basic cleaning. Next, if the initial permeate flow has not been recovered, there might still have organic fouling so a third cleaning procedure with another type of detergent can be carried out in order to remove the remaining organic. Finally the permeate flow should be recovered otherwise it means that the membranes have been damaged, that it might just have adjusted to the current operating conditions or that the fouling is deep inside the membrane.

Cleaning methodology

The detergent[2] is diluted in 25 litres of clean water in the VSEP washing tank. Then, pH is adjusted with caustic soda or hydrochloric acid depending on the needs. It is of great concern to respect the membrane limits regarding pH in order no to damage the unit. Once the solution is ready, it is circulated in the unit for about 20 minutes at low pressure (3-4 bars) so as to make sure that the cleaning mixture has filled the entire unit. Then, the membranes have to soak in the washing solution for at least five hours. Subsequent to soaking, the washing tank is flushed until it is emptied and filled several times with clean water to rinse the unit. At least 150 litres of water must be flushed through the unit in order to remove all remaining detergent. Figure 11 illustrates the procedure described above.

Step	**Characteristic**
1. Washing Mixture preparation	✓ NC2 2 % Basic Mixture: 500 ml of pure NC2, pH adjustment to 10.2-11, 25 litres of water. or ✓ NC4 4% Acid mixture 1000 ml of pure NC4, pH adjustment to 2.5-3, 25 litres of water or ✓ Ariel 4%, 1000 ml of Ariel Color, 25 litres of water, pH should be naturally around 8.
2. Recirculation	✓ 20 minutes of recirculation to the washing tank at 3 to 4 bars.
3. Soaking	✓ The membrane stack is left soaking in the washing mixture for at least 8 hours.
4. Flushing and Rinsing	✓ The unit is free from any detergent left-over.

Figure 11: Cleaning methodology

---

[2] The specification for each detergent is presented on appendix 4

3.3. Sampling and Analysis

Several types of analyses are carried out in order to study the pilot membrane stack behaviour, the incidence of fouling and its characteristics as well as the characteristics of the permeate and concentrate produced.

3.3.1. Batch test samples

Samples are taken automatically by the system and they are set to have different volumes depending on where the sample is to be analyzed. If analysis is carried out at location, no more than 200 ml are taken. If Alcontrol Laboratory carries them out, the required volume is 1.5 l (1000 ml for Alcontrol and 500 ml stored at location). Samples are taken at several stages of operation regarding the concentration factor (see table 3). A special procedure is followed to get an average permeate sample composition: after every hour of operation, 100 ml of permeate are taken and mixed with all previous permeate average samples.

Stage	Characteristic
0	Start
50	50% volume reduction
80	80% volume reduction
M	Maximum volume reduction

Table 3: Characteristics of sampling

Parameters followed during the experiments as well as analysis locations are shown on table 4. Actually, several important aspects of the operation can be determined by the evolution of these factors:

- amount of precipitation (if occurred)
- type of precipitation
- membrane stack performance
- chemical compound degradation or production

Parameter	Analyzed on site	Analyzed by Alcontrol
pH	✓	✓
Conductivity	✓	✓
Alkalinity	✓	✓
SS		✓
COD		✓
TOC		✓
FA_{tot}		✓
N_{tot}		✓
Ammonium (NH_4^+)	✓	✓
P_{tot}		✓
$P_{phosphate}$	✓	✓
Potassium (K^+)		✓
Sulphate (SO_4^{2-})		✓
Total Sulphur (S_{tot})		✓
Calcium (Ca^{2+})		✓
Magnesium (Mg^{2+})		✓
Sodium (Na^+)		✓
Chloride (Cl^-)		✓

Table 4: Parameters analyzed for each batch test and the analysis location

The analytical instruments used on location are conductivity meters, pH-meters, one flow meter, one Ammonia electrode and one spectrophotometer. Their specifications are given on table 5.

Instrument	number	Specifications	Operated
pH-meters	4	− Dulcometer DMT, electrode PHER 112SE ProMinent	Automatically
		− Handilab 1, SCHOTT	Manually
Conductivitymeters	4	− JUMO 640	Automatically
		− Handilab LF1, SCHOTT	Manually
Ammonia electrode	1	Expandable ion analyzer EA 940, Orion Research	Manually
Photometer	1	Lasa 20 Photometer, Dr Lange LPG 300	Manually
Flowmeter	1	Promag 33A, ENDRESS+HAUSSER	Automatically

Table 5: Instrument specification used at location

As it is shown on the system description (see paragraph 3.1), some parameters are registered automatically by the Programmable Logic Control (PLC). The instruments measuring automatically

are conductivity meters, pH-meters, thermometers and flowmeters. Alkalinity is measured manually by establishing a titration curve. Samples are titrated with hydrochloric acid until reaching a pH-value of 2.5. The acid solution concentration depends on the expected amount of alkaline species. Usually hydrochloric acid at 0.005 M is used to titrate permeate samples and hydrochloric acid at 0.05 M is utilized to titrate concentrate and feed samples

3.3.2. Washing water samples

Sometimes, after performing cleaning procedures, it was found that inorganic scaling occurred during the test. When acid cleaning is performed, inorganic precipitates should be removed; therefore it is interesting to analyze the acid washing water before and after the cleaning procedure to asses what might have precipitated. Consequently, the parameters followed are presented on table 6. Samples of washing water with NC4 of 1500 ml (1000 ml for Alcontrol, 500 ml stored at location) are taken before and after the cleaning procedure

Parameter	Measured at location	Measured by Alcontrol
PH	✓	✓
Alkalinity (back titration curve)	✓	
Calcium		✓
Magnesium		✓
Phosphates		✓
Ammonium		✓
Suspended solids		✓

Table 6: Parameters analyzed for washing water study

Moreover, back-titration curves were carried out on samples before and after the washing procedure. They were carried out with sodium hydroxide at 0.05 M.

3.3.3. Final tank concentrate study analyses

Before finishing the series of batch tests, it was decided to make a study of the concentrate left in the feed tank after the batch test has been carried out. The goal of this study is to find out how the chemistry of the concentrate is modified with time. Therefore, samples of feed are taken at two characteristic moments of one batch test: before fouling and at the end of operation. This study is carried out only for batch III. Therefore, five litres of concentrated feed are collected for each moment. A first series of analyses is carried out at location just after sampling. Then, a second series of analyses is carried out 20 hours after sampling and a last series of analyses is carried out 96 hours after sampling. The parameters followed are shown on table 7.

Parameter	Analyzed on site	Analyzed by Alcontrol
pH	✓	✓
Conductivity	✓	✓
Alkalinity	✓	✓
SS		✓
COD		✓
TOC		✓
FA_{tot}		✓
N_{tot}		✓
Ammonium	✓	✓
P_{tot}		✓
$P_{phosphate}$	✓	✓
Potassium		✓
Sulphate		✓
S_{tot}		✓
Calcium		✓
Magnesium		✓

Table 7: Analyses for final concentrate study

Moreover, titration curves with hydrochloric acid are made for each sample just like they were made for the batch test samples.

3.4. Calculations

3.4.1. Mass balances

Mass balances are performed in order to determine the amount of recovered nutrients after the concentration of black water. Moreover, it is also a way to determine if some other compounds have precipitated somewhere else than in the feed tank. A concentration factor can be determined by making a mass balance on a chosen trace element. This latter should be either found in the permeate, the concentrate or the feed as it can only precipitate and it is not degraded. As this is the case of potassium, sodium and chloride, it is possible to use one of those elements determine the concentration factor.

Then, a global mass balance over the unit for one of the elements can be expressed as:

$$V_0 \cdot C_0 = V_{max} \cdot C_{max} + V_P \cdot P_A \qquad (1)$$

where V_0: initial feed tank volume C_0: feed initial concentration

V_{max}: maximal concentrate volume P_A: permeate average concentration

V_P: total permeate volume produced C_{max}: maximum concentration achieved

Knowing that $V_0 = V_P + V_{\max}$ and by rearranging (1):

$$C_0 = \frac{V_{\max}}{V_0} C_{\max} + (1 - \frac{V_{\max}}{V_0}) P_A \qquad (2)$$

The concentration factor *F* is then given by equation (4):

$$C_0 = f \cdot C_{\max} + (1 - f) \cdot P_A \qquad (3)$$

$$F = \frac{1}{f} \qquad (4)$$

where $f = \dfrac{V_{\max}}{V_0}$

Consequently, it is possible to determine if some other species (e.g. ammonia, phosphates, calcium) have been lost or gained during the operation based on factor *f*.

A theoretical maximum concentration $C_{\max th}$ can be calculated and compared with the measured maximum concentration of those species.

$$C_{\max th} = \frac{C_0 - (1 - f) P_A}{f} \qquad (5)$$

Then, knowing that some compounds are lost through the permeate, the amount of compounds lost by other meanings (e.g. biological degradation, precipitation) can be determined.

$$\%Lost = \frac{V_0 C_0 - V_{\max} C_{\max th} - V_p P_A}{V_0 C_0} \cdot 100 = \frac{(C_0 - (f \cdot C_{\max th} + (1 - f) P_A))}{C_0} \qquad (6)$$

3.4.2. Saturation index and estimation of precipitate type and amount

In order to make an estimation of which compounds can precipitate during a batch operation, saturation indexes are calculated for several species using a chemical equilibrium modelling system software: MINEQL+® [14].

The Saturation Index (SI) is defined by equation (6):

$$SI = \frac{Q}{K_S} \tag{7}$$

where Q represents the ion product of the solid

and K_S is the solubility constant for the solid

If,

- SI<0, the solution is undersaturated for the chosen compound.
- SI=0, the system is in equilibrium.
- SI>0, the solution is supersaturated for the chosen compound.

The choice of the different compounds that are going to be in the input data is based on equilibrium equations (see § 2.2.). Moreover, the solutes that are high concentrated in black water will be also added since they can influence the saturation index.

Knowing that, the input data of the program will consist of:

- Measured concentrations of calcium, potassium, hydroxides, carbonates, magnesium, sodium, ammonium, chlorides and sulphates.
- pH
- Alkalinity (until pH=5.5)

The program is also used to determine theoretically the type and amount of precipitates. This can be an indication of the types of precipitates that occur during a concentration of black water.

3.4.3. Calculations based on alkalinity

Alkalinity corresponds to the amount of acid equivalents needed to take down the pH to a determined value. This value depends on the type of species that is going to be studied, since compounds can influence alkalinity in a different way depending on pH (cf. §. Theoretical Background). Alkalinity measurements can be used to estimate the concentration of carbonates and organic acids (OA). In the case of black water, alkalinity down to pH 5.5 or less can be estimated as follows:

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [NH_3] + \\ + m[OA] + m_1[PO_4^{3-}] + m_2[HPO_4^{2-}] + m_3[H_2PO_4^-] - [H_3O^+] \tag{8}$$

The factors m_i vary depending on pH since the different species described in equation (8) influence alkalinity at only certain pH ranges.

Down to pH= 5.5, equation (8) can be estimated as:

$$Alk_{5.5} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [NH_3] +$$
$$+ 0 \cdot [OA] + 2 \cdot [PO_4^{3-}] + 1 \cdot [HPO_4^{2-}] + 0 \cdot [H_2PO_4^-] - [H_3O^+]$$

(9)

Down to pH=3, equation (8) can be estimated as:

$$Alk_3 = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [NH_3] - [H_3O^+]$$
$$+ 1 \cdot [OA] + 2 \cdot [PO_4^{3-}] + 1 \cdot [HPO_4^{2-}] + 0 \cdot [H_2PO_4^-] - [H_3O^+]$$

(10)

The evaluation of the amount of carbonates and organic acids is made from alkalinity measurements. These estimations are not very accurate; they are just carried out to have a measure of the cited compounds at different stages of operation. By neglecting the concentration of hydronium ions in equations (10) and (9), the measure of organic acids can be estimated by making the difference between alkalinity measures until pH= 5.5 and alkalinity measures until pH=3. This difference is a measure for the organic compounds buffering between pH 5.5 and pH 3.

$$Alk_{5.5} - Alk_3 = [OA]$$

(11)

4.   <u>Results and Discussion</u>

4.1. <u>Feed characteristics</u>

Black water was collected during approximately 24 hours before performing each batch test. The characteristics of the feed for each batch are described in appendix 5 and on table 8.

Parameter	Batch I	Batch II	Batch III
pH	6.11	7.10	7.33
Initial temperature (ºC)	23.8	21.3	22.1
Alkalinity (pH=3) (meq/l)	7.6	14.6	13.6
Conductivity (µS/cm)	1442	1633	1543
Suspended Solids (mg/l)	450	930	530
COD (mg/l)	980	1900	1200
TOC (mg/l)	250	550	260
Fatty acids (mg/l)	140	180	190
Ptot (mg/l)	15	25	17
PO_4-P (mg/l)	18	18	17
Ntot (mg/l)	130	220	190
NH_4^+ (mg/l)	110	140	150
K^+ (mg/l)	42	55	53
Ca^{2+} (mg/l)	33	45	36
Mg^{2+} (mg/l)	5.6	8.2	6.7
Cl^- (mg/l)	210	110	100
SO_4^{2-} (mg/l)	31	19	24
Na^+ (mg/l)	68	87	87

Table 8: Feed characteristics

The following comments can be made about these measures:

- Alkalinity titrated down to pH 5.5 is similar for batches III and II while it is 50% lower for batch I. This is due to the acidification of batch I with hydrochloric acid. 172 ml of acid at 6 M (2.1 meq/l of black water) were added to the 500 litres of black water. This also explains the difference in pH and in chloride concentration (much higher for batch I).

- Batch II has a suspended solid concentration almost 50% higher than the other batches. This is consequently reflected in the COD and TOC values which are also almost 50% higher for batch II.

- All the phosphorus of batch III is in the form of phosphate while 72% of the total phosphorus of batch II is in the form of phosphate. The total phosphorus concentration for batch I is lower than the phosphate concentration but should of course be higher or equal to the phosphate concentration of batch I. This difference can probably be due to an analytical failure.

- Around 80% of the total nitrogen corresponds to ammonium for batches III and I, while for batch II only 60% of the total nitrogen is in the form of ammonium.

- Bath II shows a slightly higher concentration in potassium calcium and magnesium than the other two batches. These latter have similar concentrations.

From the general description of black water given in chapter 2, it can be said that all batches have characteristics similar to the ones described there. Although, it can be outlined that batch II had generally higher concentrations, more organic nitrogen and phosphorus amounts and much more suspended solids. Consequently, batch II might have been composed of more food left-over than the other two batches.

4.2. Final Concentrate characteristics

End of operation feed characteristics are presented in appendix 6 and table 9. It can be observed that the product obtained has very high concentrations of COD, suspended solids, calcium among others and a very high conductivity value (>8000 µS/cm).

Parameter	Batch I	Batch II	Batch III
PH	7.5	7.7	7.9
Temperature ($^{\circ}$C)	28.7	28.2	29.9
Alkalinity (pH=3) (meq/l)	75.6	125.2	103.6
Conductivity (µS/cm)	8440	8960	8150
Suspended Solids (mg/l)	5400	9500	2200
COD (mg/l)	12000	9300	5900
TOC (mg/l)	2400	2600	1700
Fatty acids (mg/l)	1400	2200	480
Ptot (mg/l)	180	100	93
PO_4-P (mg/l)	110	97	72
Ntot (mg/l)	1500	1100	1200
NH_4^+ (mg/l)	1200	1100	1000
K^+ (mg/l)	500	400	420
Ca^{2+} (mg/l)	380	220	180
Mg^{2+} (mg/l)	69	28	35
Cl^- (mg/l)	2400	850	890
SO_4^{2-} (mg/l)	460	240	350
Na^+ (mg/l)	790	670	670

Table 9: concentrate characteristics

The total residence time for each batch was:
- Batch I: 14 hours and 10 minutes
- Batch II: 13 hours
- Batch III: 13 hours and 40 minutes

The concentration factor attained for each batch was:
- Batch I: 15.2 times
- Batch II: 8.5 times
- Batch III: 8.7 times

Comments
After approximately 14 hours of operation, the following comments can be made about the final product obtained:

- The concentration of chlorides is higher in batch I because hydrochloric acid was added at the beginning and also the concentration factor attained was higher. The alkalinity value also reflects the acidification since it is almost 50% lower than for the other two batches.

- Batch II has a higher concentration of suspended solids than the other batches, which is reflected in the COD values. This is of course due to higher content of suspended solids and can be due to the fact that when the last concentrate samples were taken at the end of batch II, it was possible to reach the bottom of the tank, were a lot of sediments were accumulated.

- More calcium and magnesium are found in batch I, this can be the consequence of two factors: as batch I was acidified, precipitation started later; a higher concentration factor was reached.

- The total nitrogen at the end of batch II is in the form of ammonium, while approximately 80% is in the form of ammonium for batches III and I. This can be the result of high ammonification rates for batches II and a lower ammonification rates for batch III and I, since for the latter the ammonium to total nitrogen ratio was kept at the same level.
- The phosphate to total phosphorus ratio was also changed along the operation. It went from 100% to 70% for batch III and from 72% to 97% for batch II. This can be due to the fact that during batch III, the degradation rate of organic phosphorus to phosphate was lower than the precipitation rate of phosphates and vice-versa for batch II.
- For batch I, the phosphate to total phosphorus ratio found for the final concentrate is coherent, contrary to the ratio of the initial feed.

More conclusions can be made about the total recovery of compounds in the concentrate but this point is studied later in paragraph 5.4.

Furthermore, a study of the influence of time on the concentrate quality was carried out. The results are given in table B of appendix 6. It can be observed that the amount of fat is dramatically decreased as well as the COD values and pH, while alkalinity increased. Moreover, the concentration of ammonium increases with time while the total nitrogen concentration decreases. This can be due to ammonification. However, the differences in alkalinity, calcium and magnesium between filtrated and un-filtrated samples do not increase with time, so no precipitation takes place afterwards in the concentrate tank.

4.3. Permeate quality

Samples of permeate were taken at different concentration stages. The results are presented in appendix 7. It can be observed that the concentrations for all compounds increase with the concentration factor as well as pH. The study of this phenomenon is made later in chapter 4.7.

The reverse osmosis process should produce sufficiently clean water from wastewater to be able to be discharged it into the local river. Therefore it is interesting to see if the levels of total nitrogen and COD meet the Swedish legislation. Table 10 presents the Swedish National requirement for total nitrogen and COD when wastewater is to be discharged into water near the coast or in the sea, for an community of more than 10, 000 IE. But for smaller communities, there is usually no N- or COD-demands unless the local recipient is very sensitive. This might be the case for Skogaberg. What has to be noted is that the samples taken at the end of the experiments are overestimated since the samples volume to permeate flow ratio is increased a lot during the operation due to permeate flow decrease.

Parameter	Maximum concentration allowed (mg/l)
Total Nitrogen	15 (as Ntot)
COD(Cr)	125

Table 10: Swedish standards for wastewater release [16 -18]

The concentrations of the permeate average for batch I, batch II and batch III were 38 mg/l, 33 mg/l and 51mg/l for Nitrogen, respectively, and for COD the concentrations were equal or inferior to 35 mg/l. It can be seen that for COD the permeate average is under the maximum allowed while for nitrogen it is above. The concentration of total nitrogen in the permeate before fouling occurs is below the discharge limit since most of the nitrogen present in the permeate is gained after fouling has occurred at high concentration factors. So it could be possible to discharge the permeate directly to the local water recipient if fouling is controlled. However, this is strongly dependant on the concentration factor. Moreover, microbiological analyses of permeate were carried out for batch III. Actually, the membranes are supposed to keep microorganisms on the concentrate since the pores are not large enough to let them go through.

The results are presented on table 11.

Table 11: Microbiological analysis of permeate

Samples	Faecal Coliforms (cfu/100 ml)	Escherichia Coli (cfu/100 ml)	Intestinal Coliforms (cfu/100 ml)
PO	98	<50	<10
P50	950000	2300	240
P80	43	<50	<10
PM	190000	61000	1200
PA	410000	11000	460

P0: permeate at start   PM: permeate at maximum volume reduction
P50: permeate at 50% volume reduction   PA: permeate average
P80: permeate at 80% volume reduction
Comments:

The results show that some organisms were found in the permeate. However, it can be because of microorganism development in the pipes or in the bottles. As the bottles were not sterilized before sampling, it is possible that they were contaminated in the laboratory. Still, an indication that bacteria can be removed is the P80 sample.

4.4. Mass balance results

All the results from the mass balances are shown in tables 12, 13 and 14. It is then possible to visualize the amount of compounds lost through the permeate and the ones lost through other ways. All the calculations performed are based on the balance equations presented in paragraph 3.4.1.

Batch I

Compound	Amount in feed (mg/l)	% in concentrate	% in permeate	% lost or gain by other ways or inaccuracy
NH_4^+	110	72.6	31.4	+4.0
N_{tot}	130	76.8	27.3	+4.1
$N_{tot}-NH_4^+$	20	99.9	4.6	+4.7
K^+	42	79.3	22.2	+1.5
P_{tot}	15	79.9	0.9	-19.2
PO_4-P	18	40.7	0.22	-59.1
SO_4^{2-}	31	98.8	6.0	+4.9
Ca^{2+}	33	76.7	1.4	-21.9
Mg^{2+}	5.6	82.1	1.7	-16.2
TOC	250	63.9	4.7	-31.2
TOC filtrated samples	120	98.2	10.1	+5.3
COD	980	81.5	2.8	15.7
COD filtrated samples	400	127.7	7.0	+37.8
Total fat	140	66.6	6.6	-26.8
Suspended Solids	450	79.9	0.0	-20.1
Alkalinity (pH=5.5)	2.5	83.1	56.0	+39.1
Alkalinity (pH=3)	7.6	66.2	34.1	+0.3
Organic acids[3]	5.1	58.0	29.8	-12.2
conductivity	1442 (μS/cm)	39	16.6	-45.4
Na+	68	77.4	23.3	+0.7
Cl-	210	76.1	32.9	+9

Table 12: Mass balance results for batch I

---

[3] The measure of organic acids are taken from the calculations made in paragraph 4.5

Batch II

Compound	Amount in feed (mg/l)	% in concentrate	% in permeate	% lost or gain by other meanings or inaccuracy
NH_4	140	91.9	20.8	+12.7
N_{tot}	220	58.5	13.3	-28.2
N_{tot}-NH_4^+	80	0.0	0.0	-100
K	55	85.1	8.3	-6.6
P_{tot}	25	46.8	0.5	-52.7
PO_4-P	18	63.1	0.6	-36.3
SO_4	22	127.6	8.0	+35.7
Ca	45	57.2	0.7	-42.1
Mg	8.2	39.9	1.1	-59.0
TOC	550	55.3	2.4	-42.3
TOC filtrated samples	370	155.4	4.2	+59.7
COD	1900	57.3	1.6	-41.1
COD filtrated samples	730	130.0	3.6	+33.2
Fatty acids	180	144.0	1.3	+44.3
Suspended Solids	930	119.5	0	+19.5
Alkalinity (pH=5.5)	6.9	101.0	25.6	+26.6
Alkalinity (pH=3)	14.6	100.3	21.7	+22.0
Organic acids4	7.7	99.7	18.3	+18.0
conductivity	1633	64.2	10.7	-25.1
Na+	87.0	90.1	9.8	-0.1
Cl-	110	90.4	11.2	+1.6

Table 13: Mass balance results for batch II

---

[4] The measure of organic acids are taken from the calculations made in paragraph 4.5

Batch III

Compound	Amount in feed (mg/l)	% in concentrate	% in permeate	% lost or gain by other meanings or inaccuracy
NH_4	150	77.4	20.6	-2.0
N_{tot}	190	73.3	23.7	-3.0
$N_{tot}-NH_4^+$	40	93.3	0.0	-6.7
K	53	90.0	10.0	±0.0
P_{tot}	17	63.5	0.7	-35.8
PO_4-P	17	43.1	0.78	-50.0
SO_4	24	169.2	7.4	+77.4
Ca	36	58.0	1.0	-41.0
Mg	6.7	60.6	1.3	-38.1
TOC	260	75.9	3.1	-21.0
TOC filtrated samples	180	71.5	4.4	-24
COD	1200	57.0	2.2	-40.8
COD filtrated samples	600	83.8	4.4	-11
Total fat	190	29.3	1.7	-68.9
Suspended Solids	530	48.1	0	-51.9
Alkalinity (pH=5.5)	7.3	88.9	26.6	+15.6
Alkalinity (pH=3)	13.6	88.4	24.1	+12.4
Organic acids5	6.3	87.6	21.1	+8.7
conductivity	1543	61.3	12.3	-26.4
Na+	87	89.3	11.2	+0.5
Cl-	100	103.2	15	+18.2

Table 14: Mass balance results for batch III

As explained before the objective of black water concentration is to achieve the maximum recovery of nutrients (e.g. nitrogen, potassium and phosphorus) in order to produce fertilizers for agricultural use. Therefore, it is interesting to determine how much nutrients were lost during one batch operation. The nutrient loss can be due to several reasons such as biological degradation; water chemistry change and loss through permeate production.

---

[5] The measure of organic acids are taken from the calculations made in paragraph 4.5

Nitrogen and ammonium recovery

- Batch I (acidified) had the highest recovery of nitrogen (76.8%). It is followed by batch III (no dosing) with 73.3% and finally by batch II (antiscalant dose) with 58.8%. This is due to the fact that batch I had a higher membrane rejection than the other two batches, and therefore less nitrogen was lost through the permeate.

- The recovery of nitrogen is more than 70% for batches III and I while for batch II it is only of 59% but this can probably be a consequence of analytical failure on the nitrogen feed concentration.

- By looking at the ammonium values, batch II had the highest recovery, but this can depend on the transformation of organic nitrogen to ammonium during concentration. For batch III and I, no organic nitrogen was lost ($Ntot- NH_4$) and here the recovery for nitrogen was about the same (ca. 75%).

It is surprising that the recovery of ammonium is not better for batch I compared with the other two batches. At low pH, the concentration of ammonia is low, hence the loss of ammonia gas to the air and permeate should be small. However, it must no be forgotten that the pH of batch I was low only at the beginning of the operation while at 80% volume reduction (when losses through permeate start to be significant) it was already at the same level as for the other batches.

Total phosphorus and phosphate recovery

- The best total phosphorus and phosphate recovery was observed for batch I.

- The loss of phosphorus through permeate is very low for all batches, so phosphorus must have been lost by precipitation in places that could not be reached when sampling was done: e.g. the bottom of the tank, pipes and at membrane surfaces.

Sulphates

- In the feed a large part of the sulphates (ca. 50%) is bound to organics or protein, so when these latter are degraded, free sulphates are produced. This would explain the high concentration increase of sulphates in the concentrate.

Calcium and magnesium

- Batch I had the highest recovery of calcium and magnesium even if all batches had very low losses through permeate (<2%). Actually bi-valent ions are always well rejected by the membrane. Still, it has to be kept in mind that batch I was acidified and a higher degree of concentration was achieved. However, the loss of calcium and magnesium by other meanings is two times higher for batches III and II. This is probably due to precipitation of insoluble metal salts at the bottom of the

tank or in the pipes. As the pH in batch I was lower, less precipitation took place. More precise conclusions about precipitation are made later in paragraph 4.4.

Chlorides and sodium
▪ Batches III and II had a higher percentage of recovery than batch I because batch I had a lot of ion losses through permeate (>20%) while the amount loss through permeate did not exceed 15% for batches III and II. This is due to the fact that batch I reached a higher concentration factor and had a higher ionic strength because of the hydrochloric acid. Indeed, membrane rejection of monovalent ions goes down with time (see paragraph 4.7) due to concentration polarization. The value of the amount gained by other meanings must be due to inaccuracy in measuring or calculating since neither sodium nor chloride were added during the tests.

Conductivity
Conductivity is proportional to the activity of ions in solution. The conductivity loss by other meanings of batches III and II is quite similar, while the one of batch I is almost two times higher. This could be a pH-effect since the pH of batch I increases relatively more (a low pH gives a higher conductivity) but it can also depend on a lower activity coefficient due to higher ionic strength.

Alkalinity
▪ All batches seem to have gained alkalinity, the greatest one being for batch I until pH=5.5 and batch II for until pH=3. This phenomenon is probably due to ammonification.

TOC, COD, Suspended solids, total fat and organic acids
▪ Batch II shows an increase of suspended solids and total fat while only 60% of the initial COD and TOC is found in the concentrate. This is not possible so it must be due to errors in analysis.
▪ For the other batches, a lot of suspended solids are lost, probably due to sedimentation. This is consistently observed in the COD values which go down in the same way as the suspended solid values: batch I lost 20% of SS and 15% of COD while batch III lost 51.9% of SS and 40.8% of COD.
▪ The loss of COD due to other things is almost three times higher for batches III and II than for batch I. There was probably more sedimentation in those batches.
▪ The permeate leakage of TOC, COD, suspended solids and total fat is kept low for all batches (5%). So the membrane rejection for those compounds is kept high during the whole operation.
▪ The concentration decrease of COD and TOC for filtrated samples should give an indication of biological degradation. It is the case for batch III. But in the case of batch II and I, it can be observed that TOC and COD increase. Maybe organics bound to particles were hydrolysed into smaller soluble compounds.
▪ Organic acids were better recovered during batches III and II while for batch only 60% was found in the concentrate. This can be explained by the fact that batch I reached a higher concentration

factor and therefore a higher amount of organics were lost through permeate. There is also a pH effect increase: at low pH a lot of organic acids are neutralized and therefore they become more permeable to the membrane.

From a global point of view it can be said that batch I (acidified) showed the best nutrient recovery amounts. In fact, the initial acidification of batch I probably prevented the loss of ammonium through evaporation of ammonia.

4.5. Precipitation

4.5.1. Experimental Results

The occurrence of precipitation can be determined by analyzing alkalinity of filtrated and un-filtrated samples. Therefore, samples at 50%, 80% and maximum concentration were filtrated (over 1 µm) and analyzed. The same procedure was followed for each batch performed. The results are presented in table 13. The higher the difference in alkalinity values between filtrated and un-filtrated samples, the higher the amount of precipitation. The alkalinity values until pH=5.5 were used for the precipitation analysis in order to avoid the interference of organic acids.

Table 15: Alkalinity until pH=5.5 in meq/l

Sample at % volume reduction	Batch I	Batch II	Batch III
Initial feeed	2.5	6.9	7.3
Initial feed filtrated	2.1	6.7	6.9
Difference	0.4	0.2	0.4
50%	7.2	16.9	16.2
50% filtrated	6.7	17.8	15.7
Difference	0.5	+0.9	0.5
80%	16.6	36.2	38.0
80% filtrated	16.6	35.0	34.6
Difference	0.0	1.2	3.4
Maximum concentration	35.0	75.2	57.8
Maximum concentration filtrated	33.0	65.0	47.8
Difference	2.0	10.8	10.0

Batch II and III

It can be seen that before starting the operation, there are already some precipitates in the feed. The alkalinity difference between filtrated and un-filtrated samples is slightly increased as the concentration factor rises. This was expected because black water is getting more and more concentrated and therefore it is getting more and more supersaturated. This will lead to a precipitation rate increase of several compounds. Finally it can be seen that at the maximum volume concentration, the highest amount of precipitation is reached.

Batch I

As it was explained in chapter 3 (Methodology), batch I was acidified to pH=6.11. It can be observed that the alkalinity of all the samples taken during batch I are approximately 50% lower than the ones from the other two batches. It can also be observed that the alkalinity differences between filtrated and un-filtrated samples are lower for batch I than for batches II and III.

Precipitation can also be evaluated by observing the differences in concentration between filtrated samples and un-filtrated samples for several compounds susceptible to precipitate. The tables in appendix 8 show the concentration differences for each compound and each batch test.

Comments:

Only the measures of filtrated and un-filtrated samples for calcium, magnesium, phosphate, sulphates and ammonium are considered in this analysis.

- It can be seen that samples of initial feed for batch I have always a smaller difference between filtrated and un-filtrated samples than the samples of the other two batches. This is due to the acidic conditions of batch I.
- The difference between filtrated and un-filtrated samples increases gradually for all batches. However, at the beginning of operation, the difference between filtrated and un-filtrated samples is not as significant as the difference between samples from 80% volume reduction and samples from maximal volume reduction. Consequently, the largest amount of precipitation probably takes place after reaching a concentration factor of five.
- Phosphates: at the beginning of operation, the difference between filtrated and un-filtrated samples is quite low (<5%) while it can be seen that this difference increases dramatically at a concentration factor of 5 and at maximum concentration. It is then probable that phosphate precipitates have been formed during all batches.
- Calcium and magnesium: contrary to phosphate, calcium and magnesium differences between filtrated and un-filtrated samples were already significant for all batches (>10%). So, there might have been precipitates from the beginning of the operation. Along the batch, these differences are increased, therefore precipitation is increased. This is due to the concentration

increase of the feed which enhances an oversaturation of the solution and also to the gradual pH increase.

▪ Ammonium and sulphates: the difference in ammonium between filtrated and un-filtrated samples is kept under 10%. It is therefore difficult to say if the differences are due to precipitation or inaccuracy in calculating and measuring. Sulphate concentration often rises after filtration, which is hard to explain.

Hence, it is cleared that precipitation occurred for all batches. The analyses show that the probable precipitates contained calcium, magnesium, phosphates and carbonates. Use of antiscalant as well as initial acidification of feed water were not helpful to prevent precipitation. Consequently, there was risk of membrane scaling for all batches.

4.5.2. Theoretical results

The chemical equilibrium program MINEQL+ was used to determine:

▪ the saturation index of several solids that can probably precipitate
▪ the theoretical concentration of the remaining ions in solution after precipitation during a batch test.

The input data consisted of the measured characteristics of the feed and concentrate at several stages of concentration. The data is presented in appendix 9. Indices and concentrations were determined at three stages of operation: at the beginning, at 80% volume reduction and at the maximum volume reduction. The results are presented in appendices 10 to 12.

Comments:
It is observed that the program presents several types of solids that can be formed from the ions entered in the input data. But only some of them have a positive saturation index and therefore can precipitate. Table 16 shows the possible precipitates that can occur during the batch test.

Test	Possible precipitates[6]		
	In the feed	At 80% volume reduction	At maximum volume reduction
Batch I	No precipitates	Aragonite, calcite, dolomite	Calcium phosphate, acidic calcium phosphates, hydroxyl apatite, Aragonite, Calcite, Huntite, Dolomite, Magnesite,
Batch II	Hydroxyl apatite, calcite, tricalcium phosphate	Calcium phosphate, acidic calcium phosphates, hydroxyl apatite, aragonite, calcite, huntite, dolomite	Calcium phosphate, acidic calcium phosphate , hydroxyl apatite, Aragonite, Calcite, Huntite, Dolomite, Magnesite,
Batch III	hydroxyl apatite, calcite, tricalcium phosphate	Calcium phosphate, acidic calcium phosphate, hydroxyl apatite, aragonite, calcite, huntite, dolomite	Calcium phosphate, acidic calcium phosphate, hydroxyl apatite, Aragonite, Calcite, Huntite, Dolomite, Magnesite

Table 16: Possible precipitates found in black water and black water concentrate

Comments:
- It can be observed that the calculated precipitates can be composed of calcium, magnesium, phosphate or carbonate.
- When observing the values of the remaining components in solution after precipitation, it can be seen that the cited compounds in the point above have the lowest concentration remaining.
- The amount of precipitation increases with the concentration factor but a lot more precipitates are formed between 80% volume reduction and maximum volume reduction rather than before 80% volume reduction.

4.5.3. <u>Conclusion from experimental and theoretical results</u>

A very interesting fact can be outlined from the analysis of experimental and theoretical results: the same conclusion that precipitates are probably composed of calcium, magnesium, phosphates and carbonates was made. The theoretical calculations gave although more precise information about the type of precipitate. This information can be used to estimate the type of precipitations if the conditions of the tests were to be changed, since saturation indices are known. For instance, precipitates like hydroxyapatite or tricalcium phosphate will be more difficult to avoid given that their calculated saturation indexes were kept very high. On the other hand, solids like magnesite and acidic calcium phosphate will be easy to eliminate since their saturation indexes were kept very low (<1.5).

---

[6] The chemical formulas of the solids cited in the table are given at the end of appendix 10.

In addition to that, it can be seen that the highest saturation index found for all batches is for hydroxyl apatite. This is probably one of the major and first precipitate that appears. It can be seen on its chemical formula that it has 10 molecules of calcium and 6 molecules of phosphates. So this precipitate can be one of the major reasons for phosphate and calcium decrease in solution. But what must be taken into account is that the precipitate type estimation was carried out considering that the solution was only composed of some ions. However, black water has a very high concentration in organics that influences the saturation conditions of the solids. Actually a higher concentration of ions that form precipitates is needed in a solution containing high amounts of organics compared to a solution without organic compounds (due to complexes).

Moreover, as for batches III and II there were already some positive saturation indices, inorganic fouling could have been expected, contrary to batch I. But the washing procedures carried out showed different results (see paragraph 4.6.2): inorganic scaling affected batches III and I. In that case, what has to be kept in mind is that precipitation can occur in the membrane cake boundary layer. Indeed when fouling starts, a layer is formed at the surface of the membranes so precipitation can take place there (precipitates are imbedded into organic fouling). If that is the case, then the precipitates in the layer will be removed when cleaning of organic matter is carried out.

To conclude, it can be said that the calculations as well as the experiments show that the best way to prevent precipitation is acidification as the use of antiscalant was not efficient at all. Acidification could then be a good method to prevent the membrane from inorganic scaling.

4.6. Organic Acids

A concentration measure of organic acids can be estimated by making the difference between alkalinity titrated to pH=5.5 and pH=3 (cf. paragraph 3.4.3). The table below shows the concentrations of organic acids at the beginning and at the end of each batch test, for both filtrated and un-filtrated samples.

Table 17: Concentration of organic acids determined from alkalinity in meq/l

Samples	Batch I	Batch II	Batch III
Initial feed	5.1	7.7	6.3
Initial feed filtrated	5.0	6.9	6
Difference	0.1	0.8	0.3
Final concentrate	47.6	78	42.2
Final concentrate filtrated	41	76.6	36.8
Difference	6.6	1.2	5.4

The concentrations of organic acids are higher for batch II at the beginning of the operation as well as at the end. The difference in concentration between filtrated and un-filtrated samples is relatively small compared to the actual values for each batch, hence the biggest part of the organics was soluble. This was also expected.

4.7. Fouling analysis

4.7.1. Permeate flow decrease

The incidence of fouling is characterized by a dramatic decrease of permeate flow. During operation, the permeate flow can decrease for two main reasons: the drop of shear rate due to less cross-flow (the feed is getting more and more viscous) and the increase of osmotic pressure due to concentration rise. These factors will lead to a gradual decrease of permeate flow of five to ten percent every two hours while fouling will give rise to a decrease of 70% to 80% in two hours. Table 18 shows the occurrence of fouling for the three tests performed and appendices 13 to 15 show the graphics with the evolution of permeate flow and pressure for each batch test.

Test	Characteristics	Hours of operation before fouling	Concentration factor attained before fouling	Maximum concentration factor attained	Permeate flow decrease in two hours (%)
Batch I	Acid dosing	8.3	5	15.5	80
Batch II	Antiscalant dosing	9.2	4	8.9	62
Batch III	No dosing	8.9	4	8.7	74

Table 18: Characteristics and concentration factors reached for each batch performed.

- For batch I, the highest concentration factor was reached before and after fouling, as well as the higher permeate flow decrease. But as it can be seen in the graphics, it also had an overall higher permeate flow during the whole operation. Moreover, the supersaturation point for that batch was attained later. So maybe for these reasons batch I reached a higher concentration factor.

- Moreover it can be seen in table 20 and 21 that the initial permeate flows for batches II and III were the same. These batches were concentrated up to the same level (see table 18).

- A comparison of the change in slope of the permeate flow curve can be done when fouling occurs. It can be observed for the three batches a dramatic change of slope after 8 to 9 hours of operation. The curves get almost vertical in a very short time period for batches III and II, while for batch I, the change is made gradually in a longer time period and with a less steep slope. Therefore, it can be concluded that batch one was affected by fouling in a smoother way than the other two batches.

From a general point of view, it can be concluded that fouling affected all batch permeate flows in the same way. However, batch I was less heavily affected considering that a higher concentration factor was reached.

Note:
A remark can be made regarding the gradual permeate flow decrease which is not due to fouling. The first batch test was performed with automatic pressure control and unfixed feed pump recirculation flow (controlled by the feed pump frequency). During operation it was observed that the feed pump frequency went down gradually from 35 Hertz to 25 Hertz in five to ten hours[7]. This phenomenon can be caused by the increase of suspended solid concentration and therefore viscosity of the feed along the experiment (see result summary in appendix 20). Therefore, the gradual decrease of permeate flow during the first seven hours (see graphics on appendix 13, 14 and 15) of operation can be explained as an effect of shear rate drop due to cross-flow fall and increase of osmotic pressure due to concentration raise.

During batch II, a feed pump failure was detected. There were some fibrous materials accumulated on the valve springs, which held up the creation of cross-flow at the surface of the membranes. Therefore the system could not work as it should. To overcome this difficulty, it was decided to run on fixed pump frequency (45 Hertz) and manual pressure control in order to guarantee cross-flow. Consequently, the rest of the tests were performed with these parameters. It can be seen that even if the unit was working at fixed frequency there was still a gradual decrease of permeate flow before fouling took place. Therefore, it is concluded that the influence of osmotic pressure increase during operation is not negligible and that a gradual raise of operating pressure to avoid permeate flow loss should compensate it. It is believed that vibration amplitude also has an effect on shear rate; the higher the vibration amplitude the higher the shear rate. But the study of the influence of this factor on permeate flow conservation will be performed in the future.

4.7.2. Type of fouling

Membrane fouling can have an organic origin due to fatty acid or bacteria deposition. It can also have an inorganic origin because of precipitation of inorganic salts such as calcium carbonate and calcium phosphate. The type of fouling was determined through the cleaning procedure.

Batch I
The following washing procedures were performed:
   1. NC2 at 2% and pH=10.20 the next day after the end of the batch test. As shown on table 19, the clean membrane permeate flow was not recovered, so a second cleaning was needed.

---

[7] In order to create enough cross flow so as not to accumulate concentrate at the membrane surface which rapidly foul the membrane, the feed pump frequency should be higher than 30 Hertz.

2. NC4 at 4% and pH= 2.99. Some permeate flow was regained but not the initial one. Therefore a third cleaning was needed.

3. Ariel at 4% and pH= 8.00. Still, the clean membrane permeate flow was not recovered.

Clean membrane permeate flow (ml/min)	Permeate flow after Batch I (ml/min)	Permeate flow after first cleaning procedure (basic) (ml/min)	Permeate flow after second cleaning procedure (acid) (ml/min)	Permeate flow after third cleaning procedure (pH=8) (ml/min)
930[8]	390	500	610	700

Table 19: Permeate flows before and after each operation/washing procedure

A visual inspection of the washing water was also made before and after the cleaning procedure. It can be seen in figure A, appendix 16 that there was a product removal from the system. It can therefore be concluded that after batch I, the membranes were fouled with organic and inorganic compounds.

Note:
Not all organic fouling was removed with NC2. The initial clean permeate flux could not be recovered after three washing procedures. So, for batch II, an average flow of 700 ml/min was considered as the one of a clean membrane stack. Moreover, analyses of acid washing water were made before and after the acid cleaning procedure. The objective of the analysis was to have an idea of the possible compounds that could have precipitated on the membrane. Appendix 17 shows the characteristics of the washing water and the results from the back titration with sodium hydroxide.

▪ No significant differences were found to be neither in suspended solids nor in ammonium concentrations. Nonetheless, it can be seen that there is a significant difference in calcium and magnesium concentrations before and after washing (higher concentration for the washing water).

▪ The back titration curves show that titration to pH of 6, the difference between before and after washing water starts to be significant. Finally, in order to reach a pH of 8.3, the water before washing needed more NaOH than the water after washing. This means that the water after washing was likely to have compounds that consumed carbonates that could have precipitated, like calcium and phosphate.

▪ Another indicator of this phenomenon is pH difference. It was observed that pH of after washing water was higher than the one of before washing water. This can be due to the dissolution of carbonated precipitates when carrying the acid washing procedure.

---

[8] This permeate flow was obtained when the first water test was carried out after the installation of the pilot membrane stack.

- Finally it can be seen that the amount of phosphates is higher for the water before washing. The contrary result was expected but as the detergent contains a high amount of phosphates (see appendix 4), the analysis of phosphates cannot lead to any conclusion regarding precipitation.

It can be assumed that the membranes were scaled with calcium carbonate and calcium magnesium carbonate (dolomite). Unfortunately, these analyses do not provide enough information to predict other types of precipitates.

Batch II

The following washing procedures were performed:

1. The membranes soaked in water during three days before carrying out any chemical cleaning procedure.

2. A basic cleaning procedure with NC2 2% (pH=10.6) was carried out.

As shown in table 20, this was enough to recover the capacity of the membrane stack to its original value.

Clean membrane permeate flow (ml/min)	Permeate flow after Batch II* (ml/min)	Permeate flow after first cleaning procedure (basic) (ml/min)
700	550	698

* The membrane stack soaked in water during three days after batch 2 before performing the water test.

Table 20: Permeate flow before and after washing following batch II

A visual inspection of the washing water also shows removal of organic fouling from the unit (see figure B, appendix 16).

It is therefore concluded that after batch II, there was probably only organic fouling on the membrane surfaces. Moreover, it was found of great help to soak the membranes in water for a longer period (a few days) before using chemicals to clean the unit. Some compounds must have been dissolved in water during that time.

Batch III

The following washing procedures were performed:

1. The membrane stack soaked in water during three days before performing the detergent cleaning process

2. First chemical washing procedure with NC2 detergent at 2% and at pH=10.6. A visual inspection of the basic washing water before and after the cleaning procedure as well as the recovery of some permeate flow (see table 19) show that there was removal of organic fouling

(see figure C, appendix 16). However, the clean permeate flow was not recovered, an acid washing procedure was needed.

3. Acid cleaning with NC4 at 4% and at pH=2.87.

Clean membrane permeate flow (ml/min)	Permeate flow after Batch III (ml/min)	Permeate flow after first cleaning procedure (basic) (ml/min)	Permeate flow after second cleaning procedure (acid) (ml/min)
698	584	650	707

Table 21: Permeate flows before and after each operation/washing procedure

After the acid washing procedure, the clean membrane permeate flow before batch III was recovered. Consequently, organic fouling and inorganic scaling occurred during the test.

Moreover, the analysis of acid washing water before and after the cleaning procedure was carried out. The analyses results are given on appendix 17, tables C and D. Based on those results the same kind of conclusion as for batch I can be made: the membrane was probably scaled with calcium carbonate and magnesium carbonate and no conclusions can be made about phosphates.

It was observed that batches III and I contained inorganic scaling. However, less precipitation was expected for batch I. But as the concentration factor reached with this latter was two times higher, it is possible that the solution was supersaturated enough in order to allow precipitation on the membrane surfaces (see theoretical precipitation study on paragraph 4.5.2).

4.7.3. <u>Permeate flow loss and precipitation</u>

It was observed in paragraph 4.5 that major precipitation happened after concentrating five times. Moreover, by looking at the graphics in appendix 13-15, it was observed that fouling affected batch I (acidified) in a more gradual way than the other two batches. So it is interesting to plot the permeate flow against the alkalinity difference between filtrated and un-filtrated samples which represents the amount of precipitation, since it is likely that precipitation and fouling are related. In order to draw the graphics, points at the beginning of the operation, at 50% volume reduction, at 80% volume reduction and at maximum volume reduction were taken.
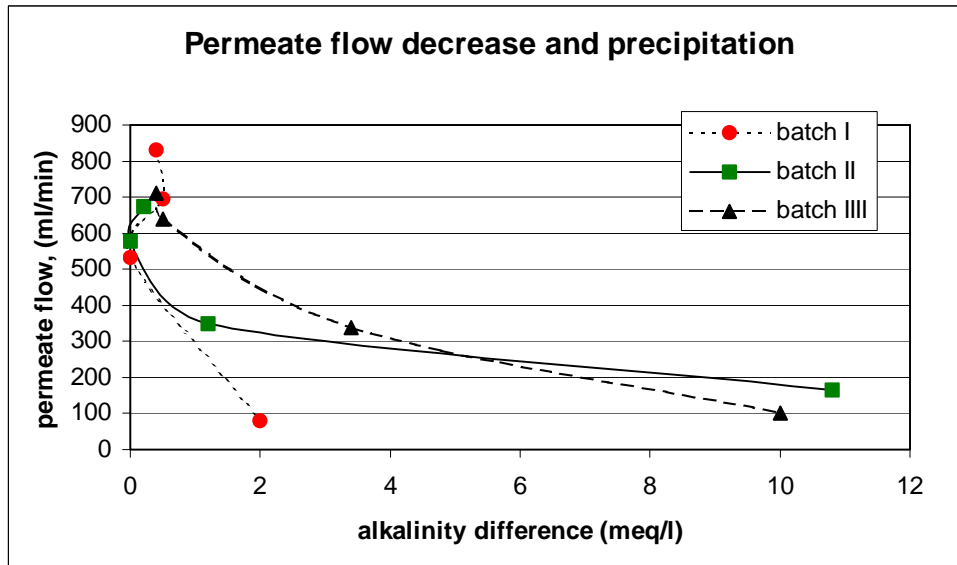
Figure 12: Permeate flow and precipitation

From this figure it can be said that the permeate flow loss might not be due to precipitation up to a concentration factor of 2 because the alkalinity differences are quite low (this can also be observed for the phosphate differences between filtrated and un-filtrated samples). However, when a concentration factor of five is reached, the permeate flow loss becomes larger (50%) for batches II and III, while for batch I the biggest loss is made after that point. Therefore it is possible that as precipitation increases, the effect of fouling becomes stronger.

4.8. Membrane rejection decrease

By following conductivity of permeate and concentrate not only during batch tests but also during clean water tests, another consequence of fouling can be studied: the membrane rejection decrease. When the membrane is operating correctly, the permeate/concentrate conductivity ratio should be kept constant at the order of two percent. If that ratio increases, it means that some compounds that were rejected by the membrane before are not anymore, so the membrane performance and the permeate quality have deteriorated [15].

Table 22 and figure 13 show the evolution of permeate/concentrate ratio for the different batches carried out as well as the average ratio for the clean membrane water test before each batch.

	Batch I	Batch II	Batch III
Water test average ratio (%)	2.09	2.37	2.69
Concentration factor	Test ratio (%)	Test ratio (%)	Test ratio (%)
1	2.3	2.2	2.5
1.2	1.8	2.2	2.5
1.6	1.6	1.9	2.5
2	1.7	2.4	2.9
3	1.8	3.2	3.0
4	2.3	4	3.8
5	3.0	5.3	4.9
7	5.1	7.2	7.8

Table 22: permeate to concentrate ratio regarding conductivity
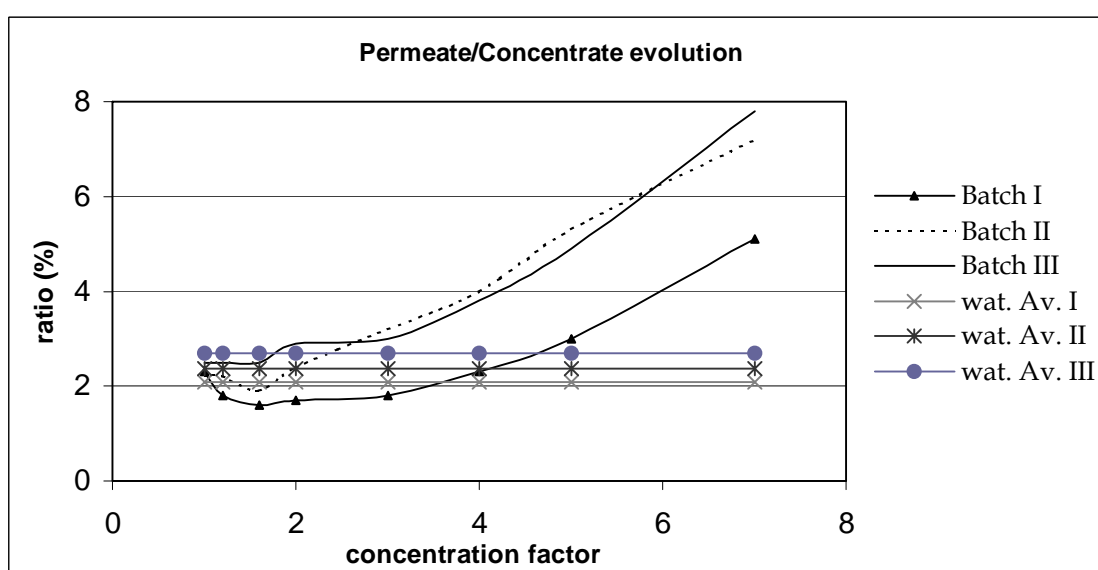
Figure 13: Evolution of the permeate/concentrate ratio regarding conductivity

Comments:

▪ When fouling begins, the permeate concentrate ratio increases dramatically for all of the batch tests.

▪ The ratio of batch I is kept lower than the one of the other batches during the whole operation. This is probably due to the acidic conditions of batch I. Indeed the lower the pH, the higher the rejection [15].

This phenomenon can also be observed with other parameters than conductivity. Indeed, the same type of reaction is observed for compounds like ammonium, sodium or chloride. In that case, the permeate/concentrate ratio is called Solute Passage (SP). However, this reaction is not observed for bivalent ions like magnesium and calcium. As it is shown on table 23, the permeate to concentrate ratio for bivalent ions is much lower than the ones of monovalent ions and the ratio increase is also less significant than for monovalent ions. It is then proved that monovalent ion rejection is lower than bivalent ion rejection.

	Ion	Before fouling (%)	After fouling (%)
Batch I	Na^+	1.6	7.2
	Cl^-	2.3	7.6
	NH_4^+	3.0	10.6
	Mg^{2+}	0.3	0.5
	Ca^{2+}	0.3	0.3
Batch II	Na^+	2.0	3.3
	Cl^-	1.9	5.8
	NH_4^+	4.4	8.7
	Mg^{2+}	0.3	0.3
	Ca^{2+}	0.2	0.2
Batch III	Na^+	2.2	6.2
	Cl^-	2.2	9.4
	NH_4^+	4.0	13.0
	Mg^{2+}	0.3	0.9
	Ca^{2+}	0.3	0.6

Table 23: Solute Passage before and after fouling for bi- and mono-valent ions

Other important parameters that have to be observed during the batch tests are pH and temperature. In fact, these parameters also influence the rejection coefficient of the membrane: the higher the temperature, the lower the rejection [5]. So the increase of permeate/concentrate ratio is not only due to fouling.

An increase in pH of one to two units was observed for all batches as shown in the graphics in appendix 18 as well as a temperature increase from five to eight Celsius degrees. The tables below present the initial and final pH-values and temperatures for all batches.

	Initial pH			Final pH			Average
	Permeate	Concentrate	Feed	Permeate	Concentrate	Feed	Permeate
Batch I	5.00	6.46	6.11	8.2	7.58	7.50	7.25
Batch II	5.95	7.32	7.10	8.59	7.90	7.90	8.33
Batch III	6.00	7.44	7.33	8.54	7.85	7.73	8.37

Table 24: pH evolution for the three batches performed

	Batch I	Batch II	Batch III
Initial feed temperature (°C)	23.8	21.3	22.1
Final feed temperature (°C)	28.7	28.2	29.9

Table 25: Temperature evolution of the three batches performed

pH

The pH of permeate varies dramatically for all batches during the operation:

- At the beginning, pH is kept low because of the presence of CO_2. In fact, the membranes are permeable to gases, so they will let CO2 pass through. Once in the permeate, CO_2 is transformed into carbonates and therefore the solution is acidified.

- When the operation approaches its end, the permeate pH is dramatically increased. This can be due to the increase of ion and/or ammonia passage.

- The permeate average pH for batch I is one unit lower than the pH of the other two batches. This is due to the initial acidification of batch I.

From a general point of view it can be said that membrane rejection can be maintained by preventing pH increase during operation.

4.9. Cleaning procedure

Firstly, The main difference between the cleaning procedures performed on the three batches was the fact that only one of them didn't soak in water before starting the chemical washing process. The water soaking without any chemical washing agent was found to be very effective for batches II and III since 50% of the initial permeate flow was recovered after three days of water soaking. Therefore, no Ariel cleaning was necessary for those batches. However, after batch I, no water soaking was carried out, but a final cleaning procedure with Ariel detergent was needed in order to try to recover the initial permeate flow.

It is then concluded that water soaking was a good option to clean the membranes before starting a chemical cleaning procedure, but it is time demanding. If the washing procedure ought to be carried as fast as possible, then no water soaking should be done but only several cleaning procedures with different chemical agents.

4.10. Pilot-mode test and laboratory-mode test comparison

First of all, the feed characteristics for each mode have to be compared. The feed characteristics of all batches carried out in L-mode are presented in appendix 19 and the ones of the P-mode are presented in appendix 5. It can be seen that the feed solutions are quite similar; the concentrations are at the same order of value.

Comments:

It can be seen that the initial clean permeate flow in the P-mode is a little bit higher than the one expected from the L-mode. However it was shown in chapter XX that the clean permeate flow in the P-mode decreased to 700 ml/min after batch I. This value is lower than the one expected (app. 800 ml/min). It is possible that the P-stack was damaged after that batch.

Table 26: L-mode and P-mode general comparison

	L-mode			P-mode		
number of reverse osmosis membranes	1			38		
Initial clean permeate flow	23 ml/min			930 ml/min		
Concentration factor	*Batch I*	*Batch II*	*Batch III*	*Batch I*	*Batch II*	*Batch III*
▪ before fouling	▪ 5	▪ 5	▪ 5	▪ 5	▪ 4	▪ 4
▪ maximum concentration factor	▪ 9	▪ 6.8	▪ 11.3	▪ 15.1	▪ 8.5	▪ 8.7
Total residence time (hours)	49 hrs 40 min	47 hrs 50 min	70 hrs28 min	14 hrs10 min	13 hrs	13 hrs 40 min
Initial pressure (bar)	10	12	11.5	12	12	12
Final pressure (bar)	18	20	19	17	17	15
Initial permeate flow (ml/min)	12	19	23	831	674	710
Final permeate flow (ml/min)	6	10	10	80	166	102
Initial feed temperature (°C)	26	17	21.2	23.8	21.3	22.1
Final feed temperature (°C)	29	32	30	28.7	28.2	29.9
% permeate flow decrease due to fouling	50	47.3	56.5	80	62	74
Type of fouling	Organic	Organic	Organic	Organic and inorganic	Organic	Organic and inorganic
Initial pH						
▪ feed	▪ 6.20	▪ 7.28	▪ 7.69	▪ 6.11	▪ 7.1	▪ 7.33
▪ permeate	▪ 5.62	▪ 6.19	▪ 8.40	▪ 5.00	▪ 5.95	▪ 6.00
Final pH						
▪ feed	▪ 7.45	▪ 8.41	▪ 8.32	▪ 7.5	▪ 7.90	▪ 7.73
▪ permeate	▪ NA	▪ 9.86	▪ 8.89	▪ 8.2	▪ 8.59	▪ 8.54
Permeate average pH	6.56	6.32	8.70	7.25	8.33	8.37

Comments (move to next page otherways hard to read):

- The maximum permeate flow decrease due to fouling for batch I was 56%; whilst for the P-mode it was 80%. It can be said that fouling affected in a stronger way the P-mode permeate flow. This can be due to the fact that both organic and inorganic fouling occurred in the P-mode while in the L-mode only organic fouling was determined.
- The residence time of the L-mode was approximately four times longer than in the L-mode. This could have created a difference in the recovery of nutrients since the chemistry and the biological activity in black water changes significantly with time
- The permeate flows of the P-mode are not exactly 38 times bigger than the ones of the L-mode. Nonetheless, it has to be noted that there were temperature, pressure and pH differences that could influence the membrane response in both modes.
- The same type of reaction regarding pH is observed for both modes: pH is kept low in the first hours of operation, then, near the end of operation it is increased. It can be seen that the final pH-values of the L-mod were higher that the ones of the P-mode. This can be due to the fact that the residence time in the L-mode was longer, therefore it allowed more processes to take place and influence pH like ammonia evaporation and ammonification.

Probably, the higher flows existing in the P-mode configuration induced a different response of the membrane stack compared to the response of the single membrane in the laboratory mode. But what must also be outlined is that before each batch test in the L-mode, a new membrane was installed while in the P-mode, the same membrane stack was used for all the test series.

Table 27: L-mode and P-mode amount of precipitation comparison

	L-mode			P-mode		
	Batch I	*Batch II*	*Batch III*	*Batch I*	*Batch II*	*Batch III*
Difference between filtrated and un-filtrated samples at for: (%)	Initial feed			Initial feed		
▪ Calcium	NA	0	21	18	NA	30
▪ Magnesium	NA	0	9	10	14	19
▪ Phosphates	NA	0	25	2	5	2
▪ Ammonium	NA	7	20	1	7	+6
▪ Alkalinity (meq/l)	0	2.3	1.4	0.4	0.2	0.4
Difference between filtrated and un-filtrated samples at for: (%)	At 80% volume reduction			At 80% volume reduction		
▪ Calcium	1	11	14	NA	NA	NA
▪ Magnesium	0	8	13	3	27	30
▪ Phosphates	17	NA	25	10	28	41
▪ Ammonium	0	NA	5	1	1	8
▪ Alkalinity (meq/l)	NA	3.3	1.1	0	1.2	3.4
Difference between filtrated and un-filtrated samples at for: (%)	At maximum volume reduction			At maximum volume reduction		
▪ Calcium	20	42	51	41	37	51
▪ Magnesium	15	54	65	43	60	33
▪ Phosphates	NA	58	63	57	36	49
▪ Ammonium	17	10	15	0	+6	10
▪ Alkalinity (meq/l)	10.5	19	NA	2	10.8	10

Comments:

▪ The same type of reaction can be observed for both modes: the values at the beginning of operation and at 80% volume reduction are quite similar while at maximal volume reduction, the differences increase a lot. So the same conclusions were made for both batches: most of the precipitation occurs after reaching a concentration factor of five.

▪ Less precipitation is observed in the L-mode batch I (acidified) at the end of operation, whilst in the P-mode there are not so many differences between each batch. However, up to a concentration degree of five, the acidification prevents from precipitation for both modes.

▪ The differences in ammonium values are higher for the L-mode. However, in the P-mode, the differences are kept quite low. Therefore it can be said that there were probably more chances to have precipitates derivate from ammonium (e.g. $MgNH_4PO_4$) in the L-mode concentrate (pH-values are higher in the L-mode).

▪ As the theoretical estimation of precipitates was not performed in the laboratory mode, no comparison can be carried out. However, from the experimental results it can be seen that probably the same type of precipitates were formed. They were probably composed of calcium, phosphate, magnesium or carbonate.

Acidification up to an initial pH of 6 was more effective in the L-mode rather than in the P-mode since less precipitates were formed at the maximum concentration degree.

Table 28: Nutrient recovery comparison

Nutrient recovery comparison	L-mode			P-mode		
	Batch I	*Batch II*	*Batch III*	*Batch I*	*Batch II*	*Batch III*
Nutrient:	% in concentrate			% in concentrate		
▪ Total nitrogen	78.9	104.3	69.5	76.8	58.5	73.3
▪ Total phosphorus	65.8	82.6	70.4	79.9	46.8	43.1
▪ Potassium	85.8	102.7	90.6	79.3	85.1	90
▪ Ammonium	87.2	97.7	76.3	72.6	91.9	77.4
▪ Phosphates	52.3	85.9	66	40.7	63.1	43.1
▪ Sulphates	370	166.3	136	98.8	127.6	169.2
▪ TOC	44.9	73	61.4	63.9	55.3	75.9
	% in permeate			% in permeate		
▪ Total nitrogen	6.95	7.9	15.3	27.3	13.3	23.7
▪ Total phosphorus	0.2	0.16	0.12	0.9	0.5	0.7
▪ Potassium	4.52	2.8	7.1	22.2	8.3	10
▪ Ammonium	7.95	8.5	18.2	31.4	20.8	20.6
▪ Phosphates	0.03	0.05	0.0	0.22	0.6	0.78
▪ Sulphates	0	0	0	6.0	8	7.4
▪ TOC	0	0	1.2	4.7	2.4	3.1
	% lost or gained(+) by other meanings			% lost or gained(+) by other meanings		
▪ Total nitrogen	14.1	+12.2	15.2	+4.1	28.2	3
▪ Total phosphorus	33.9	17.2	29.5	19.2	52.7	35.8
▪ Potassium	9.62	+5.5	2.3	+1.5	6.6	0
▪ Ammonium	4.18	+6.2	5.5	+4.0	+12.7	2
▪ Phosphates	47.7	14.1	33.9	59.1	36.3	50
▪ Sulphates	+270	+66.3	+36	+4.9	+35.7	+77.4
▪ TOC	+55.0	27	37.4	31.2	42.3	21

Comments:

- The same behaviour of sulphates is observed for both modes: the concentration of sulphates increased beyond the maximum expected. This phenomenon is even more significant for the L-mode tests, maybe because the residence time was longer and more sulphates were produced.

- In terms of performance, the best results in the L-mode for nutrient recovery were obtained in batch II, with antiscalant dose; whilst the best results in the P-mode were obtained in the batch with acid dose.

- It can be observed that for all batches in the P-mode, there was more nutrient losses through permeate than in the L-mode. This partly explains the general lower nutrient recovery of the P-mode compared to the L-mode.

The general lower nutrient recovery in the P-mode tests can be explained by two main reasons:

- Fouling had a stronger influence in these tests, therefore it could also make the membrane more permeable to certain compounds.

- In the L-mode new membranes were installed before each batch test so no damaged membranes were used. In the P-mode the same membrane stack was used for all the test series even if after batch I no initial clean membrane permeate flow was recovered. So the P-mode stack was not at its full potential during batches III and II.

5. <u>Recommendations</u>

It is recommended for future work to perform a batch test with a fixed pH of 6 since a good nutrient recovery and low degree of precipitation were obtained with an acidified feed. By that, it will be interesting to explore if fouling can be delayed and if the initial membrane rejection is kept. Besides, a two-stage concentration should be foreseen. For instance the unit could be stopped before fouling began to appear (at a concentration degree of five), then the membranes could be cleaned and the concentration process could be started again with the remaining concentrated feed. Moreover, it is recommended to perform tests with higher cross-flow by increasing the feed pump recirculation flow (higher feed pump frequency) to see if fouling can be controlled easily. It is also important to study the influence of vibration amplitude on the occurrence of fouling. Maybe higher concentration degrees could be achieved with increased vibration amplitudes.

Last but not least, it is important to keep the inhabitants of Skogaberg aware about the project that is being carried at their neighbourhood so that they don't create technical problems due to plastic material and tissue disposals into the black water system.

6.   <u>Conclusion</u>

The concentration of black water from 130 houses in the city area of Skogaberg was carried out using a VSEP reverse osmosis pilot unit composed of 38 membranes. This was made in order to study the evolution of black water chemistry, the incidence and the characterisation of fouling, as well as nutrient recovery. Therefore, three batch tests at different operating conditions were performed: batch I dosed with acid until reaching a pH of 6, batch II dosed with antiscalant at a concentration of 10 ppm and batch III not dosed at all.

The results showed that after approximately 14 hours of operation, fouling had affected all batches in the same way: a dramatic permeate flow decrease was observed after reaching a concentration factor exceeding four. However, there were some differences between each batch. Firstly, the final concentration factors attained were not the same: batch III and II were concentrated up to a factor of 8.5 and 8.7, respectively, while batch I was concentrated up to 15 times. Some other differences were found when nutrient recovery and precipitation were evaluated. The acidified batch showed the highest amount of compound retention in the concentrate (>70% for nitrogen, >75% for phosphorus, >79 % for potassium and >98% for sulphates) and also the lowest incidence of precipitation up to a concentration factor of five.

From a general point of view it can be said that precipitation occurred in a similar way for all batches: most of the precipitation probably took place after reaching a concentration degree of five. A theoretical study of precipitation enabled the determination of the main possible precipitates that could have been formed. It revealed that the solids were probably composed of calcium, magnesium, phosphate or carbonate. The main ones were hydroxylapatite, calcite, tricalcium phosphate, and aragonite among others.

The membrane cleaning revealed that inorganic and organic fouling had occurred for batches III and I, while batch II (antiscalant) only had organic fouling. Moreover, the analysis of acid cleaning water showed that the membranes were probably scaled with precipitates composed of calcium, magnesium or carbonates.

In addition to that, a comparison of the performances of the pilot unit was made with the ones of the laboratory unit. In fact, the same tests were carried out in the VSEP RO unit composed of only one membrane, the so called "laboratory mode (L-mode)". It was found that the pilot stack response (P-mode) was similar to the one of the laboratory mode: dramatic permeate flow decrease after reaching a concentration factor of five, high precipitation rates after concentrating five times, less precipitation for the acidified batch.

So, from all the analyses performed, it can be said that the best operating conditions in order to recover the maximum amount of nutrients and to protect the unit from inorganic scaling is the acidification of feed.

For the future, it might be interesting to perform acidic fixed pH tests in order to see if fouling is delayed. Moreover, two-stage operations should be explored in which the objective of the first step could be to concentrate up to a degree of five and then send the concentrate to a second stage, which could be operated in a different way (e.g. purge mode). In any case, a lot of investigation has to be done before deciding about the final process that will operate in the real wastewater treatment plant. The recirculation mode should not be aimed at since it cannot operate continuously, it demands a lot of time and energy and the membranes are fouled before reaching a high concentration factor.

Another important aspect that must not be left aside is the citizen information. Actually, many of the technical problems encountered during the project were due to unawareness of the public. For instance, plastic materials and tissues often blocked the feeding pump of the station. People from Skogaberg were then throwing objects that shouldn't be found in the black water pipes. This could only be avoided by a continuous education of the people. If a good quality product ought to be prepared, good quality raw materials ought to be used. The same idea can be applied to the production of agricultural fertilizers from household wastewater.

It is very stimulating to see a project of this type carried out by the City Council. It demonstrates that the City Council is thinking in long-term profits and trying to gain back the natural geochemical cycle equilibriums. Other cities around the world should learn from this example and try to go one step further in order to give back what has been taken from the land.

References

[1]   *Environmental System Analysis of sewerage alternatives in an urban district, Black Water System-Skogaberg, A pilot Project in Göteborg,* Geira Torjusen, Kretsloppskontoret Göteborg Stad, Linköping University, June 2002.

[2]   *Brief Project Description*, Pascal Karlsson, Kretsloppskontoret - Göteborg Stad, May 2004

[3]   *Behandlingsmöjligheter för att återvinna näringsämnen ur svartvatten från Skogaberg, Orienterande förstudie*, Mark de Blois, Kretsloppskontoret - Göteborg Stad, July 2004.

[4]   *Undersökning av pågående processer i svartvatten från Skogaberg*, Mark de Blois, Krestlopp Kontoret - Göteborg Stad, August 2004.

[5]   *Water treatment plant design,* Third edition, American water works Association, American Society of Civil Engineers, 1990 McGraw-Hill Companies.

[6]   *Lenntech, Technologie des membranes*, http://www.lenntech.com/français/membrane-technologie.htm, (21-06-05)

[7]   *Technology*, New Logic Research, http://www.vsep.com/solutions/technology.html, (22-06-05)

[8]   *Advanced Separation Technology Course Material 2004-2005 Chapter 7: Membrane separation processes*, Anders Rasmuson, Chalmers University of Technology, Department of Chemical Engineering Design.

[9]   *Influence of shear on flux in membrane filtration of integrated pulp and paper mill circulation water*, Tiina Huuhilo, Pasi Väisänen, Jutta Nuortila-Jokinen and Marianne Nyström, Desalination, volume 141, Issue 3 , 30 December 2001, Pages 245-258.

[10]   *Membrane filtration of manure wastewater, A comparison of conventional treatment methods and VSEP, a Vibratory RO Membrane System*, Greg Jonhson, Dr Brad Culkin Ph.D, Larry Stowell, New Logic Research Incorporated, August 2004

[11]   *Make Equilibrium Diagrams Using Sophisticated Algorithms (MEDUSA)*, Ignaci Puigdomenech, Inorganic Chemistry, Royal Institute of Technology, Stockholm, Program version: 18/02/04, http://www.kemi.kth.se/medusa (07/06/05)

[12]   *Aquatic Chemistry, Chemical Equilibria and rates in natural waters*, Third Edition, Werner Stum, James J. Morgan, 1996 John Wiley & Sons.

[13]   *Analysis of fouling on RO-VSEP (LFC 1) membrane system used in recovering nutrients from household sewage water of Skogaberg*, Shadab Ahmad, 2005 Department of Civil and Environmental Engineering, Water Environment Technology, Chalmers University of Technology, Sweden.

[14]   *MINEQL + version 4.5, Chemical Equilibrium modelling system*, William D Schecher, Drew C. Mc. Avoy, Environmental Research Softwares.

[15]   *Technical Service Bulletin: Foulants and Cleaning Procedures for composite polyamide RO Membrane elements (ESPA, ESNA, CPA, LFC and SWC)*, Hydanautics, July 2003 TSB107.10, www.membranes.com (15-07-05).

[16]   Naturvårdsverkets författningssamling, ISSN 1403-8234, NFS July 2004

[17]   Statens naturvårdsverks författningssamling Miljöskydd, ISSN 0347-5301, SNFS July 1994.

[18]   Statens naturvårdsverks författningssamling Miljöskydd, ISSN 0347-5301, SNFS July 1998

ix

<u>Appendix</u>

Appendix 1: Some important Equilibrium to be considered

- Water-carbonate equilibrium:

$HCO_3^- + H_2O \longleftrightarrow CO_3^{2-} + H_3O^+$ $\qquad$ $pK_a = 10{,}25$

$CO_2 + 2 H_2O \longleftrightarrow HCO_3^- + H_3O^+$ $\qquad$ $pK_a = 6{,}36$
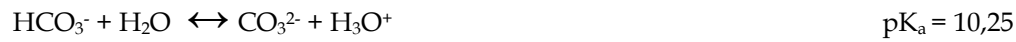
- Water-phosphate equilibrium:

$HPO_4^{2-} + H_2O \longleftrightarrow PO_4^{3-} + H_3O^+$ $\qquad$ $pK_a = 12.32$

$H_2PO_4^- + H_2O \longleftrightarrow HPO_4^{2-} + H_3O^+$ $\qquad$ $pK_a = 7.21$

$H_3PO_4 + H_2O \longleftrightarrow H_2PO_4^- + H_3O^+$ $\qquad$ $pK_a = 2.13$

- Ammonium equilibrium

$NH_4^+ + H_2O \longleftrightarrow NH_3 (g) + H_3O^+$ $\qquad$ $pK_a = 9{,}24$

- Fatty acids equilibrium, e.g. acetic acid

$CH_3COOH + H_2O \longleftrightarrow CH_3COO^- + H_3O^+$ $\qquad$ $pK_a = 4{,}77$

- Calcium carbonate equilibria

$Ca^{2+} + HCO_3^- + H_2O \rightarrow CaCO_3 (s) + H_3O^+$ $\qquad$ $Ks = 3.8 \cdot 10^{-9}$

- Calcium phosphate:

$3 Ca^{2+} + 2 HPO_4^{2-} + 2 H_2O \rightarrow Ca_3(PO_4)_2 (s) + 2 H_3O^+$ $\qquad$ $Ks = 1.3 \cdot 10^{-32}$

- Magnesium ammonium phospate:

$Mg^{2+} + NH_4^+ + HPO_4^{2-} + H_2O \rightarrow MgNH_4PO_4 (s) + H_3O^+$ $\qquad$ $Ks = 10^{12{,}6}$
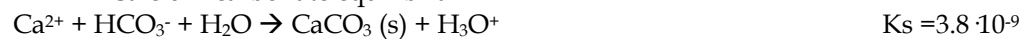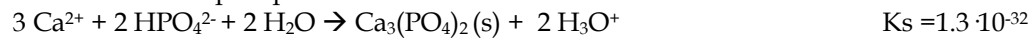
Appendix 2: Schematic of the Pilot mode VSEP unit [13]

Series LP Machine in "P Mode"
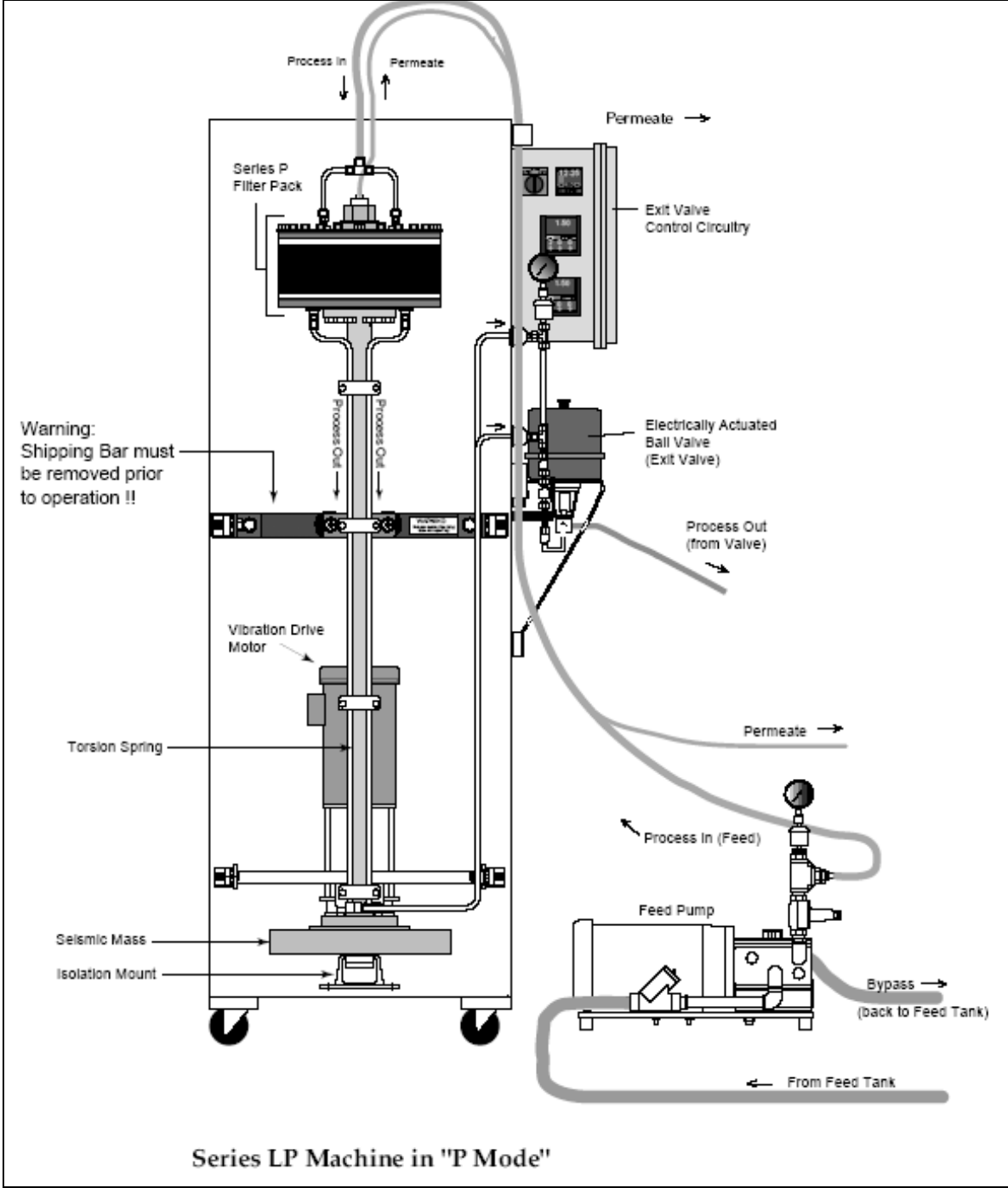
Appendix 3: Technical information about LFC-1 membranes

LFC

Test Conditions

NaCl Solution, PPM	1500
Applied Pressure, psig (MPa)	225 psi (1.55)
Operating Temperature, °F (°C)	77° (25°)
Permeate Recovery	15%
pH Range	6.5-7.0

Application Data

Maximum Applied Pressure, psig (MPa)	600 (4.14)
Maximum Feed Flow, GPM (m^3/h)	4040-16(3.6), 8-inch -75(17.0)
Maximum Operating Temperature, °F (°C)	113° (45°)
Feedwater pH Range*	3.0-10.0
Maximum Feedwater Turbidity, NTU	1.0
Maximum Feedwater SDI (15 mins)	5.0
Maximum Chlorine Concentration, PPM	<0.1
Maximum Ratio of Concentrate to Permeate Flow for Any Element	5:1
Maximum Pressure Drop for Each Element, psig	10

Element Performance

Element Type	Min Salt Rejection, %	Nominal Salt Rejection, %	Permeate Flow, GPD	(m^3/d)
LFC1	99.2	99.5	11,000	(41.6)
LFC1-4040	99.0	99.4	2,300	(8.7)
LFC3	99.5	99.6	9,500	(35.96)
LFC3-4040	99.0	99.6	1,980	(7.49)
LFC3-LD	99.5	99.7	11,000	(41.6)

Appendix 4: Specifications of the detergents used to clean the membranes

NC2 detergent, product of Norcap

---

1. KEMISK PRODUKT OCH TILLVERKARE/LEVERANTÖR

Produktens ändamål: Producent:

Neutralt rengöringsmedel för membran.   Nordcap Membrane Consulting
                                             Styrbordsgatan 12, 426 76 VF
                                             Tel. 031-691670 Fax 031-698557

---

2. SAMMANSÄTTNING/KLASSIFICERING

		Halt	CAS nr.
Hälsofarliga ämnen:	Natriumdodecyl-bensensulfonat	2-4 %	25155-30-0
	Natriumkapryl-iminopropionat	2-4 %	94441-92-6
Andra ämnen:	Trinatriumetylen-diamintriacetat	1-2 %	64-02-8
	Vatten		7732-18-5

Märkning   Irriterande

---

3. FARLIGA EGENSKAPER

Största hälsofaran: Kan irritera hud och ögon.

---

4. FÖRSTA HJÄLPEN

Inandning: Frisk luft.
Hudkontakt: Ta av nedstänkta kläder. Tvätta rikligt med vatten.
Stänk i ögonen: Skölj med vatten i flera min. Håll ögonlocken isär.
Förtäring: Skölj munnen med vatten. Rådfråga läkare.

---

5. ÅTGÄRDER VID BRAND

                  Ej brandfarligt.
Åtgärder: Flytta emballage från brandhärd.
Släckningsmedel: Samma släckningsmedel som omgivande brand.

---

6. ÅTGÄRDER VID SPILL/OAVSIKTLIGA UTSLÄPP

Miljömässiga
försiktighetsmetoder: Förhindra genom att valla in med sand, jord eller sågspån.

Saneringsmetoder: Absorbera större mängder med sand, jord eller sågspån.
                             Skölj bort återstående spill med vatten.

7. HANTERING OCH LAGRING

Hantering: Normal kemikaliehantering. Skall spädas vid användning.

Lagring: Normal kemikalielagring. Väl tillslutet på torr plats.

8. BEGRÄNSNING AV EXPONERING, PERSONLIGA SKYDDSÅTGÄRDER

Personlig skydds-
utrustning: Skyddsglasögon, plast- eller gummihandskar(Nitrilgummi).
                              Flaska för ögonsköljning. Skyddskläder.

Teknisk utrustning: Se till att friskt vatten finns lättillgängligt.

Hygieniska gränsvärden för denna produktkategori enligt AFS 2000:3 ej kända.

9. FYSIKALISKA OCH KEMISKA EGENSKAPER

Utseende: klar svagt gulbrun vätska.
Kokpunkt: 100° C.
Smältpunkt/fryspunkt: 0° C.
Densitet: $1.05 \ g/cm^3$.
Ångtryck: -
Rel. ångdensitet (luft=1):   -
Flampunkt: -
Tändpunkt: -
Löslighet i vatten: löslig.

Övriga data: lukt - förnimbar.

10. STABILITET OCH REAKTIVITET

Specifika egenskaper
och risker: Stabil under normala betingelser.

Hälsofarliga sönder-
delningsprodukter: Ej kända.

11. TOXIKOLOGISK INFORMATION

Hälsofara: Inandning kan ge hosta och nysningar vid långvarig inandning.
                              Hudkontakt ger avfettning. Förlängd kontakt ger hudrodnad.
                              Ögonkontakt kan ge lätt irritation.
                              Förtäring i små mängder ger ingen större effekt. I stora mängder
                              låg akuttoxicitet.

12. EKOTOXIKOLOGISK INFORMATION

Toxicitet för fisk: - .

Toxicitet för djur-

plankton: -

Toxicitet för växt-
plankton: -

13. AVFALLSHANTERING
Bortskaffas i enlighet med lokala regler. Tillfråga kommun.
Förpackning i enlighet med lokala regler. Tillfråga kommun.

14. TRANSPORTINFORMATION

Ej farligt gods enl ADR/ADR-S, RID/RID-S, IMDG eller DGR

15. GÄLLANDE BESTÄMMELSER

Varningssymbol för emballage: Irriterande

Risk-fraser: R 22   Farlig vid förtäring.
                R 36   Irriterar ögonen.

Skydds-fraser: S 23   Undvik inandning av dimma.
               S 26   Vid kontakt med ögonen, spola genast med mycket vatten
                            och kontakta läkare.
               S 2   Förvaras oåtkomligt för barn. Enbart för industriellt bruk.

16. ÖVRIG INFORMATION

Produktens användning: Rengöring av membran. Sädes innan användning.

Leveransformer: Vattenlösning - plastemballage.

MSDS handläggare   Carl-Henrik Hansson   Tel 031-691670

Utfärdare: Bengt Åke Andersson

Reviderad: 1 maj 2005

17. KÖPARENS INTERNA INFORMATION

Hos köparen granskad av: Datum:

....

NC4 detergent, product of Norcap

MSDS

---

1. KEMISK PRODUKT OCH TILLVERKARE/LEVERANTÖR

Surt rengöringsmedel för membran.	Nordcap Membrane Consulting Styrbordsgatan 12, 426 76 VF Tel. 031-691670 Fax 031-698557

2. SAMMANSÄTTNING/KLASSIFICERING

		Halt	CAS nr.
Hälsofarliga ämnen:	Fosforsyra	20-30 %	7664-38-2
	Dodecylbensen-sulfonsyra	2-4 %	27176-87-0
	Kumensulfonsyra	1-3 %	28631-63-2
Andra ämnen:	Hydroxietyletylendiamin-triacetat	1%	139-89-9
	Vatten		7732-18-5

Klassificering: R 22 Farlig vid förtäring
                     R 34 Frätande.
                     R 36/38 irriterar ögonen och hud

---

3. FARLIGA EGENSKAPER

Symbol: Frätande, C, irriterande Xi
Hälsa: Frätande. Irriterar ögonen och huden.
Brand: Produkten ej brandfarlig.
Miljö: Produkten är klassificerad som miljöfarlig. pH<2.

---

4. FÖRSTA HJÄLPEN

Inandning: Frisk luft, värme och vila. Ev andningshjälp. Kontakta läkare.
Hudkontakt: Tag av nedstänkta kläder. Skölj rikligt med vatten.
Stänk i ögonen: Spola med vatten i minst 15 min. Håll ögonlocken isär.   Kontakta läkare.
Förtäring: Drick några glas med vatten. Kontakta läkare.

---

5. ÅTGÄRDER VID BRAND

Ej brandfarligt.
Åtgärder: Flytta emballage med NC4 till brandsäker plats. Risk för
bildning av giftiga och irriterande gaser.
Släckningsmedel: Samma släckningsmedel som omgivande brand.

---

6. ÅTGÄRDER VID SPILL/OAVSIKTLIGA UTSLÄPP

Miljömässiga
försiktighetsmetoder: Undvik spill till ytvatten och avlopp. Valla in med sand, jord
eller sågspån. Vid större spill, kontakta kommunen.

Saneringsmetoder: Absorbera spill med neutral absorbent t ex sågspån eller sand,
                          samla upp. Behandla mark med kalk. Späd rikligt med vatten.

---

7. HANTERING OCH LAGRING

Hantering: God luftväxling samt skyddsutrustning så att direktkontakt med vätskan förhindras. Skall spädas före användning.

Lagring: Slutna originalemballage i ventilerad samt mörk och sval   plats. Undvik behållare av aluminium, järn eller tenn.

8. BEGRÄNSNING AV EXPONERING, PERSONLIGA SKYDDSÅTGÄRDER

Personlig skydds-
utrustning: Ögonspolningsmöjlighet samt nöddusch. Skyddsglasögon, skyddskläder samt skyddshandskar(PVC).
Hygieniska gränsvärden: NGV= 1mg/m3,   KTV= 3 mg/m3.
Enl AFS 2000:3

9. FYSIKALISKA OCH KEMISKA EGENSKAPER

Utseende:	lätt gul, klar lösning
Kokpunkt:	110° C
Smältpunkt/fryspunkt:	5° C
Densitet:	1.1 kg/m^3
Ångtryck:	-
Flampunkt:	-
Tändpunkt:	-
Explosionsområde:	-
Löslighet i vatten:	obegränsad löslig
pH i koncentrat:	<2

10. STABILITET OCH REAKTIVITET

Specifika egenskaper   Baser och starkt oxiderande ämnen bör undvikas.   .
och risker: Löser sig obegränsat i vatten under värmeutveckling.
Hälsofarliga sönder-
delningsprodukter: I kontakt med metaller finns risk för bildning
av giftig fosfin.

11. TOXIKOLOGISK INFORMATION

Akut toxicitet: Fosforsyra: LD_{50} oralt i råtta: 1530 mg/kg.
                              LD_{50} dermalt på kanin:2740 mg/kg.
          Dodecylbensensulfonsyra: LD_{50} oralt i råtta: ca 1000 mg/kg.
Hälsofara: Inandning. Höga halter ger irritation i andningsvägarna.
                              Hudkontakt. Ger hudirritation.
                              Stänk i ögon. Ger irritation med risk för ögonskador.
                              Förtäring. Ger irritation och risk för skada på magslemhinna och
                              matstrupe. Symptom är brännande smärta och kräkningar.

12. EKOTOXIKOLOGISK INFORMATION

Toxicitet för fisk: 85% fosforsyra:LC50 96 timmar (Gambusia affinis) = 138 mg/l.
                    Dodecylbensensulfonsyra: fisk 3-8 mg/l.
Toxicitet för Daphnia: 85% fosforsyra:LOEC, Daphnia (NaH2PO4) = 59 mg/l.
                    Dodecylbensensulfonsyra: EC50 Daphnia, 48h: 10 mg/l.
Toxicitet för alg: . Dodecylbensensulfonsyra; EC50 alg, 96h: >10 mg/l.

Bioackumuleras ej i vattenmiljö.

13. AVFALLSHANTERING

Utsläpp till miljön undvikes.
Spill kan neutraliseras med kalkslurry.
Rådfråga lokala myndigheter vid hantering av avfall.
Tömda engångsförpackningar lämnas till lokala återvinningsstationer eller hämtas av
lokala entreprenörer då alla risker eliminerats.

14. TRANSPORTINFORMATION

FN nr.   1805   IMDG: Klass:8 EmS nr: 8-08, MFAG nr: 700

ADR/ADR-S: Klass: 8, ämnesnr: 17(c)

RID/RID-S: Klass: 8, ämnesnr: 17(c)

15. GÄLLANDE BESTÄMMELSER

Klassificering: Frätande

Varningssymbol för emballage: C, Xi

Risk - fraser: R22   Xi   -farlig vid förtäring
R34   -frätande
                          R36 och R3   - irriterar ögon och hud
Skydds - fraser: S2   - förvaras oåtkomlig för barn.
                                      endast för industriellt bruk
                          S26   - vid kontakt med ögonen, spola genast
                                        med mycket vatten och kontakta läkare.
                          S39   -använd lämpliga skyddshandskar samt
                                        skyddsglasögon eller ansiktsskydd

16. ÖVRIG INFORMATION

Produktens användning: Rengöring av membran. Produkten spädes före användning.

Leveransformer: Vattenlösning - plastemballage.

MSDS handläggare   Carl-Henrik Hansson   Tel:031-691670

Utfärdare: Bengt Åke Andersson

Reviderad: 1 maj 2005

17. KÖPARENS INTERNA INFORMATION

Hos köparen granskad av: Datum:

Appendix 5: Feed composition and characteristics

Parameter	Batch I	Batch II	Batch III
PH	6.11	7.10	7.33
Initial temperature ($^{\circ}$C)	23.8	21.3	22.1
Alkalinity (pH=3) (meq/l)	7.6	14.6	13.6
Conductivity (μS/cm)	1442	1633	1543
Suspended Solids (mg/l)	450	930	530
COD (mg/l)	980	1900	1200
TOC (mg/l)	250	550	260
Fatty acids (mg/l)	140	180	190
Ptot (mg/l)	15	25	17
PO_4-P (mg/l)	18	18	17
Ntot (mg/l)	130	220	190
NH_4^+ (mg/l)	110	140	150
K^+ (mg/l)	42	55	53
Ca^{2+} (mg/l)	33	45	36
Mg^{2+} (mg/l)	5.6	8.2	6.7
Cl^- (mg/l)	210	110	100
SO_4^{2-} (mg/l)	31	19	24
Na^+ (mg/l)	68	87	87

Note: The values for filtrated samples can be found in appendix 20

Appendix 6: Final concentrate composition and characteristics

Table A

Parameter	Batch I	Batch II	Batch III
pH	7.5	7.7	7.9
Temperature (ºC)	28.7	28.2	29.9
Alkalinity (pH=3) (meq/l)	75.6	125.2	103.6
Conductivity (µS/cm)	8440	8960	8150
Suspended Solids (mg/l)	5400	9500	2200
COD (mg/l)	12000	9300	5900
TOC (mg/l)	2400	2600	1700
Fatty acids (mg/l)	1400	2200	480
Ptot (mg/l)	180	100	93
PO_4-P (mg/l)	110	97	72
Ntot (mg/l)	1500	1100	1200
NH_4^+(mg/l)	1200	1100	1000
K^+(mg/l)	500	400	420
Ca^{2+}(mg/l)	380	220	180
Mg^{2+} (mg/l)	69	28	35
Cl^- (mg/l)	2400	850	890
SO_4^{2-}(mg/l)	460	240	350
Na^+ (mg/l)	790	670	670

Note: The values for filtrated samples can be found in appendix 20

Appendix 6 (continuation): Final concentrate composition and characteristics

Table B

	pH	NH4-N	N tot	SS	PO4-P	P tot	COD(Cr)	Ca	Mg	Fat	K	TOC	SO4
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
BF 0	7.7	710	1600	1500	56	76	4500	160	30	450	280	1200	200
BF 20h	7.7	480	1300	830	67	72	3300	130	25	360	210	870	NM
BF 96h	7.5	550	1500	1000	65	71	3100	130	24	380	210	680	NM
BF-f 20h	NM	520	1300	110	57	58	2200	97	23	58	200	770	160
BF-f 96h	NM	540	1200	13	58	47	1600	95	22	49	200	540	130
TSED	7.9	1000	1200	2200	72	93	5900	180	35	480	420	1700	350
AF 20h	7.9	1000	2000	2100	110	120	6200	220	45	490	420	1900	360
AF 96h	7.8	1100	2000	2100	110	120	6100	220	45	530	430	1900	290
AF-f 20h	NM	980	1900	98	44	56	4200	130	16	150	410	1600	360
AF-f 96h	NM	1100	1900	38	49	62	4200	110	24	140	430	1700	400

Table C

mg/l		BF20h	BF96	AF20h	AF96h
mg/l	ammonium	289	314	391	461
uS/cm	conductivity	4710	4340	7460	7620
	pH	7.55	7.84	7.89	7.8
C	Temperat.	20.9	23.2	22.3	23.4

BF: before fouling (80 %) vol.red.
AF: after fouling
20h: measure made 20 Hours later
96h: measure made 96 Hours later
TSED: final concentrate

Appendix 6 (cont.)
Table D: Alkalinity measures

X: Until pH=5.5

Sample	HCl volum (ml)	Concent. M	alkalinity mEq/l
BF20h	15.3	0.1	30.6
BF-f20h	15	0.1	30
AF20h	27.6	0.1	55.2
AF-f20h	25.4	0.1	50.8
BF96h	17.8	0.1	35.6
BF-f96h	17.5	0.1	35
AF96h	27.1	0.1	54.2
AF-f96h	25.8	0.1	51.6

Y: Until pH=3

Sample	HCl volum (ml)	Concent. M	alkalinity mEq/l
BF20h	25.6	0.1	51.2
BF-f20h	24.9	0.1	49.8
AF20h	49	0.1	98
AF-f20h	45.3	0.1	90.6
BF96h	27	0.1	54
BF-f96h	25.4	0.1	50.8
AF96h	50.6	0.1	101.2
AF-f96h	46.3	0.1	92.6

Difference between X and Y

Sample	HCl volum (ml)	Concent. M	alkalinity mEq/l
BF20h	10.3	0.1	20.6
BF-f20h	19.9	0.1	39.8
AF20h	21.4	0.1	42.8
AF-f20h	19.9	0.1	39.8
BF96h	9.2	0.1	18.4
BF-f96h	7.9	0.1	15.8
AF96h	23.5	0.1	47
AF-f96h	20.5	0.1	41

Appendix 7: Permeate sample characteristics at different stages of concentration

P0: permeate at the beginning of the operation
P50: permeate at 50% volume reduction
P80: permeate at 80% volume reduction
Batch I (acidified)

PM: permeate at maximum volume reduction
PA: permeate average
NM: Not Measure

Samples	pH	COD mg/l	TOC mg/l	Fatty acids mg/l	Ptot mg/l	PO4-P mg/l	Ntot mg/l	NH$_4$ mg/l	K mg/l	Ca mg/l	Mg mg/l	Cl mg/l	SO$_4$ mg/l	Na mg/l
P0	5.0	NM	7.6	NM	NM	NM	NM	4.6	NM	NM	NM	6.7	NM	3.5
P50	6.6	NM	4.6	NM	NM	NM	NM	4.9	NM	NM	NM	8.1	NM	3.1
P80	7.5	<30	9.2	12	NM	NM	41	21	3.9	NM	NM	34	NM	7.7
PM	8.2	95	44	6.9	0.42	0.41	170	160	45	1.2	0.4	380	2.5	72
PA	7.7	30	13	9.9	0.14	0.043	38	37	10	0.51	<0.1	74	<2.0	17

Batch II (antiscalant dosed)

Samples	pH	COD mg/l	TOC mg/l	Fatty acids mg/l	Ptot mg/l	PO4-P mg/l	Ntot mg/l	NH$_4$ mg/l	K mg/l	Ca mg/l	Mg mg/l	Cl mg/l	SO$_4$ mg/l	Na mg/l
P0	5.95	NM	8.8	NM	NM	NM	NM	4.2	NM	NM	NM	2.5	NM	4.1
P50	6.7	NM	8.7	NM	NM	NM	NM	9.3	NM	NM	NM	3.5	NM	3.3
P80	7.7	35	13	2.8	NM	NM	35	32	4.3	NM	NM	11	NM	7.9
PM	8.7	90	36	2.5	0.28	0.27	170	140	22	0.64	0.1	76	2.3	37
PA	8.2	35	15	2.7	0.13	0.13	33	33	5.2	0.35	<0.1	14	<2.0	9.7

Batch III (no dose)

Samples	pH	COD mg/l	TOC mg/l	Fatty acids mg/l	Ptot mg/l	PO4-P mg/l	Ntot mg/l	NH$_4$ mg/l	K mg/l	Ca mg/l	Mg mg/l	Cl mg/l	SO$_4$ mg/l	Na mg/l
P0	6.0	NM	5.2	NM	NM	NM	NM	3.9	NM	NM	NM	2.1	NM	2.3
P50	7.1	NM	3.8	NM	NM	NM	NM	10	NM	NM	NM	3.5	NM	3.6
P80	8.1	30	8.2	4.9	NM	NM	43	NA	5.7	NM	NM	13	NM	10
PM	8.7	80	26	3.6	0.49	0.51	150	130	26	1.0	0.3	82	<2	42
PA	8.3	30	9.1	3.8	0.14	0.15	51	35	6.6	0.43	<0.1	17	<2	11

Appendix 8: Concentration and concentration differences in mg/l of filtrated and unfiltrated samples

Ca^{2+}	Initial feed			80% volume reduction			Maximum volume reduction		
Sample	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)
Batch I	33	27	18	170	NM	NM	340	200	41
Batch II	45	NA	NA	190	NM	NM	350	220	37
Batch III	36	25	30	160	NM	NM	180	87	51

Mg^{2+}	Initial feed			80% volume reduction			Maximum volume reduction		
Sample	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)
Batch I	5.6	5	10	32	31	3	74	42	43
Batch II	8.2	7	14	37	27	27	33	16	60
Batch III	6.7	5.4	19	30	21	30	33	22	33

NH_4^+	Initial feed			80% volume reduction			Maximum volume reduction		
Sample	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)
Batch I	110	100	1	700	690	1	1500	1500	0
Batch II	140	120	7	730	720	1	1600	1700	+6
Batch III	150	160	+6	710	650	8	1000	900	10

SO_4^-	Initial feed			80% volume reduction			Maximum volume reduction		
Sample	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)
Batch I	31	39	+2	240	250	+4	830	610	26
Batch II	22	19	1	200	230	13	NA	770	NA
Batch III	24	38	+36	200	250	+20	320	390	+18

PO$_4$-P	Initial feed			80% volume reduction			Maximum volume reduction		
Sample	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)
Batch I	18	14	2	80	72	10	180	69	57
Batch II	18	17	5	82	59	28	120	77	36
Batch III	17	13	2	76	45	41	65	33	49

K$^+$	Initial feed			80% volume reduction			Maximum volume reduction		
Sample	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)
Batch I	42	NM	NM	280	NM	NM	620	600	3
Batch II	55	NM	NM	280	NM	NM	350	220	37
Batch III	53	NM	NM	280	NM	NM	430	410	4

Cl$^-$	Initial feed			80% volume reduction			Maximum volume reduction		
Sample	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)
Batch I	210	NM	NM	1500	NM	NM	5000	NM	NM
Batch II	110	NM	NM	720	NM	NM	NA	NM	NM
Batch III	100	NM	NM	600	NM	NM	870	NM	NM

Na$^+$	Initial feed			80% volume reduction			Maximum volume reduction		
Sample	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)	Un-filtrated	Filtrated	Difference (%)
Batch I	70	NM	NM	470	NM	NM	1000	NM	NM
Batch II	87	NM	NM	490	NM	NM	1100	NM	NM
Batch III	87	NM	NM	450	NM	NM	680	NM	NM

Appendix 9: input data of MINEQL saturation index and concentration calculations

Concentrations in mol/l

		Na	Ca	Mg	K	Cl	NH4	PO4	SO4	Carbonates	pH
Batch I	CM	4.3E-02	8.5E-03	3.0E-03	1.6E-02	1.4E-01	8.3E-02	2.1E-03	8.6E-03	3.5E-02	7.8
	CMf	NM	5.0E-03	1.7E-03	1.5E-02	NM	8.3E-02	8.1E-04	6.4E-03	3.3E-02	7.9
	feed	3.0E-03	8.5E-04	2.3E-04	1.1E-03	2.5E-03	6.1E-03	1.6E-04	3.0E-04	2.5E-03	7.6
	C80	2.0E-02	4.3E-03	1.3E-03	7.2E-03	4.2E-02	3.9E-02	9.4E-04	2.5E-03	1.7E-02	7.7

		Na	Ca	Mg	K	Cl	NH4	PO4	SO4	Carbonates	pH
Batch II	CM	4.8E-02	8.8E-03	1.4E-03	1.6E-02	3.7E-03	8.9E-02	1.4E-03	5.4E-03	7.5E-02	8.0
	CMf	NM	5.5E-03	6.6E-04	1.6E-02	NM	9.4E-02	9.1E-04	8.0E-03	6.5E-02	8.1
	feed	3.8E-03	1.1E-03	3.4E-04	1.4E-03	3.1E-03	7.8E-03	2.1E-04	2.3E-04	6.9E-03	7.3
	C80	2.1E-02	4.8E-03	1.5E-03	7.2E-03	2.0E-02	4.1E-02	9.6E-04	2.1E-03	3.6E-02	7.7

		Na	Ca	Mg	K	Cl	NH4	PO4	SO4	Carbonates	pH
Batch III	CM	3.0E-02	4.5E-03	1.4E-03	1.1E-02	2.5E-02	5.6E-02	7.6E-04	3.3E-03	5.5E-02	7.9
	CMf	NM	2.2E-03	9.1E-04	1.1E-02	NM	5.0E-02	3.9E-04	4.1E-03	4.8E-02	8.1
	feed	3.8E-03	9.0E-04	2.8E-04	1.4E-03	2.8E-03	8.3E-03	2.0E-04	2.5E-04	7.3E-03	7.5
	C80	2.0E-02	NM	1.3E-03	7.2E-03	1.7E-02	3.9E-02	8.9E-04	2.1E-03	3.8E-02	7.7

CM: maximum concentration
CM: maximum concentration filtrated
C80: concentration at 80% volume reduction
feed: initial feed
NM: not measured

Appendix 10: Results from the MINEQL program calculations

Chemical formulas of the main compounds that precipitate:

Tricalcium phosphate: Ca_3PO_4
Acidic calcium phosphate: $CaHPO_4$
Hydroxyl apatite: $Ca_{10}(PO_4)_6(OH)_2$
Aragonite: $CaCO_3$

Calcite: CaO_3
Huntite: $CaMg_3(CO_3)_4$
Dolomite: $CaMg(CO_3)_2$
Magnesite: $MgCO_3$

Samples: Batch I feed
pH=6.11
Saturation indexes calculated:

solid	lime	Portland	Artinite	Hydromag	Periclas	Brucite	Mg(OH)2	Gypsum	Nesqueho	Thermona	Natron	Epsomite
Sat. index	-23.75	-13.86	-11.87	-25.5	-13.19	-8.45	-10.40	-2.435	-5.99	-12.6	-10.66	-5.46

Solid	Mirabili	Aragonit	Calcite	Huntite	Dolomite	Anhydrit	Halite	Magnesit
Sat.indx	-7.79	-1.82	-1.64	-12.15	-3.69	-2.68	-6.85	-3.21

Samples: Batch I 80% volume reduction
PH=7.7
Saturation indexes calculated:

solid	lime	portland	Artinite	Hydromag	Periclas	brucite	Mg(OH)2	Gypsum	Nesqueho	Thermona	Natron	Epsomite
Sat. index	-20.17	-10.284	-5.40	-10-63	-9.5	-4.78	-6.73	-1.41	-3.2	-8.77	-6.82	-4.35

Solid	Mirabili	aragonit	Calcite	Huntite	Dolomite Ca3(PO4)	Anhydrit	Halite	Magnesit
Sat. index	-5.63	0.89	1.07	-1.03	1.82	-1.66	-4.88	-0.40

Samples: Batch I maximum concentration
PH=7.8
Saturation indexes calculated:

solid	lime	portland	Ca4HPO4	CaHPOa:2	Hydroxyl	Artinite	Hydromag	Periclas	brucite	Mg(OH)2	MgHPO4	Gypsum
Saturation index	-18.86	-8.94	6.98	1.01	18.10	-4.60	-8.56	-9.14	-4.4	-6.35	-1.23	-0.16

Solid	Nesqueho	Thermona	Natron	Epsomite	Mirabili	CaHPO4	Aragonite	Calcite	Huntite
Sat. index	-2.77	-7.95	-6.00	-4.07	-4.95	1.29	2.28	2.46	1.62

Solid	Dolomite	Ca3(PO4)	Anhydrit	Halite	Magnesit	Mg3(PO4)
Sat. index	3.62	6.81	-0.41	-4.11	0.019	-3.11

Samples: Batch I maximum concentration, filtrated
pH=7.9
Saturation indexes calculated:

solid	lime	portland	Ca4HPO4	CaHPOa:2	Hydroxyl	Periclas	brucite
Saturation index	-19.74	-9.85	3.106	0.019	13.31	-9.08	-4.34

Solid	Mg(OH)2	MgHPO4	Gypsum	Epsomite	CaHPO4	aragonit	Anhydrit
Sat.indx	-6.29	-1.25	-1.08	-4.01	0.29	3.922	-1.33

Samples: Batch II, feed
pH=7.3
Saturation indexes calculated:

solid	lime	portland	Ca4HPO4	CaHPOa:2	Hydroxyl	Artinite	Hydromag	Periclas	brucite
Sat. index	-21.32	-11.42	-0.77	-0.75	7.85	-7.68	-16.21	-10.71	-5.96

Solid	Mg(OH)2	MgHPO4	Gypsum	Nesqueho	Thermona	Natron	Epsomite	Mirabili
Sat.index	-7.91	-2.07	-2.53	-4.29	-11.03	-9.08	-5.51	-7.96

Solid	CaHPO4	aragonit	Calcite	Huntite	Dolomite	Ca3(PO4)	Anhydrit	Halite	Magnesit	Mg3(PO4)
Sat. index	-0.47	-0.165	0.015	-5.39	-0.34	0.81	-2.7	-6.75	-1.5	-6.33

Samples: Batch II, 80% volume reduction
PH=7.7
Saturation indexes calculated:

solid	lime	portland	Ca4HPO4	CaHPOa:2	Hydroxyl	Artinite	Hydromag	Periclas	brucite
Saturation index	-20.24	-10.35	2.66	0.040	12.37	-5.02	-9.18	-9.50	-4.76

Solid	Mg(OH)2	MgHPO4	Gypsum	Nesqueho	Thermona	Natron	Epsomite	Mirabili
Sat.indx	-6.71	-1.15	-1.57	-2.83	-8.38	-6.43	-4.43	-5.68

Solid	CaHPO4	aragonit	Calcite	Huntite	Dolomite	Ca3(PO4)	Anhydrit	Halite	Magnesit	Mg3(PO4)
Sat. indx	0.32	1.16	1.34	0.13	2.45	3.46	-1.824	-5.18	-0.04	-3.30

Samples: Batch II maximum concentration
PH=7.8
Saturation indexes calculated:

solid	lime	portland	Ca4HPO4	CaHPOa:2	Hydroxyl	Artinite	Hydromag	Periclas	brucite
Sat. index	-19.47	-9.5	4.17	0.28	14.65	-4.22	-7.19	-9.09	-4.35

Solid	Mg(OH)2	MgHPO4	Gypsum	Nesqueho	Thermona	Natron	Epsomite	Mirabili
Sat. index	-6.30	-1.27	-1.10	-2.44	-7.15	-5.20	-4.32	-4.74

Solid	CaHPO4	aragonit	Calcite	Huntite	Dolomite	Ca3(PO4)	Anhydrit	Halite	Magnesit	Mg3(PO4)
Sat. index	0.56	1.92	2.10	2.25	3.6	4.72	-1.35	-5.61	0.34	-3.11

Samples: Batch II maximum concentration filtrated
PH=8.0
Saturation indexes calculated:

solid	lime	portland	Ca4HPO4	CaHPOa:2	Hydroxyl	Periclas	brucite
Sat. index	-19.36	-9.46	3.54	0.04	14.14	-9.15	-4.4

Solid	Mg(OH)2	MgHPO4	Gypsum	Epsomite	CaHPO4	Ca3(PO4)	Anhydrit
Sat. index	-6.36	-1.69	-1.03	-4.42	0.32	4.34	-1.28

Samples: Batch III Feed=7.5
Saturation indexes calculated:

solid	lime	portland	Ca4HPO4	CaHPOa:2	Hydroxyl.	Artinite	Hydromag	Periclas	brucite
Saturation index	-21.01	-11.11	-0.64	-0.80	8.29	-7.24	-15.38	-10.39	-5.65

Solid	Mg(OH)2	MgHPO4	Gypsum	Nesqueho	Thermona	Natron	Epsomite	Mirabili
Sat.indx	-7.60	-2.12	-2.58	-4.16	-10.61	-8.66	-5.56	-7.72

Solid	CaHPO4	Aragonite	Calcite	Huntite	Dolomite	Ca3(PO4)	Anhydrite	Halite	Magnesite	Mg3(PO4)
Sat. index	-0.52	-0.03	0.14	-4.87	-0.08	1.0	-2.83	-6.68	-1.37	-6.13

Samples: Batch III, 80% volume reduction
pH=7.7
Saturation indexes calculated:

solid	lime	portland	Ca4HPO4	CaHPOa:2	Hydroxyl	Artinite	Hydromag	Periclase	brucite
Sat. index	-20.24	-10.35	2.59	0.015	12.29	-5.15	-9.40	-9.56	-4.8

Solid	Mg(OH)2	MgHPO4	Gypsum	Nesqueho	Thermona	Natron	Epsomite	Mirabili
Sat. index	-6.77	-1.24	-1.55	-2.87	-8.43	-6.48	-4.46	-5.73

Solid	CaHPO4	Aragonite	Calcite	Huntite	Dolomite	Ca3(PO4)	Anhydrite	Halite	Magnesit	Mg3(PO4)
Sat. index	0.29	1.18	1.36	0.22	2.43	1.88	-1.8	-5.29	-0.08	-3.53

Samples: Batch III maximum concentration
PH=7.9
Saturation indexes calculated:

solid	lime	portland	Ca4HPO4	CaHPOa:2	Hydroxyl	Artinite	Hydromag	Periclas	brucite
Saturation index	-18.88	-8.99	5.43	0.508	16.49	-4.66	-8.46	-9.25	-4.51

Solid	Mg(OH)2	MgHPO4	Gypsum	Nesqueho	Thermona	Natron	Epsomite	Mirabili
Sat.indx	-6.46	-1.8	-0.66	-2.71	-7.89	-5.94	-4.63	-5.51

Solid	CaHPO4	Aragonite	Calcite	Huntite	Dolomite	Ca3(PO4)	Anhydrit	Halite	Magnesit	Mg3(PO4)
Sat. indx	0.78	2.39	2.57	1.9	9.8	5.75	-0.91	-5.02	0.07	-4.34

Samples: Batch III maximum concentration filtrated
PH=8.1
Saturation indexes calculated.

solid	lime	portland	Ca4HPO4	CaHPOa:2	Hydroxyl	Periclas	brucite
Saturation index	-19.68	-9.75	1.39	-0.57	11.66	-8.94	-4.20

Solid	Mg(OH)2	MgHPO4	Gypsum	Epsomite	CaHPO4	Anhydrit	Mg3(PO4)
Sat.indx	-6.15	-1.76	-1.64	-4.50	2.80	-1.89	-3.96

Appendix 11: Results of the calculation of remaining species after precipitation with MINEQL program

Theoretical concentrations in mol/l
:

		Na	Ca	Mg	K	Cl	NH4	PO4	SO4	carbonates	pH
Batch I	CM	4.3E-02	2.7E-04	1.8E-04	1.5E-02	1.4E-01	8.3E-02	NA	8.6E-03	2.5E-02	7.8
	feed	3.0E-03	8.5E-04	2.4E-04	1.1E-03	2.3E-03	6.0E-03	NA	3.0E-04	6.9E-03	7.6
	C80	2.0E-02	4.1E-04	2.9E-04	7.1E-03	4.2E-02	3.8E-02	NA	2.5E-03	1.3E-02	7.7

		Na	Ca	Mg	K	Cl	NH4	PO4	SO4	carbonates	pH
Batch II	CM	4.8E-02	6.8E-05	4.2E-05	1.6E-02	3.7E-03	8.8E-02	4.0E-05	NA	6.9E-02	8.0
	feed	3.0E-03	7.5E-04	3.4E-04	1.4E-03	3.0E-03	7.7E-03	8.8E-07	NA	7.7E-03	7.3
	C80	2.1E-02	1.8E-04	1.2E-04	7.1E-03	2.0E-02	4.1E-02	8.7E-06	NA	3.4E-02	7.7

		Na	Ca	Mg	K	Cl	NH4	PO4	SO4	carbonates	pH
Batch III	CM	2.9E-02	3.0E-04	1.1E-04	1.1E-02	2.4E-02	5.5E-02	1.7E-06	NA	1.2E-02	7.9
	feed	3.8E-03	9.0E-04	2.8E-04	1.4E-03	2.8E-03	8.3E-03	2.6E-04	NA	7.8E-03	7.5
	C80	2.0E-02	1.7E-04	2.1E-04	7.2E-03	1.7E-02	3.9E-02	9.5E-06	NA	3.6E-02	7.7

CM: maximum concentration
C80: concentration at 80% volume reduction
feed: initial feed
NA: not available

Appendix 12: Differences between initial (input data) and remaining ion concentration values after precipitation

mol/l

Batch I		Na	Ca	Mg	K	Cl	NH4	PO4	SO4	carbonates	pH
Batch I	CM	7.8E-05	8.2E-03	2.9E-03	9.0E-04	8.5E-04	3.3E-04	NA	4.6E-05	1.0E-02	7.8
	feed	4.3E-05	0.0E+00	-4.3E-07	2.6E-06	2.1E-04	1.1E-04	NA	2.1E-06	-4.4E-03	7.6
	C80	4.3E-04	3.8E-03	1.0E-03	7.9E-05	2.5E-04	8.9E-04	NA	0.0E+00	3.9E-03	7.7

		Na	Ca	Mg	K	Cl	NH4	PO4	SO4	carbonates	pH
Batch II	CM	2.6E-05	8.7E-03	1.3E-03	1.5E-04	0.0E+00	8.9E-04	NA	NA	6.4E-03	8.0
	feed	7.8E-04	3.8E-04	4.5E-07	1.0E-05	9.9E-05	7.8E-05	NA	NA	-7.7E-04	7.3
	C80	4.3E-06	4.6E-03	1.4E-03	7.9E-05	2.8E-04	5.6E-05	NA	NA	2.1E-03	7.7

		Na	Ca	Mg	K	Cl	NH4	PO4	SO4	carbonates	pH
Batch III	CM	5.7E-04	4.2E-03	1.2E-03	2.6E-05	5.1E-04	5.6E-04	NA	NA	4.3E-02	7.9
	feed	2.6E-06	0.0E+00	-2.8E-07	-1.0E-06	1.7E-05	3.3E-06	NA	NA	-5.0E-04	7.5
	C80	-3.5E-05	NA	1.1E-03	-5.1E-07	1.4E-06	4.4E-05	NA	NA	2.0E-03	7.7

CM: maximum concentration
C80: concentration at 80% volume reduction
feed: initial feed
NA: not available

Appendix 13:: Parameter evolution during batch I

Parameter evolution batch I (acid dosing)
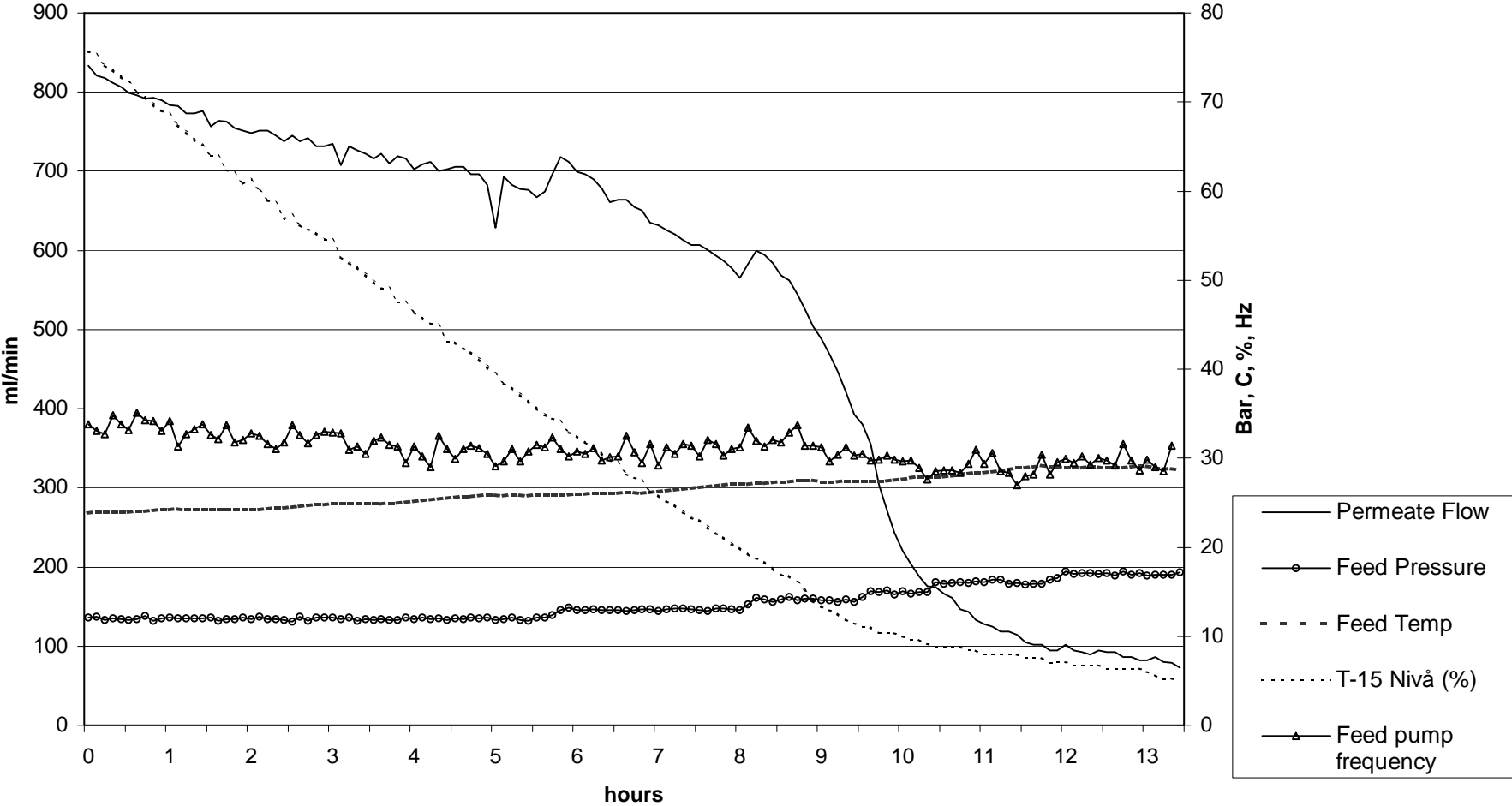
Appendix 14: Parameter evolution during batch II

Parameter evolution batch II (antiscalant dosing)
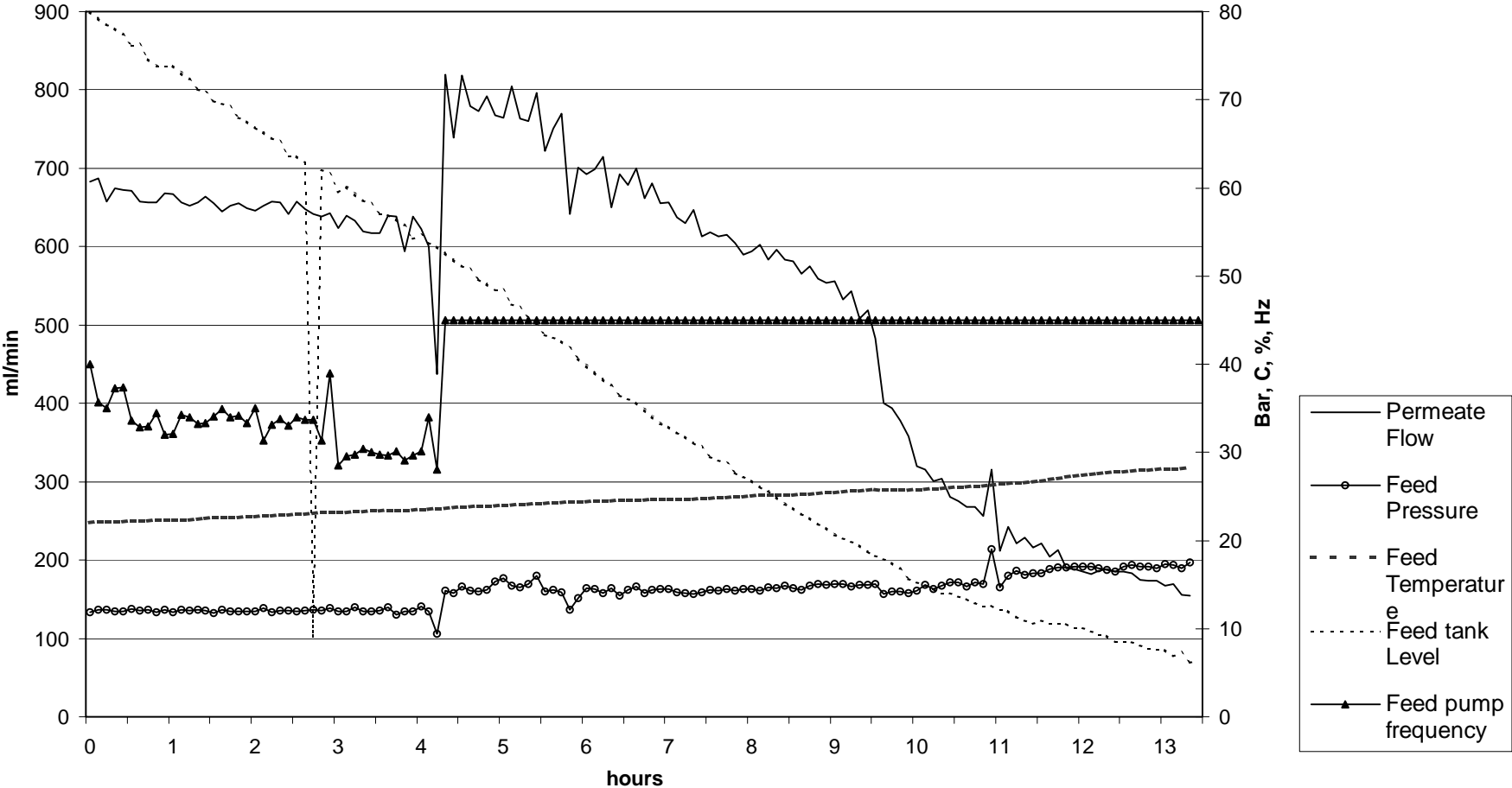
Appendix 15: Parameter evolution during batch III.

Parameter evolution batch III (no dosing)
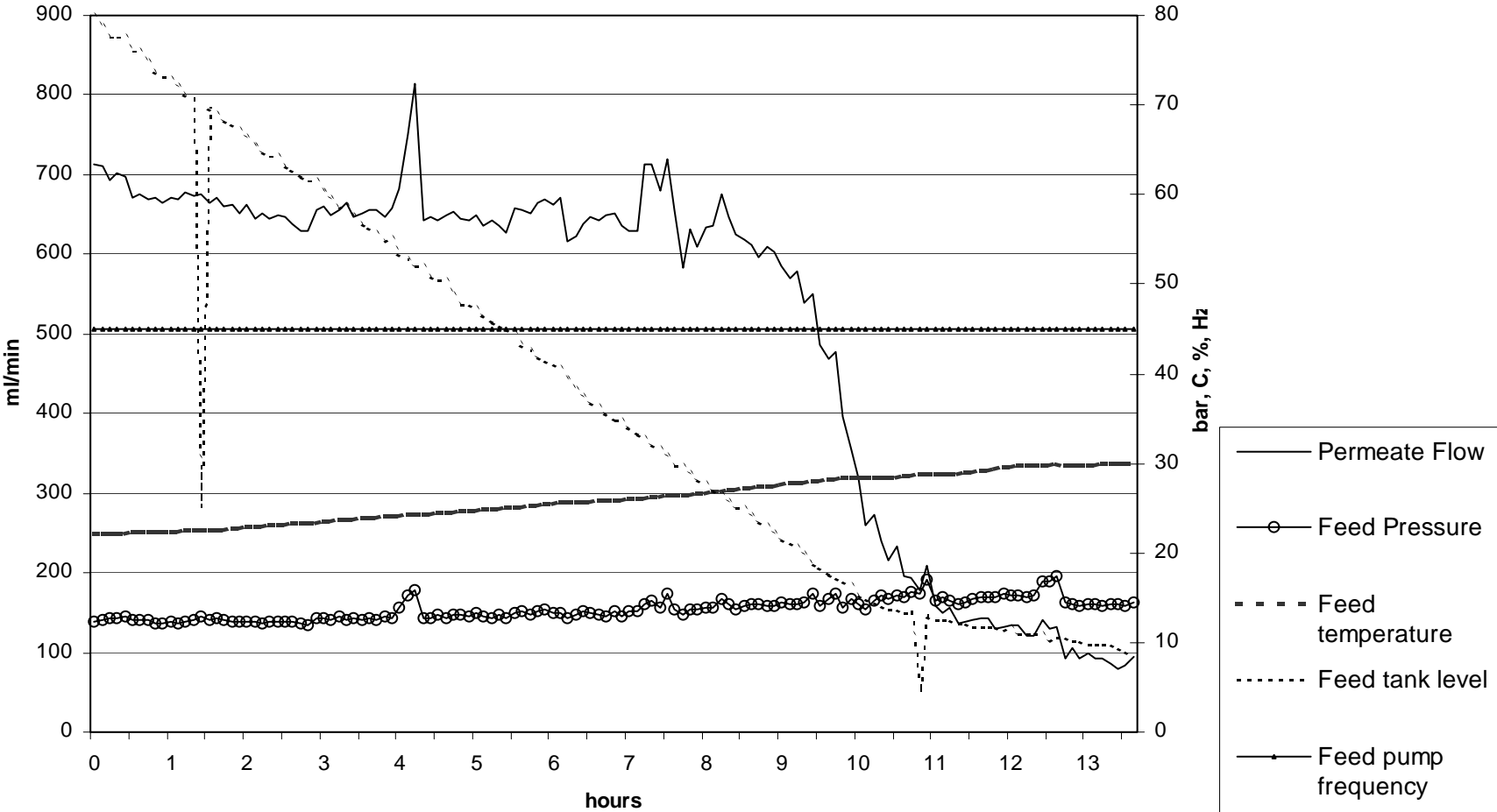
Appendix 16: Visual Inspection of washing water

Figure A: Visual inspection of washing water before and after first washing procedure of batch I.
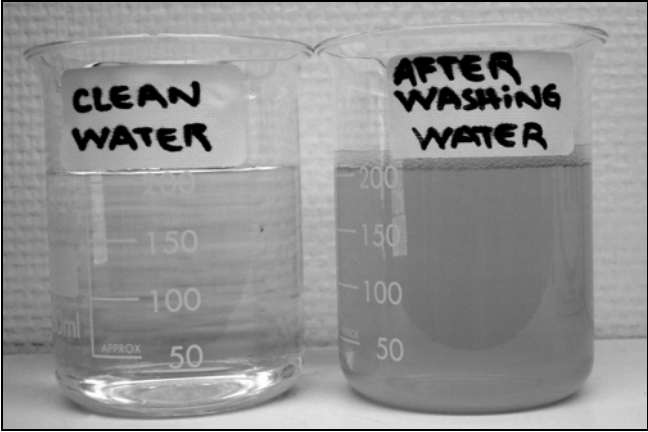
Figure B: Visual inspection of washing water before and after first washing procedure of batch II.
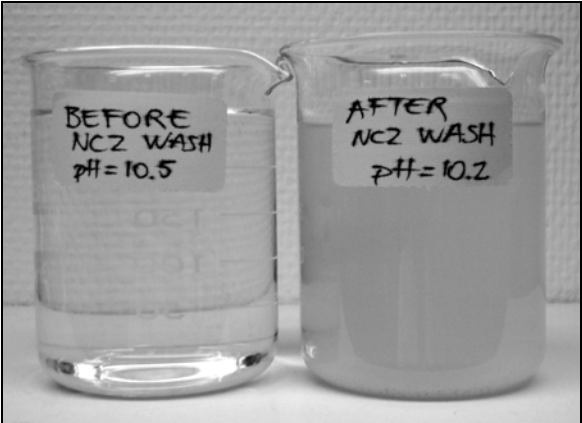
Figure C: Visual inspection of washing wat

Appendix 17: Analysis of washing water

Sample	volume of NaOH (ml)
Before washing	74
After washing	61

Table A: back titration of before and after washing water for batch I with NaOH at 0.05 M.

	pH	NH_4^+ (mg/l)	Suspended Solids (mg/l)	PO_4-P (mg/l)	Ca (mg/l)	Mg (mg/l)
Before washing	3	1.3	<5	2200	20	2.2
After washing	3.32	1.2	<5	1700	53	3.8

Table B: Before and after washing water analyses for batch I
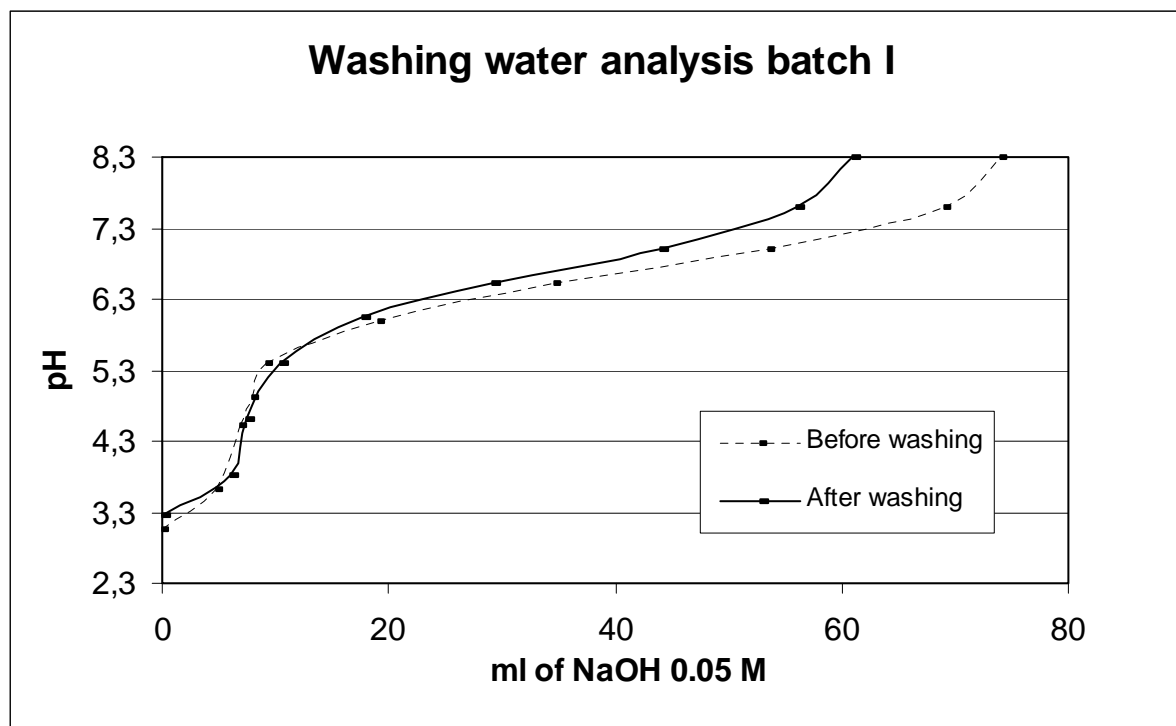
Sample	volume of NaOH (ml)
Before washing	107.6
After washing	94.5

Table C: Back titration of before and after washing water for batch III with NaOH at 0.05 M.

	pH	NH$_4^+$ (mg/l)	Suspended Solids (mg/l)	PO$_4$-P (mg/l)	Ca (mg/l)	Mg (mg/l)
Before washing	<3	1.3	<5	2200	20	2.2
After washing	<3	1.2	<5	1700	53	3.8

Table D: Before and after washing water analyses for batch III
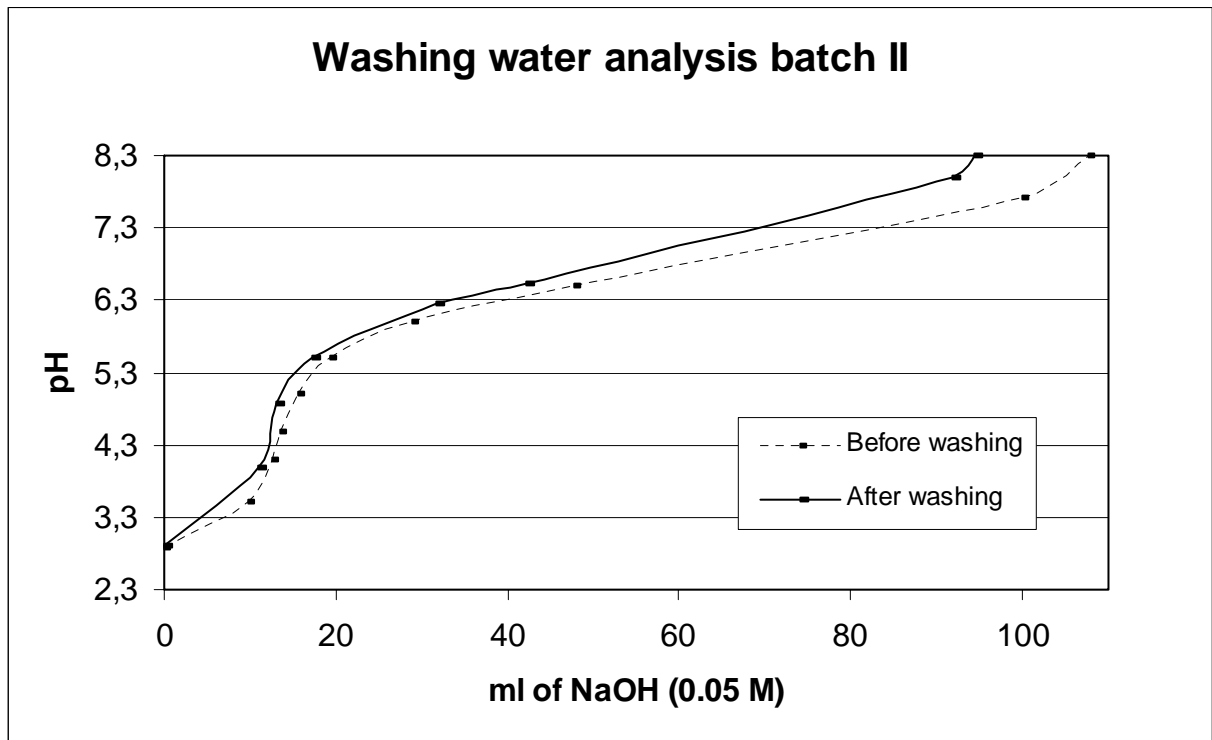
Appendix 18: pH evolution

pH evolution of batch I

pH evolution of batch II

pH evolution of batch III
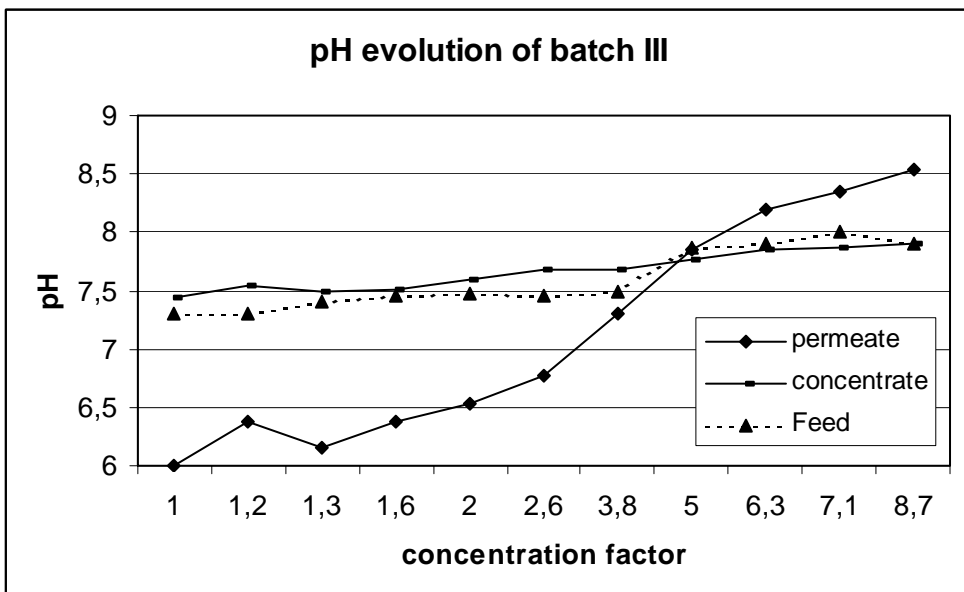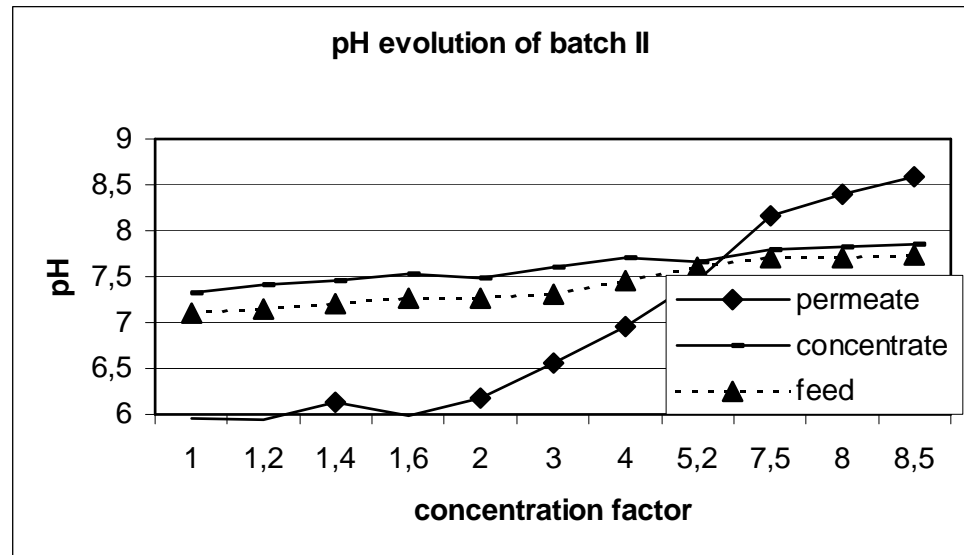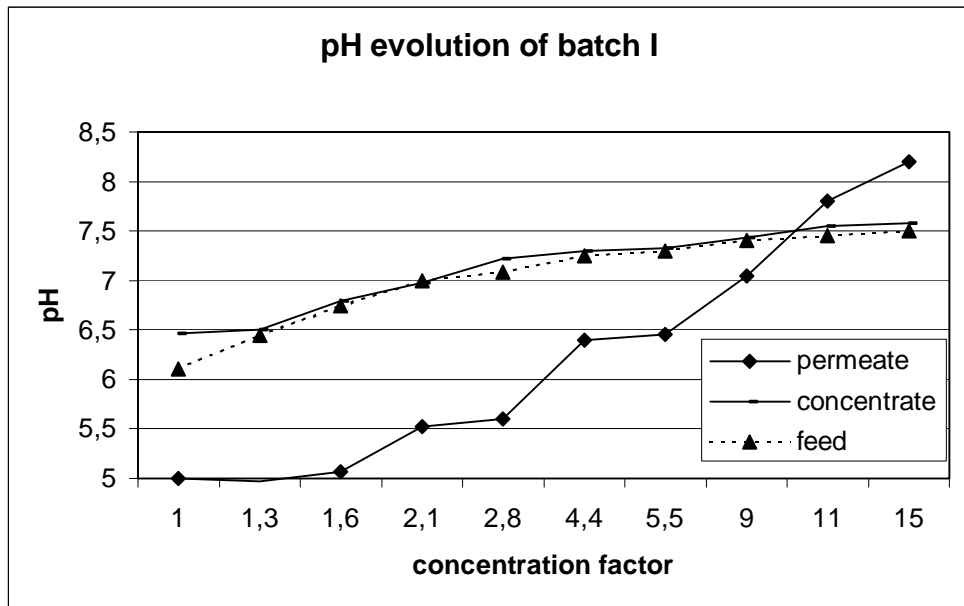
Appendix 19: Laboratory mode feed characteristics

Parameter	Batch I	Batch II	Batch III
pH	6.2	7.28	7.69
Initial temperature (ºC)	26.0	17.0	21.2
Alkalinity (pH=3) (meq/l)	NA	NA	NA
Conductivity (µS/cm)	1400	2850	1600
Suspended Solids (mg/l)	52	650	94
COD (mg/l)	710	1500	790
TOC (mg/l)	240	290	260
Total fat (mg/l)	35	120	29
Ptot (mg/l)	13	23	18
PO_4-P (mg/l)	12	18	15
Ntot (mg/l)	110	160	160
NH_4^+ (mg/l)	96	130	120
K^+ (mg/l)	48	64	65
Ca^{2+} (mg/l)	31	40	33
Mg^{2+} (mg/l)	5.1	7.2	7.3
Cl^- (mg/l)	230	110	120
SO_4^{2-} (mg/l)	33	39	33
Na^+ (mg/l)	70	85	79

Appendix 20: Summary of all chemical analyses carried out

Note: Tables A, B and C correspond to measures carried out by Alcontrol laboratories

Table A. Batch I, acid dose

	pH	Susp	COD(Cr)	TOC	Fatty acids	P tot	PO4-P	N tot	NH4-N	K	Ca	Mg	Cl	SO4	Na
Samples		mg/l	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
Feed	7.6	580	980	200	140	16	14	130	110	43	34	5.7	89	29	70
C50	7.5	370	NM	NM	NM	NM	31	NM	NM	NM	74	NM	NM	NM	NM
C80	7.7	840	3800	1200	430	96	80	790	700	280	170	32	1500	240	470
CM	7.8	2200	8500	2300	720	160	180	1500	1500	620	340	74	5000	830	1000
acid feed	6.1	450	980	250	140	15	18	130	110	42	33	5.6	210	31	68
final C.	7.5	5400	12000	2400	1400	180	110	1500	1200	500	380	69	2400	460	790
feed-f	NM	7	400	120	27	12	14	150	100	NM	27	5.0	NM	39	NM
C50-f	7.6	NM	NM	NM	NM	NM	28	NM	NM	NM	65	NM	NM	NM	NM
C80-f	7.8	NM	2700	930	100	64	72	780	690	NM	NM	31	NM	250	NM
CM-f	7.9	86	5900	2300	240	84	69	1500	1500	600	200	42	NM	610	NM
P0	6.0	NM	NM	7.6	NM	NM	NM	NM	4.6	NM	NM	NM	6.7	NM	3.5
P50	6.6	NM	NM	4.6	NM	NM	NM	NM	4.9	NM	NM	NM	8.1	NM	3.1
P80	7.5	NM	<30	9.2	12	NM	NM	41	21	3.9	NM	NM	34	NM	7.7
PM	8.2	NM	95	44	6.9	0.42	0.41	170	160	45	1.2	0.4	380	2.5	72
PA	7.7	NM	30	13	9.9	0.14	0.043	38	37	10	0.51	<0,1	74	<2,0	17

Table B. Batch II, Antiscalant

Samples	pH	Susp mg/l	COD(Cr) (mg/l)	TOC (mg/l)	Fatty acids (mg/l)	P tot (mg/l)	PO4-P (mg/l)	N tot (mg/l)	NH4-N (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Cl (mg/l)	SO4 (mg/l)	Na (mg/l)
Feed	7.3	930	1900	550	180	25	18	220	140	55	45	8.2	110	<2,0	87
C50	7.6	740	NM	NM	NM	NM	44	NM	NM	NM	97	NM	NM	NM	NM
C80	7.7	1300	5100	1700	510	89	82	890	730	280	190	37	720	200	490
CM	8.0	4200	1200	3800	830	150	120	1700	1600	630	350	33	1300	NM	1100
final C.	7.7	9500	9300	2600	2200	100	97	1100	1100	400	220	28	850	240	670
feed-f	7.6	38	730	370	19	18	17	180	120	NM	NM	7.0	NM	19	NM
C50-f	7.8	NM	NM	NM	NM	NM	39	NM	NM	NM	73	NM	NM	NM	NM
C80-f	7.9	NM	3900	1400	110	72	59	800	720	NM	NM	27	NM	230	NM
CM-f	8.1	250	9700	4100	300	75	77	1700	1700	620	220	16	NM	770	NM
P0	6.4	NM	NM	8.8	NM	NM	NM	NM	4.2	NM	NM	NM	2.5	NM	4.1
P50	6.7	NM	NM	8.7	NM	NM	NM	NM	9.3	NM	NM	NM	3.5	3.5	3.3
P80	7.7	NM	35	13	2.8	NM	NM	35	32	4.3	NM	NM	11	NM	7.9
PM	8.7	NM	90	36	2.5	0.28	0.27	170	140	22	0.64	0.1	76	2.3	37
PA	8.2	NM	35	15	2.7	0.13	0.13	33	33	5.2	0.35	<0,1	14	<2,0	9.7

Table C. Batch III, no dose

Sample	pH	Susp mg/l	COD(Cr) (mg/l)	TOC (mg/l)	Fatty acids (mg/l)	P tot (mg/l)	PO4-P (mg/l)	N tot (mg/l)	NH4-N (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Cl (mg/l)	SO4 (mg/l)	Na (mg/l)
feed	7.5	530	1200	260	190	17	17	190	150	53	36	6.7	100	24	87
C50	7.6	1400	NM	NM	NM	NM	37	NM	NM	NM	83	NM	NM	NM	NM
C80	7.7	1500	4500	1200	450	76	56	1600	710	280	160	30	600	200	450
CM	7.9	2100	6200	1800	470	97	65	1800	1000	430	180	33	870	320	680
final C.	7.9	2200	5900	1700	480	93	72	1200	1000	420	180	35	890	350	670
feed-f	7.7	24	600	180	21	14	13	210	160	NM	25	5.4	NM	38	NM
C50-f	7.7	NM	NM	NM	NM	NM	32	NM	NM	NM	57	NM	NM	NM	NM
C80-f	8.0	NM	2500	870	68	45	33	840	650	NM	NM	21	NM	250	NM
CM-f	8.1	100	3700	1300	100	43	33	1300	900	410	87	22	NM	390	NM
P0	6.7	NM	NM	5.2	NM	NM	NM	NM	3.9	NM	NM	NM	2.1	NM	2.3
P50	7.1	NM	NM	3.8	NM	NM	NM	NM	10	NM	NM	NM	3.5	NM	3.6
P80	8.1	NM	30	8.2	4.9	NM	NM	43	NM	5.7	NM	NM	13	NM	10
PM	8.7	NM	80	26	3.6	0.49	0.51	150	130	26	1.0	0.3	82	<2,0	42
PA	8.3	NM	30	9.1	3.8	0.14	0.15	51	35	6.6	0.43	<0.1	17	<2.0	11

Tables D: Measurements carried out at location

Batch I

Parameter		Feed	Feed-filtrated	C50	C50-f	C80	C80-f	CM	CM-f	TSED	P0	P50	P80	PM	PA
pH		6.11	6.43	6.98	NM	7.33	NM	7.58	NM	7.5	6.4	6.9	6.6	8.1	7.3
Alkalinity (2.5)	mEq/l	11	10.5	21	20.2	44.2	43	89	83.4	84.4	0.55	0.57	1.97	22	15.2
conductivity	uS/cm	1442	NM	3820	NM	8490	NM	16420	NM	8440	51	63	226	1808	242
ammonium	mg/l	86.2	79.2	201	NM	463	NM	869	NM	506	3.06	4.09	17.6	129	16.8
temperature	°°C	26.1	26	26.6	26.8	27.7	27.7	28.3	28.3	23	26	27.7	25.3	28.5	23

Batch II

Parameter		Feed	Feed-filtrated	C50	C50-f	C80	C80-f	CM	CM-f	TSED	P0	P50	P80	PM	PA
pH		7.1	7.45	7.49	NM	7.66	NM	7.85	NM	7.73	5.95	7.17	7.49	8.59	8.33
Alkalinity (2.5)	mEq/l	18.2	17.8	39.6	39.6	81	43	164	150.2	138	4.4	4.9	6.9	14.3	7.2
conductivity	uS/cm	1618	NM	4080	NM	8080	NM	15880	NM	8960	51	90	299	1053	197.5
ammonium	mg/l	149	139	350	NM	610	NM	1240	NM	551	3.56	8.26	32.3	151	42.0
temperature	°C	24	24	26.1	26.2	26.5	27	28	28	25.3	24	261	26.8	27	27

Batch III

Parameter		Feed	Feed-filtrated	C50	C50-f	C80	C80-f	CM	CM-f	TSED	P0	P50	P80	PM	PA
pH		7.3	7.6	7.59	NM	7.76	NM	7.9	NM	7.9	6.00	6.53	7.85	8.54	8.37
Alkalinity (2.5)	mEq/l	17.9	16.5	35.2	33.3	72.6	65.6	104.6	91	107	4.3	4.7	7.6	15	7.7
conductivity	uS/cm	1543	NM	3590	NM	7570	NM	10440	NM	8150	50	104	279	1010	215
ammonium	mg/l	132	121	272	NM	522	NM	764	NM	710	3.6	9.5	40.2	131	35.2
temperature	°C	24	24	26.8	27	29.1	29	29.5	29.3	NM	24.2	27.8	29.7	29	19