Clean Operator

Cleaning spiral wound membrane modules with a two phase solution

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Challenge the future

Clean Operator

Cleaning spiral wound membrane modules with a two phase solution

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SUMMARY

Before a bottle of champagne is opened, the gas above the champagne is almost pure carbon dioxide at a higher pressure than the atmospheric pressure. Champagne itself also contains dissolved carbon dioxide. When the bottle is opened, some of the carbon dioxide gas will escape (more CO_2 gas will escape instantly when the bottle is shaken before opening), the cork is blown away. Because the partial pressure of carbon dioxide above the champagne is decreased, some of the dissolved carbon dioxide is released from the champagne as tiny bubbles. This will continue till equilibrium between the carbon dioxide in the champagne and in the air occurs.

Clean Operator is essentially based on this natural phenomenon and is used to clean serial and horizontal placed spiral wound membrane modules, housed in pressure vessels. These modules are frequently used for water treatment. Spiral wound nanofiltration and reverse osmosis membrane modules are used to treat groundwater, surface water, effluent, seawater, from fresh to brackish and salt. Within this application, membrane fouling is a major topic. Membranes will always suffer from fouling, depending mainly on the quality of the feed water and the use of chemicals dosed to the feed water. To improve the feed water quality in order to minimize membrane fouling, raw water is often extensively pre-treated, using biological filtration and microfiltration/ultrafiltration. But even when raw water is pre-treated extensively, some membrane fouling will still occur. Normally, the remaining membrane fouling is removed by chemical cleaning (CIP: Chemical cleaning In Place). Not all types of membrane fouling can be removed completely with chemical cleaning; especially biofouling and particulate fouling are difficult to remove. Chemical cleaning will partly remove the (bio)fouling, but through killing and destroying cells, and doing so, cell fluids are released that may attach to the membrane surface and which can later act as an easily available food source for new biomass to grow. As a result the frequency of the chemical cleaning will increase over time and finally the membranes will need to be replaced earlier than planned, because every chemical cleaning also results in a tiny degradation of the membrane.

Until now, no effective cleaning method was available to remove biofouling, without destroying the cells and particles. Clean Operator is a new and innovative cleaning method that does efficiently remove biofouling and particulates. The application of Clean Operator consists of feeding a water flow, which is saturated with carbon dioxide, to the serial and horizontal placed membrane modules. When this solutions flows through a pressure vessel containing these (fouled) membranes, the pressure will gradually decrease due to hydraulic resistance. Because of this, a gradual nucleation of CO_2 gas bubbles occurs just as it occurs when opening a champagne bottle after shaking first. This is why Clean Operator is also called 'the champagne flush".

This research has shown that Clean Operator is able to efficiently remove and control biofouling and particulate fouling from spiral wound membrane modules. Even if these spiral wound modules are serial and horizontal housed in a pressure vessel. Clean Operator was able to transport the fouling from lead module, which is most fouled, through the downstream placed modules without leaving significantly quantities of the fouling behind in these modules. A Clean Operator performance typically takes only 15 minutes whereas a chemical cleaning will take between 8 and 10 hours. This means that Clean Operator reduces the down time of a stack for membrane cleaning by >97%! A chemical cleaning (CIP) however cannot be omitted completely, as other types of fouling reducing the normalised flux (for example scaling or NOM attachment to the membrane) are better removed with chemical cleanings. The CIP frequency however can be decreased significantly when Clean Operator is applied. In this research the efficiency of 12 applied CIP events was more or less the same as 13 applied Clean Operator events. The Clean Operator RO line has produced about 3.5% more permeate compared to the CIP RO line because the down time is significant less. The efficiency of Clean Operator is improved when it is applied at a high water flow (8-10 m^3/h per lead module) compared to a low flow (3 m^3/h). There was no significant difference between a co-current and a counter-current Clean Operator performance. The integrity of the membranes was not affected by Clean Operator in this applying normal CO_2 concentrations (<225% saturation). But there is a temporary decrease of the retention (based on conductivity) of 1% which is restored within one

day. This is caused by CO_2 which enters the permeate side of the membrane and will form HCO_3. When the CO_2 is responded away the retention is completely restored again. A temporary decrease of the retention is also observed after a CIP, about 0.3%, which is also restored within one day. Despite the use of CO_2 to clean the membranes, the overall CO_2 footprint of a RO system is decreased significantly when Clean Operator is applied. For the elaborated case Vechterweerd (two stacks with a 55 m^3/h feed capacity) the estimated C-footprint reduction is 7.6%. The total cost of ownership is increased with only 0.2% for the Vechterweerd case. For installations which are bigger and/or have to deal with more severe (bio) fouling the total cost of ownership will significantly decrease if Clean Operator is applied.

This research is applied with synthetic membrane fouling. Potable water was used and acetate was added to enhance biofouling. Although it is known that synthetic biofouling is quite good comparable with natural grown biofouling, next step would be to determine the effect of Clean Operator on natural fouled membranes and on membranes treating surface water with a limited pre-treatment. With a powerful tool as Clean Operator, one could allow membranes to foul more with particulates and biomass because these fouling can now relatively easy be removed. In this way the pre-treatment can be limited, thus decreasing the investment cost hugely. When membranes are less exposed to cleaning chemicals the life time of the membranes will increase. All these arguments demonstrate the high potential of Clean Operator.

In February 2013 the "champagne flush" was winner of "The WEX Global Innovation Awards" in the category "Process Technology".

PREFACE

This Master of Science thesis is the final result of my graduation project and my study at the Department of Water Management, Faculty of Civil Engineering and Geosciences at the Technical University of Delft.

After I finished the MTS Process and Environmental Engineering (1989) I did not feel the need to study further. I started working as a process operator at Memon, a part of Cebeco Handelsraad. The surplus of pig manure was a hot topic at that time and within Memon a pilot plant was operated to separate the pig manure into dry fertilizers and water. After one year the pilot project stopped and in August 1990 I ended up in the world of clean drinking water at Vitens (then WMO). From the beginning in 1994, I conducted the research with membrane filtration at Vitens. As a process engineer I designed several anaerobic nanofiltration plants for Vitens as well as for industrial projects. At a certain moment I felt the need to develop myself. In 2004, after four years, I completed the course Chemical Engineering at the Hogeschool of Utrecht as a part time student. Three years later, in September 2007, I started the mid-career course Sanitary Engineering, again as a part time student. I am Vitens grateful that they have offered me the opportunity to follow these two courses. I have experienced both pathways very interesting and motivating.

With my background it was to be expected that membrane filtration would be a part of the topic of this thesis. The basic idea behind Clean Operator sounds obvious, but good inventions are obvious most of the time. I strongly believe that, based on the results of this research, Clean Operator will be a powerful tool to clean spiral wound membranes in the future.

Off course I would like to thank some people. First the man who introduced the mid-career course, emeritus professor Hans van Dijk. Professor Walter van der Meer, not only as chair of the graduation committee but also for giving me the opportunity to start this course at the time he was my supervisor at Vitens. The members of the committee for their valuable advises and discussions. Especially Peter Wessels who is, together with professor Walter van der Meer, the inventor of the Clean Operator technology. I would like to thank the University of Twente, RWB Waterservices B.V. and WE Consult as the project members and AgentschapNL who subsidized the project. Monica Hermans and Kurt Vervalle of Messer B.V. for their discussions and input for the (full scale) design.

My colleagues Dik Brummel, Janneke Duiven and Feike van de Wal, at Vitens Innovation Centre where the research is performed, for their support during the execution of this research. All colleagues who showed their interest during this course and project. Special thanks to Frank Schoonenberg and Ron Jong who are following the same course. Thanks for your help and motivating during the last years. Doing it together made it somehow a bit easier.

Finally I would like to thank family and friends for their interest and support. Most thankful I am to my wife Chantal and our daughters Eva and Iris for their great support throughout the last six years especially the periods before the exams.

I hope you will enjoy reading my thesis!

Bas Rietman

Contents

1. INTRODUCTION

1.1. Membranes in water treatment

Membrane filtration is a state of the art water treatment technology in the production of potable water as well as in all kind of other industrial applications and water reuse. Membrane filtration can be divided in four categories; microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Microfiltration and ultrafiltration is applied to remove particles, bacteria and viruses (only UF). Nanofiltration and reverse osmosis are mainly applied to remove dissolved ions, organic matter and priority compounds. Where nanofiltration has a high retention for bivalent ions and a lower retention for monovalent ions, reverse osmosis has a high retention for both bi and monovalent ions. Nanofiltration and reverse osmosis are usually applied as spiral wound modules. A benefit of a spiral wound membrane module is the relatively large quantity of membrane surface per volume of a module. The drawback is that, due to its tight and compact construction, membrane fouling is easily built up and then hard to remove again, especially when the membrane fouling is caused by biofouling and/or particle fouling. This type of membrane fouling is mainly a feed spacer problem [Vrouwenvelder, 2009]. The fouling is more attached to the spacer, than attached to the membrane surface. This research is about a new method for cleaning spiral wound membrane modules which are fouled with biofouling and/or particle fouling. The investigated cleaning technique is called: Clean Operator.

1.2. The biggest challenge; how to cope with biofouling?

Although nanofiltration and reverse osmosis membranes are worldwide used for water treatment, there is still one big challenge: how to cope with biofouling? Biofouling is the result of biomass that has accumulated/grown in the membrane module and is hard to remove with a (chemical) cleaning. This type of fouling will lead to higher energy consumption, a higher cleaning frequency, shorter lifetime of the membranes and a decrease in permeate quality [Flemming, 2002]. Heavily fouled membrane modules suffer from channelling, and even can cause mechanical damage to the membranes through telescoping. The above mentioned effects of biofouling, explains why this type of membrane fouling has such a high impact on the operational costs of membrane plants.

Worldwide, there is only one common used method to clean spiral wound membrane modules: different types of chemical cleanings all called 'Cleaning In Place (CIP)'. During a CIP, the aim is to bring the fouling into solution and/or to detached from the spacer/membrane surface using a chemical solution, and remove the fouling from a membrane module. Especially with persistent types of membrane fouling, like biofouling and particle fouling, the removal is difficult and not very effective. As a result the cleaning frequency needs to be increased, and the operational costs will rise. In large membrane plants about 5-20% of the operational costs are related to cleaning activities [Madaeni et al., 2001]. Membrane replacement can contribute up to 20-30% of the operational costs [Butt et al., 1997]. In practice, the membrane lifetime is significantly influenced by the frequency and type of CIP during operation. Reduction of the use of cleaning chemicals generally will increase the lifetime and decrease the replacement costs.

Because of the limited effectiveness of biofouling removal with CIP, a lot of attention is given to the pre treatment of the feed water to prevent membrane fouling. Several treatment steps in series are often applied to decrease the fouling potential of the feed water. The problem here is that a pre-treatment should remove particulate matter and dissolved nutrients, in order to effectively reduce the biofouling rate. Current commonly applied pre-treatment technologies are Ultrafiltration (very effective in removing particulate matter, but limited effective in removing nutrients) and granular activated carbon filtration (very effective in removing nutrients). Such pre-treatment technologies however will increase the total investment and operational costs of a RO/NF plant.

So far, no effective, quick and low cost cleaning method is able to remove biofouling and particle fouling in an effective way. Recently the AiRO concept is developed [Cornelissen, 2007]. AiRO is a technology that uses air and water for hydraulic cleaning of spiral wound membranes. To be able to apply AiRO, the membranes should be placed vertical, in order to enable an effective distribution of water and air. AiRO is applied for the first time in the Botlek demiwater plant (1350 m^3/h, Evides, 2010). Because biofouling starts in the lead membrane modules of a membrane stack, the lead modules are parallel placed in a separate vertical stack in front of a regular horizontal stack holding the downstream membrane modules. Only the lead modules can be cleaned with water and air. With this water/air mixture the (bio)fouling is effectively removed. A disadvantage of this cleaning method is that the lead membrane modules need to be placed vertical in a separate stack. This increases the investment costs and makes the use of AiRO in existing membrane plants impossible without building an extra stack. Another disadvantage is, that only the lead modules can be cleaned in the AiRO design. And although biofouling starts in the lead modules, it is not limited to the lead modules meaning that also the downstream modules will suffer from biofouling in time.

As mentioned before, this research is about a new cleaning method (Clean Operator) that is able to remove biofouling and particulate fouling from horizontal and serial placed membrane modules in an effective way. This is achieved by a hydraulic cleaning of the membranes with a two phase solution using water and a well solvable gas (CO_2). CO_2 is dissolved in water and turned back to the gas phase during flushing this solution through the membrane modules due to the decrease of the pressure. The specific characteristics of CO_2 compared to just air, makes CO_2 more effective in cleaning of spiral wound membranes. Moreover, Clean Operator is a technology that can be applied in existing membrane plants without the need of having membranes vertically placed.

1.3.   Research objectives

With the proof of principle (paragraph 2.5.4) it is found that membrane cleaning with water and CO_2 has the highest efficiency to restore increased hydraulic resistance caused by biofouling compared to a water/nitrogen gas cleaning or just water rinsing [Ngene, 2010]. Additional research at the University of Twente showed that the nucleation and distribution of CO_2 gas bubbles does occur over the entire surface of a flat sheet membrane (20*30 cm.) irrespective of the position of the flat sheet, horizontal or vertical. Next step is to perform the Clean Operator technology on a full scale application (8 inch membrane modules in series in a horizontal pressure vessel).

Within this research two membrane lines will be running under the same conditions. Each line consists of three eight inch membrane modules, horizontal and serial placed in one pressure vessel. Both lines are fed with drinking water of water treatment plant Noordbergum of Vitens. To promote biofouling sodium acetate is dosed to the feed water. When the pressure drop from feed to concentrate increases with a certain % over one or both lines, both lines will be cleaned, one using Clean Operator, the other using regular cleaning chemicals (CIP).

Within the Clean Operator technology several variables can be changed which might increase or decreased the effectiveness of the technology. These variables are;
- Co-current or counter current
- High flow or low flow
- the concentration of CO_2
- pressure fluctuations
- dosage of additives.

The objectives of this research are;

1. To compare Clean Operator with conventional chemical cleaning (CIP)
    The <u>main objective</u> is to determine the effect of Clean Operator compared to the conventional chemical cleaning. Based on the results of the first experiments with Clean Operator on full scale applications a basic setting will be chosen to perform Clean Operator. During a period of three and a half months the application of Clean Operator, using the basic settings, is compared with a commonly used chemical cleaning (CIP) procedure.

2. To investigate the influence of variables on Clean Operator
    A second objective is to determine the influence of variables on the effectiveness of Clean Operator application. These influences will be determined based on several short experiments. The following variables were investigated: counter/co-current flush, water velocity through the feed spacer, amount of CO_2 dissolved.

3. To ensure that the membrane integrity is not decreased by Clean Operator application
    Hydraulic cleaning of membranes is a new technology, and the CO_2 nucleation in the membrane modules and application of a higher shear velocity during flush, should not deteriorate the membrane top layer. The effect of Clean Operator on the membrane integrity is monitored through on line measuring of the Electrical Conductivity.

4. To evaluate the integrated impact of Clean Operator
    Besides the cleaning efficiency, also the use of energy and CO_2 during Clean Operator cleaning, the reduction of total energy use, reduction of CIP, the duration of the Clean Operator cleaning, and the frequency of Clean Operator needed, are important aspects in order to be able to judge the total value of Clean Operator application.

5. To provide a first full scale design for Clean Operator
    How can Clean Operator be integrated in existing RO plants and in RO plants to be new designed. What are the effects on investment and operational costs?

1.4.   Structure of the report

Chapter 1 describes the problem of membrane fouling, especially biofouling, for the operations of a membrane filtration plant followed by the objectives of this research. In Chapter 2 the problem of membrane fouling is described more in detail. In addition several types of membrane fouling are described together with the existing methods to remove or prevent membrane fouling. At the end of chapter 2, Clean Operator is described as a new method. The used research installation is described in chapter 3. The results are reported in chapter 4, followed by a full scale design for Clean Operator in chapter 5. The results and full scale design are discussed in chapter 6. The conclusions are summarized in chapter 7 together with the recommendations. This report ends with the overview of used literature in chapter 8 and 12 appendixes.

2.   THEORY

2.1.   Membrane module

With nanofiltration / reverse osmosis contaminated feed water is split in two water flows: a clean permeate and a concentrate containing all contaminations in the feed water. Permeate is the water flow without almost all of the dissolved ions and the concentrate contains the remaining dissolved ions in a higher concentration. In a spiral wound membrane module several membrane envelopes are inserted. Each envelope is sealed for feed water at three sides and filled with a permeate spacer. The open side is connected to the central permeate tube. Between each envelope a feed spacer is placed to create a pathway for the feed water to flow through the membrane module, and to create turbulence in order to reduce concentration polarisation. Inside each envelope a permeate spacer is inserted to create a flow path for the produced permeate towards the central permeate tube. In figure 2.1 the feed water is entering the element from the left. At the right side, permeate and concentrate are leaving the element. At the feed side of the module a brine seal is located to provide a sealing between membrane and pressure vessels in order to avoid feed water to bypass the feed spacer.
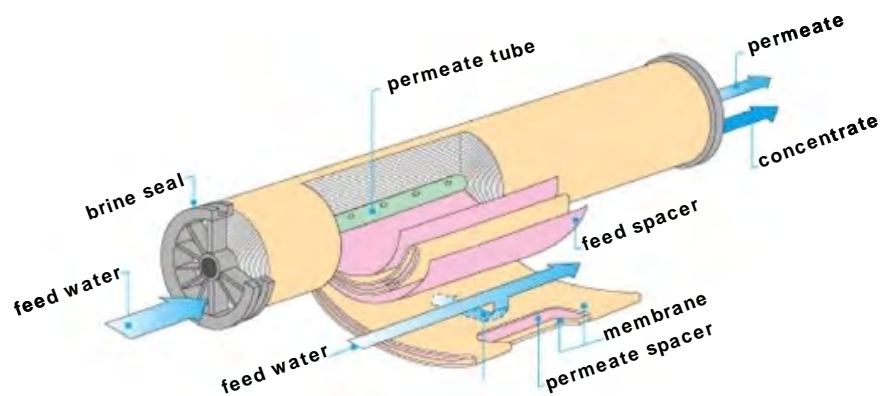
Figure 2.1 construction of a spiral wound membrane module.
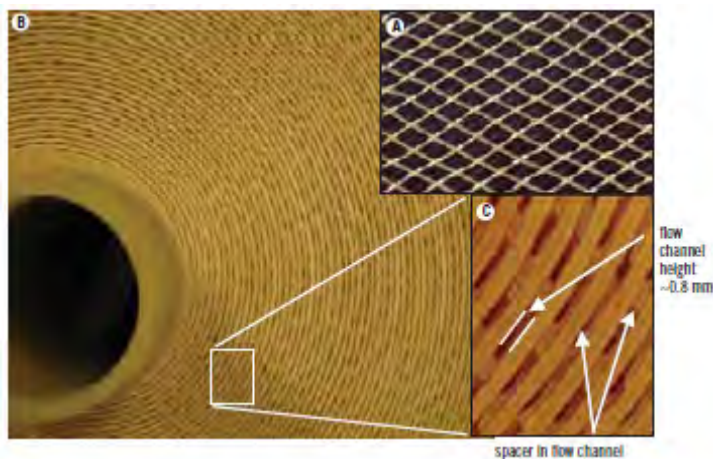
Figure 2.2 Feed spacer geometry (A) and spiral wound membrane module without end cap (B), showing the feed flow channels containing the feed spacer (C). A part of B is shown enlarged in C. The tube on the left is the central permeate collection tube (Vrouwenvelder, 2010)

The envelopes with the permeate spacers, together with the feed spacers, are coiled very tightly around the central permeate tube. As a result the height of the feed channel is limited till about 0.8 mm (figure 2.2). The maximum allowable pressure drop over one single module is limited in order to avoid damage of the construction of the module and the membrane surface (telescoping). Consequently, the maximum velocity in the feed channel is limited.

The internal volume of one single module is 13.8 litres at the feed side of the leaves and 2.6 litres inside the permeate side of the leaves (Appendix 1).

The dimension of a spiral wound module is standardized, with a length of 40 inches (1,016 mm) or 60 inches (1,524 mm). The most used diameter is 8 inch (203.2 mm). An 8 inch spiral wound module typically contains between 30 and 40 m² membrane surface. Usually, a flux between 20 and 30 l/m².h is applied. Depending on the applied flux and membrane area, one single element can produce between 600 l/h and 1200 l/h permeate. The recovery of one single module (40 inch length) is commonly about 10-20%.

2.2.   Membrane unit

A recovery of 10-20% of one single module is not sufficient for full scale applications. To increase the recovery of a system, several modules are placed in series. The modules are housed in a pressure vessel to be able to withstand the applied pressure needed for permeate production. In serial housing, each module is fed with the concentrate of the module upstream. Normally three to seven modules are serial housed in one pressure vessel. The permeate tubes of all serial placed modules are connected with so-called interconnectors. In this way permeate is collected and discharged per pressure vessel through one or two permeate outlet pipes at the vessels end. All parallel placed pressure vessels together will form a stage and are fed with the same quality feed water. The velocity of the feed water through the last module in a pressure vessel must meet a certain minimum value. With to many modules in series the velocity of the feed water will become to low, causing reduced turbulence and increased concentration polarisation. Therefore the concentrate of the pressure vessels of the first stage is collected and divided over a set of pressure vessels in a the second stage. The number of pressure vessel in the second stage is commonly a factor 2 to 4 lower compared to the first stage. In this way the velocity in the feed spacers of the membranes is kept on a sufficient high level. If needed also a third stage can be installed. With two or three stages in series a recovery of 80 to 90% can be obtained in many different designs (figure 2.3).
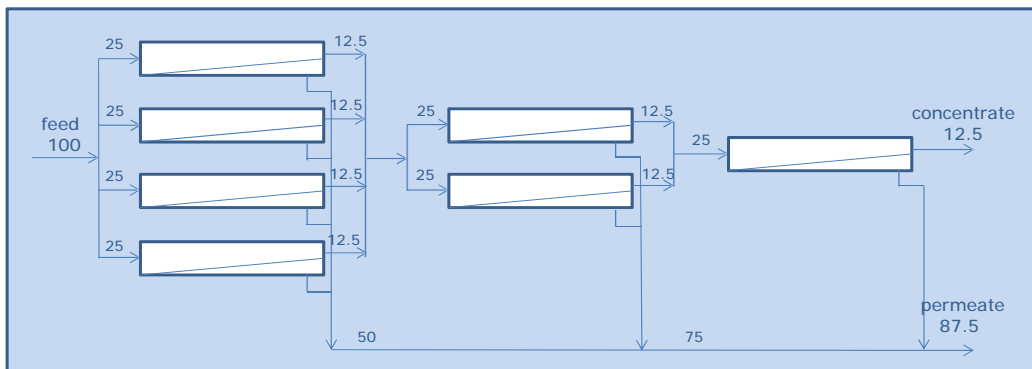
Figure 2.3 Design example of a three stage membrane unit with a recovery of 87.5%.

2.3.   Membrane fouling

Application of membrane filtration will always result in some degree of membrane fouling. It depends on the circumstances, like the quality of the feed water or the dosed chemicals, how severe and fast the membranes will be fouled and how severe and fast the performance of a membrane filtration plant will be reduced.

There are in general four types of membrane fouling:

- Scaling
  Scaling is the precipitation of a salt onto the membrane surface. This precipitation can occur when the solubility of a specific salt has exceeded its saturation limits with a certain value. The concentration of the salt can increase until spontaneous precipitation will occur due to a recovery that is set too high. In order to achieve a reasonable recovery and still prevent scaling, an antiscalant is often dosed. Without an antiscalant

the recovery will be limited till <50%-60% and with an antiscalant the recovery can be increased till ~80-90% depending on the quality of the feed water. If the recovery of a system is a safe set point, normally scaling is absent And the system performance is maintained at the same level. Most common salts that can cause scaling on the membrane are: calcium carbonate ($CaCO_3$), calcium sulphate ($CaSO_4$), barium sulphate ($BaSO_4$), and others. Normally scaling starts in the last modules of the last stage, because there the concentration of dissolved ions is the highest. A decrease of MTC (normalized flux) in only the last stage of an installation indicates that scaling is starting to occur.

- Organic fouling
Organic fouling is a problem when certain substances in the feed water interact with and/or are attracted to the membrane surface. The charge of the membrane surface is often seen as an important factor. Natural Organic Matter is in many cases causing organic fouling of membranes. Dissolved organic substances are negatively charged. With a positive charged membrane surface, the adsorption will be enhanced through electrostatic attraction. As a result a fouling layer will appear on the membrane surface. Organic fouling will typically start over the entire installation and causes MTC decrease of the total membrane area at the same time. Selection of a membrane that has a minimal interaction with organics in the feed water will avoid or minimize organic fouling substantially.

- Particulate and colloidal fouling
Particles and/or colloids have a size between a few nm to a few μm. Examples are silica, aluminium, iron, manganese, organic colloids and suspended matter. Particles and or colloids accumulate on the membrane surface or within the membrane pores, causing pore blocking (microfiltration and ultrafiltration). In spiral wound NF/RO membranes, particulates cannot block pores. Instead, the particulates can cause rapid blocking of the feed spacers of the (lead) elements. Particle and colloidal fouling can become problematic in spiral wound NF/RO elements when the Modified Fouling Index (MFI) or the SDI of the feed water exceeds certain values. Manufactures of membranes prescribe that the SDI must be below 5. This corresponds approximately with a MFI of <3 s/l^2. Particles and/or colloids attach mainly in the first stage often in combination with a (bio)organic fouling layer.

- Biofouling
Biofouling is the accumulation and attachment of biomass to the membrane surface in a spiral wound membrane module, which will lead to unacceptable increase of the operational costs [Flemming, 2002]. Biofouling starts with the formation of a biofilm. The formation of a biofilm can be divided in five stages as illustrated in figure 2.4. In the first stage the first colonies attach to the surface. After the colonies have attached, they will anchor themselves more permanently using cell adhesion structures (stage two of formation). Then the first colonies facilitate the arrival of other cells by providing more diverse adhesion sites and begin to build the matrix that holds the biofilm together. Some species are not able to attach to a surface on their own but are often able to anchor themselves to the matrix or directly to earlier colonists (stage 3, maturation I). Once colonization has begun, the biofilm grows through a combination of cell division and recruitment (stage 4, maturation II). The final stage of biofilm formation is known as development (stage 5), and is the stage in which the biofilm is established and may only change in shape and size. This development of biofilm allows for the cells to become more antibiotic resistant [Franken, 2009]. The stages 4 and 5 are the problematic stages of biofilm formation for a spiral wound membrane module, as the biofilm at this stage is voluminous enough to block the feed channels.
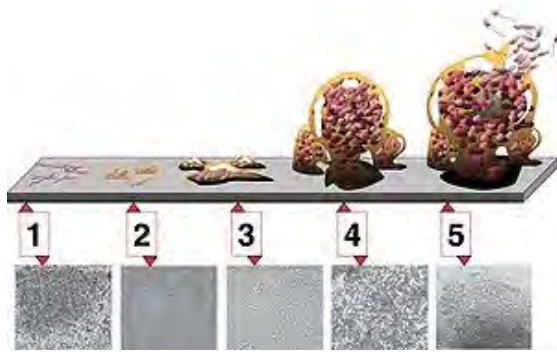
Figure 2.4 Five stages of biofilm development: (1) Initial attachment, (2) Irreversible attachment, (3) Maturation I, (4) Maturation II, and (5) Dispersion. [http://en.wikipedia.org/wiki/Biofilm]

Vitens applies nanofiltration and reverse osmosis on anaerobic groundwater to minimize biofouling (Hiemstra, 1999). With aerobic feed water, especially surface water, waste water effluent or seawater, biofouling is more problematic. To minimize biofouling, often extra pre-treatment steps are installed to clear the feed water. Using this pre-treatment, nutrients are removed and the assimilable organic carbon (AOC) of the feed water is decreased. Recent research also showed that the biomass is prominent attached to and/or captured by the feed spacer [Vrouwenvelder, 2009]. Once suffering with biofouling (stage 4 or 5 of biofilm development), a lot of effort must be put into membrane cleaning because the biofilm becomes more voluminous and inert to cleaning chemicals.

2.4. Cleaning of spiral wound modules

As much as possible of the fouling in the membranes should be removed through cleaning. Several types of membrane cleaning are available. One can divided the different cleaning methods in two major categories; physical cleaning and chemical cleaning. Cleaning In Place (CIP) is the most common used method to clean, and is a type of chemical cleaning. This method is not always successful to remove the fouling sufficiently. Especially biofouling and particulate fouling is difficult to remove with chemical cleaning. AiRO and Clean Operator are cleaning technologies that are more physical based, and very effective in removing particulate fouling and biofouling from spiral wound membrane elements.

Many researches have been performed to study and evaluate membrane cleaning. Several overviews can be found of cleaning methods that are available to clean (spiral wound) membranes (Arnal et al, 2011, Nguyen et al, 2012, Franken, 2009, Bereschenko 2010). In the following sub paragraphs a short reference is made to the previous mentioned literature.

2.4.1. Physical cleaning

There are several types of physical cleaning methods. Most of these methods, such as backwashing, are applied with microfiltration and ultrafiltration. Backwashing can not be applied with nanofiltration and reverse osmosis because the resistance over the membrane, from the feed side to the permeate side, is too high. The membrane layer would loosen from its support layer due to the high pressure needed to perform a backwash with sufficient flux.

Another physical cleaning method is the forward and reverse flush. With a forward flush the cross-flow velocity in the feed channel of the module is increased in order to remove fouling from the membrane surface. Due to the higher velocity, the turbulence is increased and mainly easily detached fouling is removed. With reverse flushing the flow direction is alternated reversed. Forward and reverse flush is applied to remove colloidal matter. But, due to the limitation of the pressure drop and velocity over one membrane module the applied turbulence is restricted. This method is not very common in practice.

Cleaning methods using air, such as air sparging, air lifting or airflush are widely used in practise for tubular and capillary microfiltration and ultrafiltration. There is one application were spiral wound ultrafiltration modules are cleaned with air, called SpiraSep (www.trisep.com). Recently a cleaning method with an air/water mixture has been developed for spiral wound nanofiltration and RO modules, called AiRO. This method is discussed in paragraph 2.4.3. Other physical cleaning methods like ultrasound or electric field for spiral wound nanofiltration or reverse osmosis membranes are not common practice. The effectiveness is questionable and the practical application is difficult. On lab scale, a chemical free cleaning method is tested with self-collapsing air micro-bubbles. With their capacity to shrink and subsequently collapse in solution it was possible to detach the biofilm from the membrane surface [Agarwal et al., 2012]. This method has not been applied at industrial scale so far.

Clean Operator is also a physical cleaning technology, but will be discussed more in detail in paragraph 2.5.

2.4.2. Chemical cleaning

The most common method to clean spiral wound membrane modules is a chemical cleaning. During a chemical cleaning, the fouling is destroyed, detached and (partially) brought in solution and then removed from the membrane element.
There are four variables which have an influence on the efficiency of a chemical cleaning:
1. Cleaning agent
   Different types of cleaning agents can be applied such as acids, bases, oxidants and surfactants or detergents. The used type of agents and the combination and order of use depends on the type of fouling that needs to be removed.
2. Mechanical action
   Mechanical action will support the removal of the fouling layer. The mechanical action is mostly provided through application of a high cross flow velocity in combination with a low trans membrane pressure.
3. Temperature
   At increased temperatures, the efficiency of the cleaning is also increased. The cleaning effect of a higher temperature is caused by different effects. Due to a higher temperature, the membrane matrix expands and opens, which makes the membrane structure more accessible for chemicals. Also at a higher temperature, the viscosity of the water is increased. Due to this, chemicals are more easily and faster transported to, and better distributed over the membrane surface. Last effect mentioned is that chemical reactions are faster at increasing temperatures. Most polymer membranes however, can be cleaned till a maximum temperature of 40 °C. Heating water from the regular 10-20 °C up to 40 °C will consume a lot of energy.
4. Time
   The longer a cleaning procedure takes place the more effective the result of the cleaning will be. The more time provided, the more chemical reactions can take place.

A chemical cleaning in place (CIP) is generally performed as follows: a cleaning solution is prepared using permeate and the required cleaning agent. In case of scaling, commonly an acid cleaning is used, for instance citric acid. In case of organic fouling or biofouling, commonly a base cleaning is used, for instance caustic soda. Sometimes the fouling requires a detergent in combination with an acid or base. An oxidizing cleaning chemical can not be applied on a regular basis because this will also partly oxidize the membrane surface. To improve the effect of a cleaning, the solution is heated till 40 °C. During the cleaning procedure, the cleaning solution is alternately soaking the membranes and circulated along the membranes. During circulation the cross-flow velocity should be higher than during production. The applied pressure however should be as low as possible to avoid too much permeation through the membrane. Chemical cleaning is most of the time applied in co-current direction and two chemical cleanings are regularly combined: first a high pH cleaning and then a low pH cleaning. A CIP generally takes 4-10 hours to perform. Normally each membrane installation has its own Cleaning In Place (CIP) unit. This unit is connected to all membrane stacks and the cleaning procedure is more or less a manual job. In case the cleaning frequency is high, the cleaning procedure can be automated. For industrial applications this is common practise.

The CIP cleaning has some important drawbacks:
1. Wear and tear of the membrane because of the chemical exposure;
2. High energy consumption (heating of the chemical solution)
3. Creation of chemical waste
4. High (and increasing) costs of the chemicals
5. It is a labour-intensive process.

Because a chemical cleaning is very labour-intensive, often an extra stack is installed to produce the required permeate quantity even during a cleaning event. Another option would be to install more buffer capacity. Both options increase the investment costs.

Bereschenko states in her PhD thesis [Bereschenko, 2010] that the results of her research suggest that chemical treatment facilitates initiation and subsequent maturation of biofilm structures on the RO membrane and feed-side spacer surfaces. Biofouling control might be possible, but only if the cleaning procedures are adapted to effectively remove the (dead) biomass from the RO modules after chemical treatment. Her research indicates that conventional cleaning with toxic chemicals has an effect on the occurrence of biofouling in RO systems, but is not effective in really cleaning the RO system. Consequently, when a RO plant is suffering from persistent biofouling, a conventional CIP cleaning might not be capable to combat biofouling good enough.

2.4.3. New development: AiRO

Recently a new cleaning method is developed called AiRO (NI octrooi 1019130, Wessels et al, 2001). It generally is a hydraulic flush with water and air through vertical and parallel placed membrane modules. Extra mechanical action is obtained by the scrubbing of the air bubbles. After a certain increase of the normalised pressure drop, the modules are flushed with the water and air mixture. During this air/water flush the fouling is not completely removed, but to an extensive level. It has proven to be an effective way to control both particle fouling and biofouling of spiral wound modules [Cornellissen et al., 2007]. The AiRO design will lead to a reduction of the chemical cleaning frequency, which will reduce the drawbacks of the CIP method. Pilot research determined that by the application of AiRO the membranes can be operated stable over a long period. Water Company Evides has introduced the AiRO method in one of their industrial water treatment plants (start operation 2010). In front of each stack a set of vertical placed pressure vessels, each containing one module, is placed. Biofouling is effectively controlled although the feed water is surface water with a minimum of pre-treatment (coagulation-media filtration-cation exchanger). KWR and Evides Industriewater have received the IWA Design Honour Award in 2012 for the AiRO technology.

Backdrops of the AiRO cleaning method are:
1. It is not directly applicable on existing installations since it is only applicable on one vertical positioned module. Application of AiRO in an existing plant requires the installation of an extra stage to each stack having modules installed in vertical pressure vessels.
2. All of the membranes should be installed parallel in vertical pressure vessels; otherwise, the membranes housed in series in horizontal pressure vessels will still suffer from fouling.

2.4.4. Other options to minimize membrane fouling

<u>Extensive pre treatment</u>
Pre-treatment is installed to remove components that promote (bio)fouling of the membranes or to decrease the biofilm formation rate. These components can be nutrients, particles and the assimilable organic carbon (AOC).

For the treatment of surface water at least a technique is installed to remove particles. Mostly this is a coagulation step followed by sedimentation and/or sand filtration. To increase the efficiency of the pre-treatment, techniques like ultrafiltration and biological activated carbon filtration are used and increasingly promoted. There are still situations that despite these extra

pre-treatment (bio) fouling of the membranes can occur [Bergman, 2010]. It is common knowledge that ultrafiltration does remove particulate matter satisfactory, but does not remove nutrients and therefore cannot prevent biofouling (particulate (biomass) formation after particulate removal). Activated carbon filtration is a very effective method for biofouling reduction (van der Maas et al, 2010), but activated carbon filtration releases particulate matter (bacteria, biomass, etc.). The combination of activated carbon filtration followed by ultrafiltration is very effective (Galjaard et al, 2008), but also very costly.

Dosage of biocides

Biocides can be dosed continuously or discontinuously to the feed water in order to control the growth of micro-organisms. The focus of biocide dosing should be prevention of biofilm development (prevention of getting above phase 3 of biofilm development (see Fig 2.4). To achieve this, biomass should be killed regularly to prevent that voluminous biofilm are being formed. Problem with the use of biocides is that they end up in the environment and that some biocides may form oxidation products that might pass the membrane partially. In that case they will end up in the permeate which might be used for drinking water production. Another drawback of dosage of biocides is that good control (dosage, frequency and continuity) is needed in order to prevent a problematic biofilm growing to large volumes. As soon as the biofilm has reached stage 4 or 5 of development (see Fig 2.4), it has overgrown the ability of biocide dosing to control the pressure drop over the feed spacer. As particulate matter and biolims cannot be physically be removed with dosage of biocides, it also cannot provide a solution for existing plants having huge biofilm problems. Moreover, biocides tend not to decrease the nutrient level that ultimately supports the biofilm.

As a biocide, monochloramine is used in practice (Newater Singapore, Waste Water Reuse Plant Veurne Ambacht (Van Houtte et al, 2010)) and promising results have been found in research with Dibromonitrilpropionamide (DBNPA) (Boorsma et al, 2011). The high pH fluid used in a normal CIP can also be regarded as a biocide.

2.5. Clean Operator

Clean Operator is a hydraulic cleaning method with water and a readily dissolvable gas, for example CO_2 (NI octrooi 2002519, Wessels et al, 2009). The water is saturated with CO_2 at a certain pressure and temperature and then fed to a membrane stack. Due to the hydraulic resistance, CO_2 is gradually released as a gas, resulting in the desired water/gas solution for effective cleaning. The higher the hydraulic resistance, the more CO_2 gas will be formed. Consequently, more CO_2 is released at the more fouled locations in the membrane, as the pressure drop is higher at such locations.

Because its hydrophilic character, CO_2 will less agglomerate compared to air. Air is more hydrophobic and agglomerates quickly when released in in water. Because of its nature, CO_2 is able to cover the entire membrane surface and preferred flow channels are prevented (Ngene, 2010.

2.5.1. Saturation of CO_2 in water

For dissolving carbon dioxide in water Henry's Law is valid. According to this law, the amount of CO_2 dissolving in water at a constant temperature is directly proportional to the partial pressure of carbon dioxide in the air in equilibrium with the water. In other words, the solubility of carbon dioxide in water is directly proportional to the partial pressure of carbon dioxide above the water. This means that if the partial pressure of carbon dioxide is twice as high, then also twice the amount of carbon dioxide will dissolve in the water.

$$p = k_H * c \tag{1}$$

p : partial pressure of gas [bar]
k_H: Henry constant [bar/mol CO_2/mol water]
c : concentration of gas [mol CO_2/mol water]

With data of Henry's constant at different temperatures (Liederkerken et al, 1998) a polynomial is calculated to determine Henry's constant at different temperatures (Appendix 2). With the calculated Henry's constant the solubility of carbon dioxide can be calculated at different pressures with formula 1.

2.5.2.   Calculation CO_2 to be dosed

The quantity of CO_2 to be dosed, to get a saturated solution, depends on the temperature, pressure and water flow. In figure 2.5 several lines give the relation between the solubility of CO_2 in water, the temperature and certain pressures. The relation between the solubility and the pressure is linear. This means that with the solubility at 1 bar the solubility at any other pressure can be calculated. For instance, at a pressure of 2 bar the solubility is double and at a pressure of 0.5 the solubility is 50%.
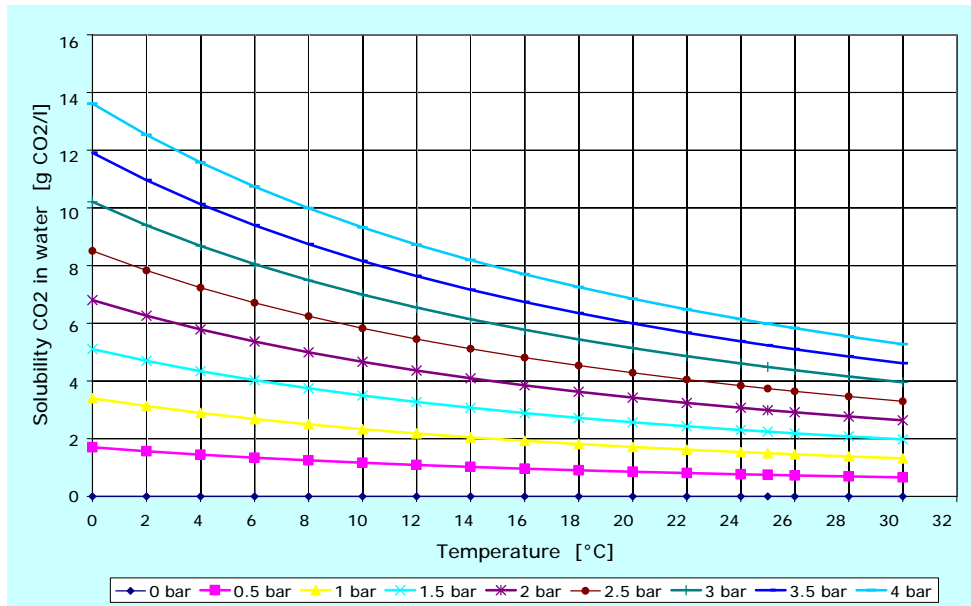
Figure 2.5 Solubility carbon dioxide at different temperatures and (absolute) pressures (100% CO_2 in gas above).

In appendix 2 the solubility at atmospheric pressure is given in a graph and a polynomial is calculated to determine the relation between the solubility and the temperature. This calculated solubility at a certain temperature and atmospheric pressure together with the actual pressure, water flow and a concentration factor determine the set point of the CO_2 to be dosed according the following formula:

$$\text{Set point [kg/h]} = CO_2\text{-factor} /100\% * SOL_T * (P+P_{atm}) / 100 \text{ kPa} * F \qquad (2)$$

With;

CO_2-factor = [0-300%]	concentration CO_2 (100%= saturated) [%]
$SOL_T = -10^{-5} \cdot x^3 + 0.002 \cdot x^2 - 0.1176 \cdot x + 3.3474$	CO_2 solubility at temperature T (x) [kg/m^3]
P	pressure at the entrance of the pressure vessel [kPa] (in kPa as overpressure)
P_{atm}	Atmospheric pressure [kPa]
F	water flow [m^3/h]

2.5.3.   Volume of CO_2 that will release

As soon as the water/CO_2 solution enters the pressure vessel the pressure will decrease due to hydraulic losses. With formula 2 the quantity of CO_2 to be dosed is calculated. This can be done for different quantities of water flows and assuming different pressures (different every time because depending on the fouling present in the membrane).

In appendix 3 a table is given with the results of this calculation. Using this calculation, the needed quantity of CO_2 is determined to get a saturated water/CO_2 solution. Based on the decline of the pressure one can calculate the quantity of CO_2 that will release per unit of pressure. This calculation is (by example) performed at a temperature of 12°C. Based on the pressure that is still present at the point of gas formation, the amount of CO_2 released takes a certain volume according the following formula (law of Boyle and Gay-Lussac):

$$p*V = n*R*T \qquad\qquad (3)$$

p : partial pressure of the gas [Pa]
V : volume of the gas [m^3]
n : amount of gas [mol]
R : gas constant [8,314472 J/K.mol]
T : temperature [K]

According to formula 3 the volume of the CO_2 already released will increase with a decreasing pressure. Due to a gradually decrease of pressure, more and more volume of CO_2 gas will be formed out of the solution. And at larger volumes, flow velocities and turbidity will increase.

2.5.4. Proof of principle

The proof of principle is performed with a laboratory set up. Three identical flow cells were fouled in parallel and cleaned using three different cleaning methods; water rinsing, water/N_2 sparging (AiRO) and water/CO_2 nucleating (Clean Operator). The increased hydraulic resistance caused by the fouling was partly removed by water rinsing (±40%) and water/N_2 sparging (±85%). With the water/CO_2 nucleating the resistance was more or less completely removed (±100%) (Ngene, 2010). Figure 2.6 shows images of the different flow cells before and after cleaning.
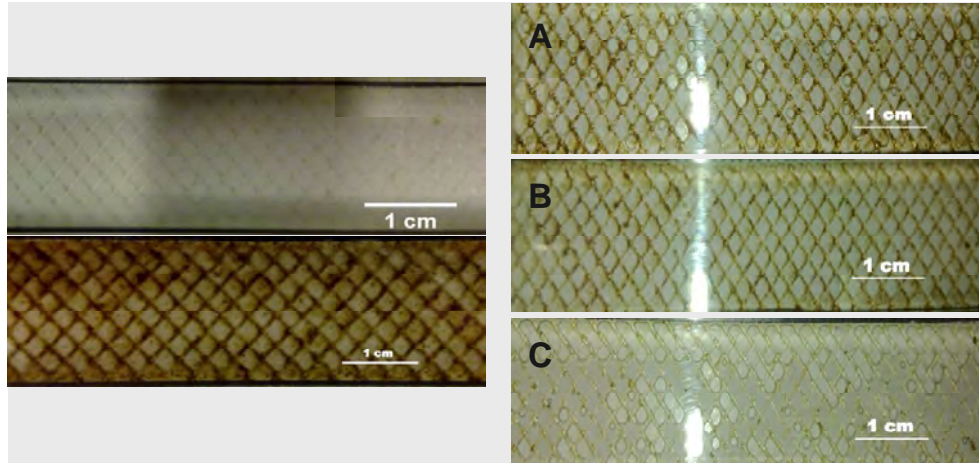
Figure 2.6 Images of a virgin membrane (left top), fouled membrane (left bottom), after water rinsing (A), after water/air (B) and after Clean Operator (C) (Ngene, 2010).

In this study it was observed that a water/gas solution clearly increased the efficiency of a hydraulic cleaning. With water/N_2 preferential flow patterns (channelling) were observed resulting in a lower efficiency. Continuous formation of CO_2 gas bubbles and their continuous detachment at every part of the flow cell resulted in the highest efficiency. The water and CO_2 solution was saturated at the inlet pressure of the flow cell. The continuous nucleation and growth of CO_2 gas bubbles within the whole flow cell resulted in the absence of stagnant bubbles. This effect improves the cleaning efficiency. During the experiment the flow during cleaning was kept constant for all three methods. In figure 2.6 it is clearly visible that most of the fouling is attached on the feed spacer or near the feed spacer (between spacer and membrane). In the research of Vrouwenvelder one of the major conclusions was that biofouling is a feed spacer problem [Vrouwenvelder et al., 2009]. The images A, B and C in figure 2.6 are

made after each specific cleaning method. It is clear that on picture C (Clean Operator) most fouling is removed. This was also concluded on the basis of the pressure drop measurements. Figure 2.7 shows an image during the Clean Operator cleaning method, the formation or nucleation of the CO_2 gas bubbles starts on every irregularity of the surface, in this case (a clean spacer) the feed spacer (figure 2.6). Again this explains the high cleaning efficiency of the method. The gas bubbles were able to transport the fouling out of the flow cell.
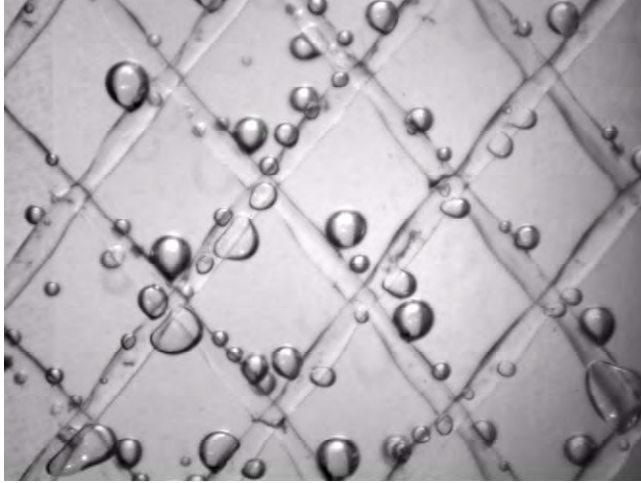
Figure 2.7 Image of the nucleation of the CO_2 gas bubbles during a Clean Operator cleaning. Flow direction is upwards [University of Twente].

3. MATERIALS AND METHODS

3.1. Research installation

To conduct the research a new research installation is designed by Vitens, WE Consult and RWB Waterservices B.V. (RWB) and build by RWB. The carbon dioxide dosage part is redesigned by RWB and build by Messer B.V.. In appendix 4 the P&ID's of the research installation are given. The research installation consisted of three parts; the membrane filtration, the chemical cleaning unit (CIP) and the Clean Operator unit.

3.1.1. Membrane filtration

The set-up of the membrane filtration installation is split in two lines (RO1 and RO2), which can be operated independently from each other. A process scheme and picture are given in figure 3.1.Each line consists of a pressure vessel with three serial placed (eight inch) spiral wound membrane modules. The pressure vessels are horizontally mounted in the stack. The membrane flux is kept constant, causing the feed pressure to be increased when the membrane / feed spacers are fouled. The feed flow is kept 4,5 m^3/h, which is lower than normal applied and according the Optiflux design [van der Meer et al., 1998, van Paassen et al., 2005]. With the Optiflux design the feed flow per pressure vessel in the first stage is decreased in order to decrease the pressure drop over the first stage. The second stage can then be operated at a higher feed pressure. As a result about 10-15% decrease of the energy consumption or membrane surface is achieved [Jong et al, 2010].
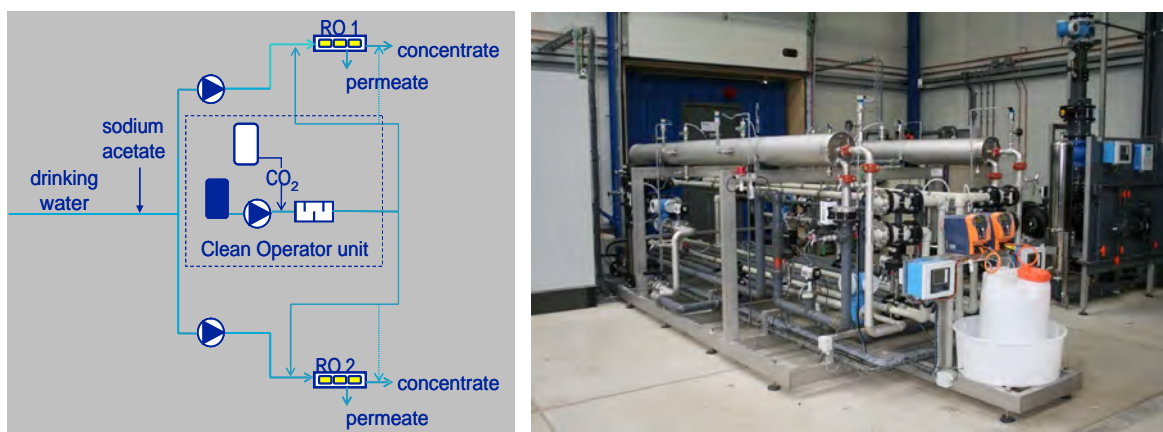
Figure 3.1 process scheme and picture of membrane installation

Permeate from RO1 and RO2 is collected in a tank. The overflow from this permeate tank is discharged. The remaining permeate in the tank is used to perform the Clean Operator cleanings and to fill the CIP tank for chemical cleanings.

To assess the operations several pressure transmitters, flow meters and conductivity sensors are installed as can be seen in appendix 4. With the different transmitters and flow meters process data is collected to calculate the normalised pressure drop (NPD) over the feed spacers and the normalised flux (Mass Transfer Coefficient). It is possible to calculate the normalized pressure drop over the pressure vessel (three membrane nodules in series) as well as over each individual membrane module. In this way, it is possible to determine if fouling is removed or partly transported between the three modules.

The process data is collected every hour and during a Clean Operator cleaning every minute.

3.1.2. Chemical cleaning unit

The chemical cleaning unit consists of a tank with a volume of 3 m^3. The tank is filled with permeate from the membrane filtration installation. The electrical heather can increase the temperature up to 40 °C. The cleaning pump has a capacity up to 21 m^3/h at 4.4 bar to feed RO1 or RO2 with the cleaning solution. After the cleaning pump a cartridge filter is installed to remove particles from the cleaning solution before it is fed to the membranes. The connection between the cleaning unit and RO1 or RO2 is accomplished with hoses. During cleaning the cleaning solution can be circulated over RO1 or RO2. The permeate discharge of RO1 or RO2 can also be returned back to the cleaning tank.

3.1.3. Clean Operator unit

The carbon dioxide (CO_2) used for the Clean Operator cleaning is stored as a liquid in ten cylinders. The pressure of a full cylinder is about 60 bar. One nitrogen gas cylinder at approximately 200 bar is installed to ensure that enough pressure is available to dose the requested amount of carbon dioxide under all circumstances. This is necessary because of the high CO_2 peak demand when Clean Operator is performed. The CO_2 is dosed in the gas phase to a permeate flow. Therefore the CO_2 in the liquid phase is heated by a heather. The required amount of CO_2 to be dosed is calculated based on the flow, pressure and temperature according to formula 2 in paragraph 2.5.2. The CO_2 is dosed with the use of a mass flow meter and flow controller (Bronkhorst model number F-206AI-AGD-55-V). The saturated permeate is fed to one of the pressure vessels, RO1 or RO2. This can be done co-current (same flow direction as during production) as well as counter-current. The discharge of flushed out permeate and CO_2 gas passes a degassing tower to remove the excess of CO_2 safely before water samples are taken. Downstream of the degassing tower a turbidity meter is installed to measure the pollution that is removed out of the modules. The flush pump to perform the Clean Operator cleaning has a capacity up to 17 m^3/h at 3 bar.

3.2. Feed water

The research installation is fed with drinking water from treatment plant Noordbergum of Vitens (table 3.1). Sodium acetate can be dosed to the feed water to promote biofouling.

Table 3.1 (average) composition feed water

Parameter	Unit	Feed water
pH	-	8.15
Conductivity	mS/m	49.7
Turbidity	NTU	0.14
HCO$_3$	ppm	135
Cl	ppm	105
SO$_4$	ppm	6
Ortho PO$_4$	ppm	<0.02
NO$_3$	ppm	4.6
Si	ppm	12
Ca	ppm	45
Mg	ppm	9.7
Fe	ppm	0.01
Mn	ppm	<0.01
Ba	ppb	13
Sr	ppb	180
TOC	ppm	4
DOC	ppm	4
Colour	ppm Pt/Co	7.6

3.3. Membrane

During the research a so called "open" RO membrane is used, TriSep 8080-ACM5 TSAN. Specifications are listed in appendix 5.

3.4. Normalisation process data

The performance of a membrane filtration installation is judged by parameters like flux and pressure drop. In order to compare the process data in time under different circumstances the process data is normalized [Huiting et al, 1999]. Most important parameters are the normalized flux (MTC, Mass Transport Coefficient), the normalised pressure drop from feed to concentrate (NPD) or the feed channel pressure drop, and the retention. In appendix 6 the set-up of the normalisation of process data is elaborated.
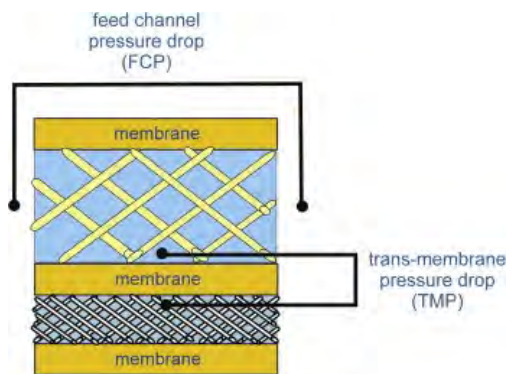
Figure 3.2 image with different pressure drops in membrane filtration, feed channel pressure drop (FCP) and trans-membrane pressure drop (TMP) (Vrouwenvelder, 2009)

Within spiral wound membrane filtration there are two types of hydraulic resistance that are important to monitor: the hydraulic resistance over the feed spacer, and the hydraulic resistance over the membrane.

The first hydraulic resistance is caused by the feed channel pressure drop. In the upper part of figure 3.2 the feed spacer between two membranes is shown. This is the space through which the feed water flows. The feed water contains a variety of ions, (dissolved) organic matter and particulate matter. Fouling will occur depending on the quality of the feed water and the height of the feed spacer channel. The height of the feed spacer channel of the used RO membrane is approximately 0.8 mm (figure 2.2). When fouling accumulates/grows in the feed channel, the resistance will increase and also the feed channel pressure drop or the normalised pressure drop will increase.

The second hydraulic resistance is caused by the membrane itself. This hydraulic resistance is called the trans-membrane pressure drop or membrane permeability. When the membrane is fouled, the trans-membrane pressure drop increases, the permeability decreases and the normalized flux (MTC) also decrease.

The lower section in figure 3.2 shows the permeate spacer between two membranes. Because permeate contains hardly any ions this spacer normally will not foul, meaning that the pressure drop will stay constant and of no importance to monitor.

4.   RESULTS

The research installation is started in July 2012 under the pretext of getting to know the Clean Operator technology. During the period July-December 2012 the first experiences with Clean Operator were conducted and the cleaning process was optimized. During the second period (February-May 2013) Clean Operator was compared to the conventional chemical cleaning over a period of 105 days. In June 2013 a number of short experiments were performed to determine the influence of certain variables on the efficiency of Clean Operator. The effectiveness of the Clean Operator technology was evaluated through monitoring of the pressure drop.

Initially it was the plan to feed the research installation with surface water (Lake Bergum), pre-treated with only inline flocculation and sand filtration. The surface water contained a huge level of Natural Organic Matter (colour ~150 mg Pt/l, DOC ~22 mg/l) together with non-oxidized Iron (~1.3 mg/l). It turned out that the pre-treatment was unable to remove the Iron and turbidity. Treated surface water led to rapid reduction of MTC, most probably due to adsorption of organic matter together with non-oxidized Iron. The membranes did not suffer from biofouling and/or particulate fouling because the membranes could not be held in operation for a long time. Attempts to improve the pre-treatment would take much time and would involve extra pre-treatment steps (for example additional ion exchange and oxidation with Potassium Permanganate dosing). The quality of surface water from Lake Bergum also is not very comparable for other surface water locations, because of its extreme Nom and Iron content. Therefore the decision was taken to feed the research installation with drinking water. To promote extra biofouling, Sodium Acetate is dosed. Sodium Acetate is used in many research projects to enhance biofouling.

4.1.   First research period

4.1.1.   Settings pilot

Both RO lines were fed with 4.5 m^3/h feed water. The recovery was regulated on 50%. In this period no anti-scalant was dosed, because no scaling was to be expected at this recovery. Sodium Acetate was dosed between 75 - 200 µg C/l but predominantly at 100 µg C/l, to accelerate biofouling.

Each chemical cleaning was performed for 2-2.5 hours, in which a chemical cleaning solution was recirculated over the membranes at a velocity of 8 m^3/h interrupted by soakings of the membranes in the chemical cleaning solution. During the chemical cleaning, the permeate valve was not closed and the flow direction was the same as during production (co-current). A chemical cleaning existed in a low pH cleaning (citric acid, pH ~2) followed by a high pH cleaning (NaOH, pH ~11.5).

Each Clean Operator cleaning was performed with a (permeate) water flow of 8 m^3/h. The order of co current and counter current is indicated by the results. During clean operator the permeate valve was closed. During the flush out at the end this valve was open.

Each Clean Operator cleaning had the following procedure;

- 3 minutes – start heater (formation of CO_2 gas from CO_2 liquid)
- 1 minute – start flush pump
- 5 minutes – dosing the CO_2 at the calculated set point and with a closed permeate valve
- 2 minutes – flush out of CO_2 with and opened permeate valve.

The membranes of RO line 1 were chemically cleaned (CIP) and at the membranes of RO line 2 were cleaned using water and CO_2 (Clean Operator). Manual collected process data was used to evaluate the performance of both RO lines.

4.1.2. Results first period

Over a period of 100 days the membranes were fouled three times due to the sodium acetate dosage to the feed water.

In figure 4.1 the development of the normalised pressure drop over RO1 and RO2 (three elements in series) is shown. Appendix 7 contains the development of the pressure drop over the three individual modules and the development of the feed pressure, the normalised flux (MTC) and the retention. As can be seen in figure 4.1, the normalized pressure drop increased from the initial ~50 kPa to ~410, ~600 and ~500 kPa. The normalized pressure drop of both RO lines was fouled almost identically in all three cases of biofouling enhancement. In total, five cleaning events took place. The followed procedures and results are described for each individual cleaning event. The results over the first 50 days were also presented and published during the IWA conference in Busan, South Korea, in 2012 [Rietman et al., 2012].
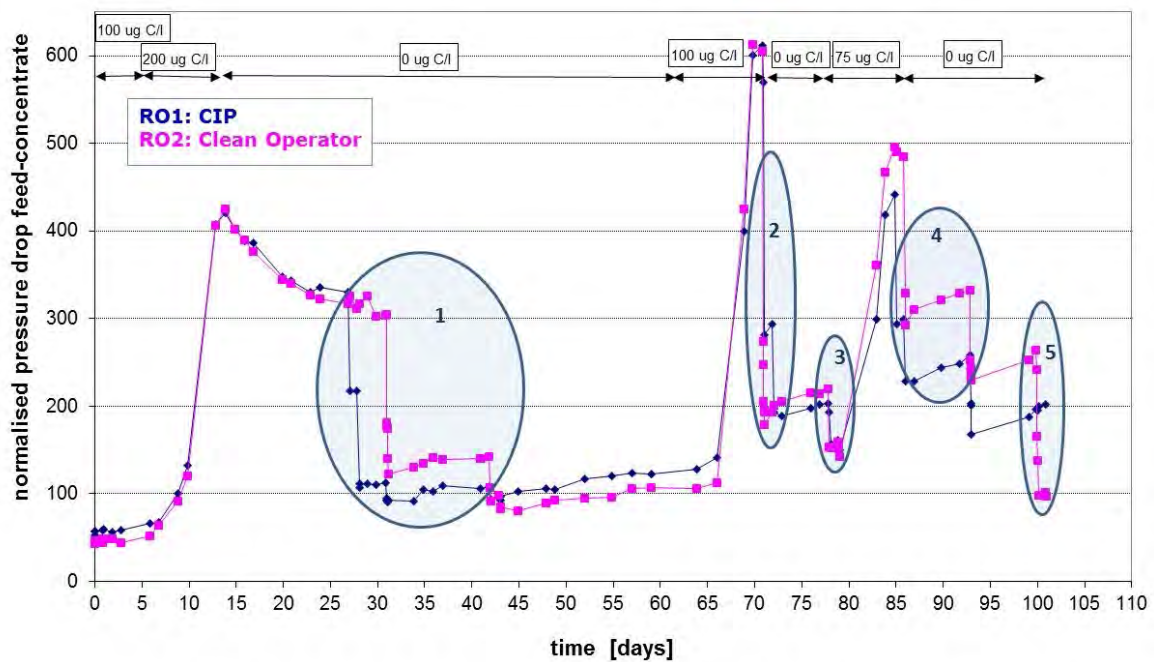
Figure 4.1 development of the normalised pressure drop during the first research period with five cleaning events

Cleaning 1

Direct at the start of the research installation 100 µg C/l was dosed to promote biofouling. After 5 days the increase of the normalized pressure drop was limited and the dosage was increased till 200 µg C/l, just before a weekend. As a result the increase of the pressure drop exploded during that weekend. On day 13 the dosage was stopped and the pressure drop started to decrease.

On day 27 RO1 was cleaned with citric acid (pH ~2) followed by a cleaning with caustic soda (pH ~11.5) at day 28. The pressure drop decreased with 41.2% due to the citric acid cleaning and with 38.7% due to the caustic soda cleaning. Overall the CIP the pressure drop is reduced by 80% (from 164 kPa down to 55 kPa).

On day 31 the first full scale Clean Operator flush was performed. Because of the high pressure drop over RO2 (due to the severe fouling), a high feed pressure and a lot of CO_2 was needed to perform the Clean Operator flush. Because the Clean Operator flush was not performed correctly (as it was the very first time it was performed), it had to be repeated four times in order to get the right flows. During the first attempt only about 40% of the needed CO_2 was dosed because the pressure regulator to dose the CO_2 was not set correctly. Due to the huge fouling Clean Operator had to be performed at a high pressure. As a consequence, the flush

water fed to the membranes was far from completely saturated. The first Clean Operator flush attempt was performed in counter current and reduced the pressure drop by 49.1%. Overall the four Clean Operator flushes reduced the pressure drop by 70.5% (from 152 kPa down to 61 kPa). Clean Operator is first performed in counter current twice followed by also twice a co current. During the last three performances the amount of CO_2 was according the settings to get a saturated solution.

On day 42, a Clean Operator flush was performed at RO1. Between the CIP on day 27 and day 28 no increase or decrease of the normalised pressure drop took place. Another 5.6% reduction of the normalized pressure drop over the feed spacers was removed with this Clean Operator cleaning.

Also on day 42 and 43, a CIP (citric acid at pH ~2 and caustic soda at pH ~11.5) was performed on RO line 2 (which was cleaned with water and CO_2 on day 31). But before the CIP, RO line 2 was cleaned with a Clean Operator flush again. The Clean Operator flush restored the pressure drop with 13.7%. The citric acid cleaning restored the initial fouling with another 3.2% and the caustic soda cleaning with another 5.3%.

During the citric acid cleaning the color of the cleaning solution turned yellowish. During the caustic soda cleaning the color changed slightly. During a CIP, no particulate flush out was observed, while during a Clean Operator cleaning solid particles were observed in the flush water. The turbidity measurements showed no clear and reproducible trend that could be use to determine the time of the Clean Operator performance.

After all applied cleanings on RO1 (CIP on day 27 and 28, followed by Clean Operator on day 42) and RO2 (Clean Operator on day 31 and CIP on day 42 and 43), the overall cleaning efficiency in terms of reduction of the increased normalized pressure drop was 86.8% for RO1 and 85.1% for RO2. Remarkable at RO1 (CIP) is that the percentage (86,8%) was applicable to module 1 and 2 but not to module 3. The increased pressure drop over the third module was only restored by 25%. At RO2 with the Clean Operator technology this was not the case, here the pressure drop over the third module was restored completely! The development of the pressure drop over the individual modules can be seen in appendix 7.

Cleaning 2
In the period between day 43 and 62 no Sodium Acetate was dosed. During this period a slight increase in normalized pressure drop was observed, equal on both lines (see figure 4.1). On day 63, the Sodium Acetate dosing was started again (100 µg/l) and a rapid increase of the pressure drop was observed from ~ 100-120 kPa on day 63 up to 600 kPa on day 71, again comparable on both RO lines.

On day 71 and 72 the membranes of RO line 1 were chemically cleaned. The pressure drop over RO 1 was restored with 81.4% by this CIP. The citric acid cleaning restored the pressure drop with 61.3% and the caustic soda cleaning with another 20.1%.

Also on day 71, RO line 2 was cleaned with a Clean Operator cleaning. The Clean Operator cleaning was performed counter-current first and co –current second. Both were performed twice. Each second attempt had a moderate contribution to the efficiency. The first performed counter-current cleaning had already an efficiency of 63.8%, whereas the total cleaning efficiency was 78.8%.

After this second cleaning the overall performance is comparable for both RO lines (normalized pressure drop feed-concentrate ~190 kPa).

Cleaning 3
Seven days after the cleaning event on day 71, the third cleaning event took place at day 78. In the period between day 71 and day 78, no Sodium Acetate was dosed, and the normalized pressure drop was only increased form ~190 up to ~210 kPa. On day 78, RO1 was chemically cleaned and RO2 was cleaned with a Clean Operator cleaning (co current followed by counter current). The results plotted in figure 4.1 shows that the pressure drop over both RO lines was reduced to a level lower than achieved after cleaning event 2.

<u>Cleaning 4</u>

Direct after the third cleaning on day 78, the Sodium Acetate dosage was started again and the membranes were fouled rapidly again.

On day 85 and day 86 the membranes of RO line 1 were chemically cleaned again. During this CIP, the pressure drop over RO1 could be resorted for 73.3%, 49.1% due to the citric acid cleaning and 24.2% due to the caustic soda cleaning.

On day 86, the membranes of RO line 2 were cleaned with a Clean Operator cleaning. The pressure drop over RO2 however was restored with 55.9%. This is clearly les effective compared to earlier performed Clean Operator cleanings (cleaning events 1, 2 and 3). The lower efficiency was found to be caused by the fact that the CO_2 stock ran empty. The cleaning was actually partially performed with nitrogen gas which is used as a propellant.

On day 93 RO line 1 and 2 are flushed with only permeate because there was still no CO_2 available. Both were first co current flushed and than counter current. All flushes are applied with permeate at 8.5 m^3/h. On both RO lines the pressure drop over the lead element was restored with 43 kPa and 48 kPa for respectively RO line 1 and 2. In terms of percentages this 307% for RO1 and 264% for RO2.

During the period day 78 - day 85, the normalized flux of RO1 and RO2 started to decrease for the first time. This is an indication that scaling took place. The chemical cleaning (cleaning event 4 on day 85/86) at RO1 restored this decline of the normalized flux. The Clean Operator cleaning on day 86 on RO line 2 however was not able to restore the normalized flux. The Clean Operator cleaning performed on day 86 was not optimal because of CO_2 shortage. From day 85, the normalized flux kept on decreasing.

<u>Cleaning 5</u>

During the period from day 93 until day 99 no Sodium Acetate was dosed. On day 100 only RO2 is cleaned with Clean Operator after new CO_2 cylinders were delivered. The efficiency increased significantly due to the interference of the flow controller of the CO_2 dosage. This had not been observed before. The pressure drop was restored down to the level after the first cleaning event (day 31). It is unknown how much CO_2 was dosed, but for sure there was an overdose of CO_2 gas. The pressure in the CO_2 cylinders was >40 bar at that time, suggesting that without the restricting of the flow controller significant more CO_2 is dosed. After this cleaning event the retention of RO2 was decreased with about 0.5% compared to the situation before this failure. The integrity of the membrane is separately described in paragraph 4.4.

From day 100 the intention was to test with lower Sodium Acetate dosages, in order to find out how much Sodium Acetate is needed to increase the pressure drop over the first module with maximum 100% in one week. This was namely considered to be a good setting for the second research period. A 100% pressure drop increase corresponds with about 10% increase of total pressure drop feed-concentrate in a full scale plant with 2 stages having 6 modules in series each. Unfortunately the MTC of the membranes was reduced rapidly again with mainly Calcium Carbonate scaling analyzed in the acid CIP released from the membranes. The Calcium Carbonate scaling was caused by a different feed water composition (temporary higher pH after softening in the Water Treatment Plant Noordbergum) together with the absence of an anti-scalant dosage and a recovery of 50%. At the end of the first research period, both RO1 and RO2 were cleaned chemically twice and also several Clean Operator flushes were performed to clean the membranes as much as possible before starting the second research period.

4.1.3. Maximum CO_2 volume that can release at different flow and pressure

After the first research period the development of the pressure drop during a Clean Operator performance on RO line 2 is determined at different feed flows with and without CO_2 dosage. The feed flow is varied between 2 (at the start of cleaning) and 8 m^3/h (at the end of cleaning). In figure 4.2 the location of the different pressure transmitters is given. The pressure drop over each individual membrane element can be calculated. The outflow of the pressure vessel is at the top of the degassing tower.
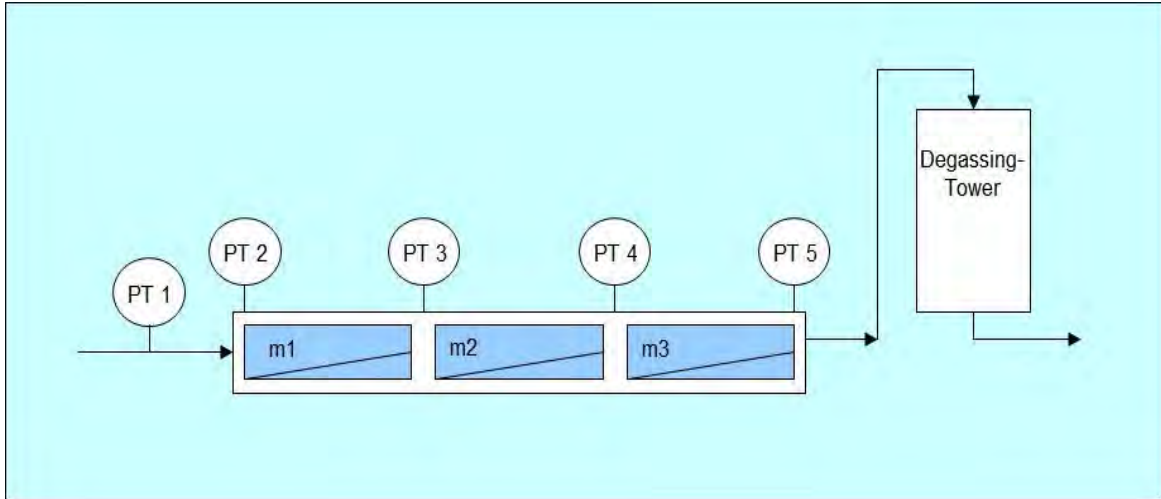
Figure 4.2 location pressure transmitters DO

In table 4.1 the pressures are given without the dosages of CO_2 and in table 4.2 with CO_2 dosage. In both tables also the calculated pressure drop over the three modules is given (Clean Operator cleaning in co-current direction).

Table 4.1 pressures and pressure drop per module without CO_2 dosage

Flow	DO 1	DO 2	DO 3	DO4	DO 5	dP m1	dP m2	dP m3
[m³/h]	[kPa]	[kPa]	[kPa]	[kPa]	[kPa]	[kPa]	[kPa]	[kPa]
2	40	37.5	25	20	14	12.5	5	6
3	49,5	47	30	23	15	17	7	8
4.1	65	63	38	28	17	25	10	11
5	82	80	47	33	19	33	14	14
6.1	99	96	55	38	21	41	17	17
6.9	122	119	68	46	24	51	22	22
8	149	145	84	56	28	61	28	28

Table 4.2 pressures and pressure drop per module with CO_2 dosage

Flow	DO 1	DO 2	DO 3	DO4	DO 5	dP m1	dP m2	dP m3
[m³/h]	[kPa]	[kPa]	[kPa]	[kPa]	[kPa]	[kPa]	[kPa]	[kPa]
2	61	60	46	38	27	14	8	9
3	79	77	58	45	28	19	13	17
4.1	103	100	71	54	29	29	17	25
5	121	119	82	60	30	37	22	30
6.1	152	149	102	75	35	47	27	40
6.9	174	171	118	88	41	53	30	47
8	222	218	155	117	54	63	38	63

With the measured pressures the amount of CO_2 gas that was release can be calculated. Since it is not possible to measure the amount of gas formed in each module directly, theoretical calculation is the only way to estimate the volume of gas formed. Per 10 kPa decline of the pressure approximately 0.223 kg CO_2 per m^3 water is released (appendix 3). With this information, combined with the information from table 4.2, one can calculate the volume per time of CO_2 that will release in a pressure vessel using formula 3 (paragraph 2.5.3). The result is given in appendix 8 and in tables 4.3 and 4.4. The release per module is calculated as well as the release over the outflow and the cumulative release.

Table 4.3 calculated release of CO_2 in m^3/h at the actual pressure (co-current)

release per module and outflow + *calculated cumulative release*

flow	module 1	module 2	module 3	outflow	*cum*
2	0,205	0,126	0,185	2,495	*3,011*
3	0,380	0,288	0,417	3,756	*4,841*
4,1	0,717	0,479	0,809	5,151	*7,156*
5	1,033	0,719	1,156	6,303	*9,210*
6,1	1,424	0,978	1,759	7,817	*11,977*
6,9	1,676	1,141	2,204	9,007	*14,028*
8	1,972	1,443	3,040	10,826	*17,280*

cumulative release + *difference in cumulative and calculated cumulative*

flow	module 1	module 2	module 3	outflow	*dif cum*
2	0,205	0,346	0,556	3,144	*0,133*
3	0,380	0,708	1,203	5,194	*0,352*
4,1	0,717	1,297	2,298	7,986	*0,829*
5	1,033	1,929	3,428	10,618	*1,407*
6,1	1,424	2,679	5,014	14,417	*2,440*
6,9	1,676	3,158	6,096	17,311	*3,283*
8	1,972	3,835	7,913	22,355	*5,075*

From table 4.3 it is clear that, when more water is fed, also more CO_2 gas is released per module due to the higher pressure drop at increased water flows. In the upper part of table 4.3 the release of CO_2 gas per module and outflow is cumulated. This is a different value compared to the lower part of the table. The difference in the cumulative volume of CO_2 that is released (e.g. 5.075 m^3/h at 8 m^3/h water flow) is caused by the influence of the gradually decline of the pressure. Gas that originally is released in module 1 will have a higher volume when entering module 2 and further downstream (p*V must be constant).

The same calculation is done for the counter-current Clean Operator cleaning. The measured pressures determined in the co-current are assumed to be the same in a counter-current situation as the same volume of (bio)fouling is present in the feed spacers of the modules and the permeate valve was kept closed. The results are given in appendix 8 and in table 4.4. Based on these calculation there is more volume of gas released in the lead module during a counter-current cleaning compared to a co-current cleaning (e.g. 2.976 m^3/h in counter current mode instead of 1.972 m^3/h in co current mode, both at 8 m^3/h water flow).

Table 4.4 calculated release of CO$_2$ in m^3/h at the actual pressure (counter-current)

release per module and outflow + *calculated cumulative release*

flow	module 3	module 2	module 1	outflow	*cum*
2	0,144	0,122	0,232	2,515	*2,869*
3	0,297	0,280	0,456	3,815	*4,551*
4,1	0,534	0,460	0,907	5,270	*6,637*
5	0,764	0,684	1,374	6,400	*8,457*
6,1	1,097	0,929	1,984	7,990	*10,903*
6,9	1,366	1,093	2,398	9,198	*12,690*
8	1,834	1,419	2,976	11,107	*15,502*

cumulative release + *difference in cumulative and calculated cumulative*

flow	module 3	module 2	module 1	outflow	*dif cum*
2	0,144	0,275	0,531	3,144	*0,275*
3	0,297	0,604	1,137	5,194	*0,642*
4,1	0,534	1,055	2,148	7,986	*1,349*
5	0,764	1,554	3,251	10,618	*2,161*
6,1	1,097	2,201	4,730	14,417	*3,514*
6,9	1,366	2,696	5,798	17,311	*4,621*
8	1,834	3,622	7,638	22,355	*6,853*

4.2. Second research period: long term biofouling research

4.2.1. Adjustments to the research installation

Before the start of the second research period several adjustments have been executed in the operation of the research installation. These adjustments are based on the experiences gained in the first research period:

- Anti-scalant dosage
  With the applied recovery of 50% and no anti-scalant dosage the membranes were polluted in the first research period with mainly $CaCO_3$ scaling because of a slightly different feed water composition. To avoid such a situation an anti-scalant dosage is installed. The applied anti-scalant is the common used OSM92, at a dosage of 2.5 ppm.

- Decreased recovery
  The recovery was decreased from 50% towards 45%. Together with the anti-scalant dosage, this provides extra security against scaling.

- Decreased Sodium Acetate dosage
  The Sodium Acetate dosage between 75-200 µg C/l in the first research period resulted in extreme and rapid biofouling. The Sodium Acetate dosage needs to be decreased in order to handle the biofouling. The aim is to let the pressure drop increase by maximum 100% over the first module (lead module) in about one week. Based on the experiences in research period 1, a Sodium Acetate dosage of 10 µg C/l was regarded as sufficient.

- Flow during Clean Operator
  The permeate flow during Clean Operator is reduced from 8 till 7 m^3/h. This is done because during the first period the pressure drop over the three membrane module was that high at 8 m^3/h that the limits of the quantity of the CO_2 to be dosed were reached. With a flow of 7 m^3/h and less membrane fouling no problems were expected.

- Modified CO$_2$ dosage
  During the first research period as much CO_2 was dosed to theoretically have just 100% in solution when the flush water enters the first module. Then, CO_2 gas will already form in the first module, causing a feed to the second module with water and CO_2 dissolved in it, plus CO_2 as a gas. This might not be an optimal situation as the second module will be fed with water and gas. Therefore the dosage is modified: at the start of the dosage as much as CO_2 will be dosed to be just in saturation when leaving

the last module. Then this dosage will be gradually increased until the level where the water is saturated with CO_2 entering the first module. Doing so, the formation of the gas bubbles will start in the last module and gradually the gas formation moves further stream up until it has reached the first module.

- Flush after Clean Operator
  After a flush with water and CO_2, only water is flushed through the RO membranes to remove the CO_2 gas that is still present in the feed spacer and in the space between membranes and pressure vessel. During the first research period this flush out was performed with an open permeate valve. As a result some gas passed through the membrane. This was visually observed as large gas bubbles passing the permeate flow meter when the membranes turned back in production again. After a Clean Operator cleaning, the retention was decreased every time for approximately one day, but was then restored every time. For the second research period the permeate valve is kept closed during this flush out with permeate, and the permeate valve is opened again only the last minute of the flush out. Most of the CO_2 gas will then removed and the effect of the decreased retention is expected to be limited.

- Exchange of the first and third membrane module
  Because there were no new membrane modules available at the start of the second research period, the same membranes were used in the second test period. The first and third modules of both RO lines were exchanged. At the end of the first research period the first modules were still fouled based on the increased pressure drop. The pressure drop over the third modules at the end of the first research period was comparable with the pressure drop at the start of the first research period. Because biofouling starts in the first module, modules 3 and 1 were exchanged. As a result the lead modules starting the second research period were the less fouled modules and the third modules in research period 2 were the most fouled.

- Exchange of the Clean Operator method and the conventional CIP
  During the first research period, the Clean Operator cleaning was mainly applied on RO2. During this period the retention based on conductivity was slightly decreased, mainly after the incident with the defect flow controller (cleaning event 5). In order to determine if the Clean Operator method really will affect the retention negatively, it is best that Clean Operator will be applied on RO2 in the second research period (using the membranes that still had their original level of retention).

- Frequency data logging
  The data will be automatically logged every hour. During a Clean Operator performance every minute the data will be logged automatically.

4.2.2. Settings pilot second period

Both RO lines were again fed with 4.5 m^3/h feed water. The recovery was regulated on 45%. In this period an anti-scalant was dosed, 2.5 ppm OSM92. Limited Sodium Acetate was dosed, 10 µg C/l, to promote biofouling.

Each chemical cleaning was performed for 2-2.5 hours, in which a chemical cleaning solution was recirculated over the membranes at a velocity of 8 m^3/h, interrupted by soakings of the membranes in the chemical cleaning solution. During the chemical cleaning, the permeate valve was not closed and the flow direction was the same as during production (co-current). A chemical cleaning existed in a low pH cleaning (citric acid, pH ~2) followed by a high pH cleaning (NaOH, pH ~11.5).

Each Clean Operator cleaning was performed twice: first a co-current cleaning (flow direction is the same as during filtration) with a water flow of ~7 m^3/h, followed by a counter-current cleaning with a water flow of ~7 m^3/h. During Clean Operator the permeate valve was closed. During the flush out at the end this valve was also closed, except in the last minute of flush out.

Each Clean Operator cleaning had the following procedure:

- 3 minutes – start heater (formation of CO_2 gas from CO_2 liquid)
- 1 minute – start flush pump
- 5 minutes – dosing the CO_2 with a dynamic calculated setpoint, the last 140 seconds the solution was saturated based on the setpoint belonging to the inflow.
- 4 minutes – flush out CO_2/mixture with closed permeate valve and the last minute with an opened permeate valve.

The membranes of RO line 1 were chemically cleaned and at the membranes of RO line 2 were cleaned with a Clean Operator cleaning.

At the end of the second research period it was found that the the setpoint of the CO_2 dosage was not as it was planned to be. It turned out to be a fixed setpoint instead of a dynamic setpoint based on pressure, flow and temperature. And above that, the theoretical saturation of the CO_2 was not 100% but approximately 225%.

4.2.3. Feed water quality

The quality of the feed water was reasonable stable during the second research period and the period that the influences of different variables have been investigated (figure 4.3). The pH fluctuated between 7.7 and 8.5, and the turbidity between 0.15 and 0.25 NTU. On day 41 an increased turbidity (up to ~5 NTU) was measured due to the collapse of a 700 mm transport pipe in the distribution network of treatment plant Noordbergum.
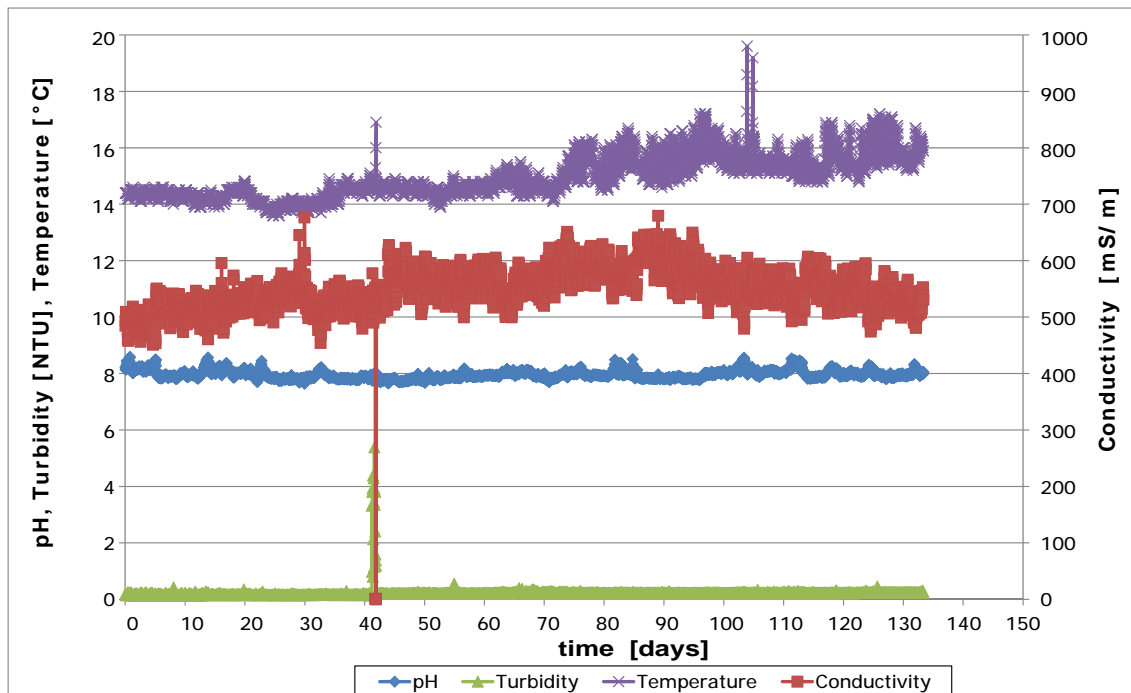
Figure 4.3 development of different water quality parameters

4.2.4. Results second period

The main objective of the second research period was to compare the efficiency of the Clean Operator technology with the conventional chemical cleaning over a longer period. In a period of 105 days twelve cleaning events took place. Figure 4.4 shows the development of the normalized pressure drop in this period. In appendix 9, the development of the pressure drop over the three individual modules and the development of the feed pressure, the normalised flux and the retention are given.
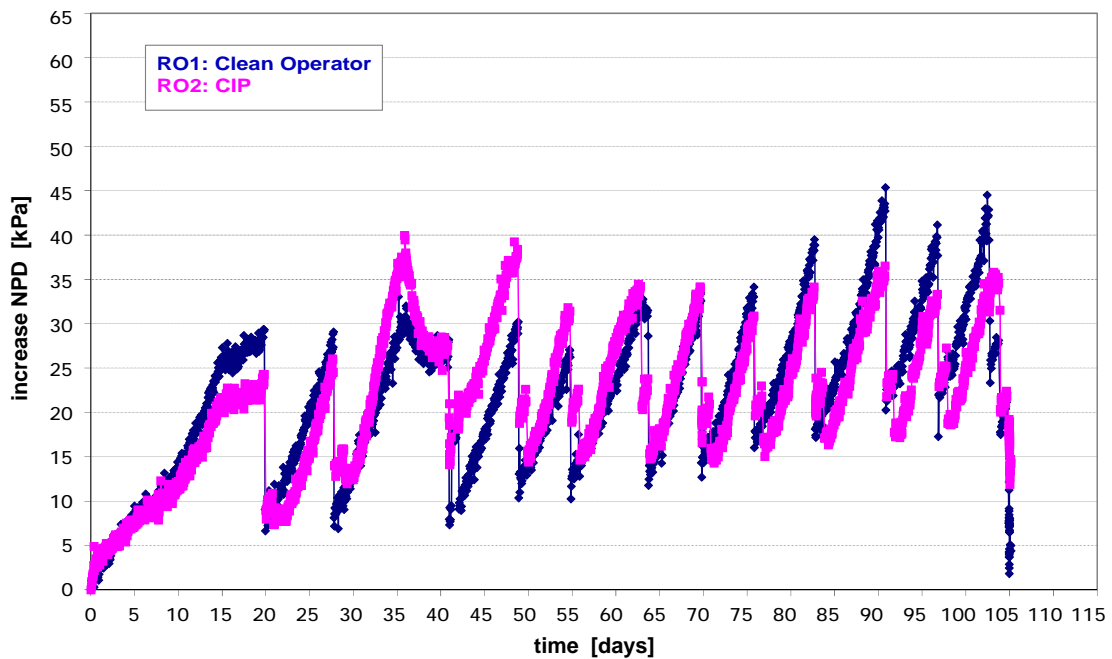
Figure 4.4 development of the increased normalised pressure drop during the second research period

Figure 4.4 clearly shows that both cleaning strategies were not able to restore the increased pressure drop completely. During these 105 days of operation there was one exceptional situation that needs extra explanation. Due to the collapse of a large transport pipe in the distribution system of production facility Noordbergum on day 41, the quality of the feed water was poor (turbidity ~3-5 NTU) and the quantity of the feed water was too low to feed both RO lines. Because of that RO2 was automatically shut down. This breakage happened just in between the citric acid and caustic soda cleaning of RO2. RO1 still produced permeate during the period of bad feed water quality (turbidity between 3 - 5 NTU) for twelve hours on day 41. Next day (day 42) a Clean Operator cleaning was performed.

The average percentage of efficiency of the restored normalized pressure drop over each RO line of all applied cleanings was more or less the same, 91.5% for the chemical cleaning (RO2) and 93.7% for Clean Operator (RO1).

RO1 started with the most fouled membranes (the old CIP cleaned membranes from the first research period). Directly from the start of the second research period, the normalized pressure drop (NPD) over the feed spacers was the highest in RO line 1 (having the most fouled membranes from research period 1). After the first 2 cleaning events (day 27), the NPD over the feed spacers in RO line 1 were lower compared to RO line 2. The extra Clean Operator cleaning on day 42 (RO1) gave an extra reduction of the NPD compared to RO line 2, but from there the NPD over the feed spacers of RO line 1 slowly increased to higher levels compared to RO line 2. From day 70 the absolute increase of the normalized pressure drop over RO1 (Clean Operator) became bigger compared to RO2 (CIP). The increase of the pressure drop is a linear process. The inclination angle of the increase of the pressure drop between two cleaning events is comparable for RO1 and RO2 over the last seven runs (appendix 10). RO2 was better able to restore the pressure drop towards the level after the cleaning event before. The average percentage of efficiency of the restored normalized pressure drop over the last seven runs was 97.1% for the chemical cleaning (RO2) and 92.6% for Clean Operator (RO1).

After 105 days of operation, both RO lines are cleaned chemically and with Clean Operator. Where RO1 was cleaned with Clean Operator it is cleaned chemically after the last Clean Operator performance. RO2 is cleaned with Clean Operator after the last regular chemical cleaning. After these combined cleaning events the NPD of RO 1 was again reduced below the

NPD value of RO line 2. The total increase of the normalized pressure drop over RO1 is approximately 2-5 kPa and over RO2 12-15 kPa (see figure 4.4.).

4.3. Major parameters of influence

There are several parameters that might have an influence on the efficiency of the Clean Operator performance. These variables are:

1. Concentration of CO_2
   The concentration of CO_2 must at least lead to nucleation of gas bubbles inside the membrane modules, especially at the location were the biofouling is attached. An increase of the CO_2 concentration will create more gas bubbles. And more gas bubbles mean a better mechanical cleaning effect. However, a disadvantage could be that the nucleation of the gas bubbles already occurs before the solution is entering the first module. In that case a preferred flow pattern and channelling may occur, which might reduce the cleaning efficiency.

2. Co-current versus counter-current
   The (biological) fouling is mainly present in the first module, concluded from the higher increase in NPD. A counter-current performance might have a higher efficiency as the fouling removed from the most fouled membrane does not need to be transported through the other serial placed modules.

3. Low versus high water flow
   The water flow is thought to have different effects on the gas formation and the cleaning efficiency. At a lower flow, less permeate and less CO_2 is needed to be dosed to prepare a CO_2 saturated solution, because the pressure is also low at lower water velocities. A lower velocity also means: less sheer and less gas formation. Secondly, at a lower pressure the volume of a single gas bubble will be larger. Contrary, at higher water flows, more CO2 and more permeate is needed (delivering more shear and more gas), but gas bubbles formed will have a smaller volume due to the higher pressure.

4. Pressure
   When applying a back pressure, using a control valve at the outflow of the pressure vessel, the volume of the released gas bubbles can be influenced. The drawback is that this will require more CO_2 to be dosed. Another possibility is that one can increase the pressure in the pressure vessel with the same control valve and feed the pressure vessel with a water/CO_2 solution. This does not necessarily need to be a saturated solution. By sudden opening of the control valve the pressure decreases and nucleation of gas bubbles will occur evenly all over the pressure vessel.

5. Adding additives
   Adding additives besides CO_2 (e.g. particulate matter, flocking agents, detergents) to the permeate that is used in the Clean Operator flush, might also increase the efficiency of the process. The idea behind this, is that particulate matter also has a cleaning effect when it is flushed through the feed spacer of a membrane.

These five major parameters together can form different settings that may increase or decrease the total cleaning efficiency. After the second research period, three short experiments were performed to investigate the influence of these major parameters (CO2 concentration, co-current / counter current, and water flow velocity). During these short experiments the Sodium Acetate dosage was increased from 10 µg C/l to 20 µ g C/l, in order to fasten the biofouling In the next three sub paragraphs the results of the tests are reported. Each experiment is applied twice in a row to see what effect a second performance of Clean Operator under the same conditions would have on the normalized pressure drop. Both RO lines are not chemically cleaned during these experiments. The effect of pressure increase and adding of additives isnot tested in this research.

In the figures in appendix 11, the development of the normalized pressure drop is plotted during these experiments. The graph of the increased pressure drop during the second research period and during these experiments is also presented in appendix 11. The impact of the increased Sodium Acetate dosage is clearly visible.

4.3.1. Influence of CO_2 concentration

This experiment is performed on day 111. As mentioned before in this report, during the second research period Clean Operator is performed not with a 100% saturated solution but with a 225% saturated solution. In this experiment Clean Operator is applied with a 100% saturated solution on RO1 and with a 225% saturated solution on RO2 (table 4.5). For both RO lines Clean Operator is first applied as co-counter and second as counter-current. The water flow during Clean Operator cleaning at both RO lines was 7 m^3/h.

Due to the Sodium Acetate dosage the normalised pressure drop increased with 18.4 kPa and 18.8 kPa (RO1 and RO2). An increase of the CO_2 concentration had a positive effect on the efficiency (table 4.5). The second performance of Clean Operator did not remove more fouling, a negative effect was even measured. Both results are significantly less compared to research period 2.

Table 4.5 efficiency and normalised pressure drop decrease with different concentration CO_2

	RO1		RO2	
	100% saturated		200% saturated	
First performance (co)	52.2%	9.6 kPa	78.9%	14.8 kPa
Second performance (counter)	-2.6%	-0.5 kPa	-12.8%	-2.4 kPa
Overall	49.6%	9.1 kPa	66.1%	12.4 kPa

4.3.2. Influence of co-current vs counter-current cleaning

This experiment is performed on day 125. Clean Operator is performed with a 100% saturated solution and a water flow of 7 m^3/h.

Due to the Sodium Acetate dosage the normalised pressure drop increased with 68.4 kPa and 56 kPa (RO1 and RO2). A minor difference in cleaning efficiency is observed in favour for the co-current performance (table 4.6). The first performance showed a clearer difference, after two performances the difference stayed.

Table 4.6b efficiency and normalised pressure drop decrease applied co-current and counter-current

	RO1		RO2	
variable	Co-current		Counter-current	
First performance	75.2%	51.5 kPa	64.7%	36.2 kPa
Second performance	4.1%	2.8 kPa	8.7%	4.9 kPa
Overall	79.3%	54.3 kPa	73.4%	41.1 kPa

4.3.3. Influence of cleaning at high flow vs low flow

This experiment is performed on day 133. First Clean Operator was performed on RO1. With the lowest possible flow, the pump delivers 3 m^3/h and only about 13 kg/h of CO_2 was dosed for a 100% saturation. At a high flow (11 m^3/h), about 135 kg/h of CO_2 was needed for 100% saturation on RO2. The pressure of the pump was so high (8 bars), that the flow had to be reduced until 10 m^3/h during the first performance. The second Clean Operator cleaning is performed at 9 m^3/h (and 90 kg CO_2/h). All events were performed as co-current and with a 100% saturated solution, except the third event with a low flow. This was performed with a 200% saturated solution.

Due to the Sodium Acetate dosage the normalised pressure drop increased with 81.4 kPa and 81.6 kPa (RO1 and RO2). A higher flow resulted in a higher cleaning efficiency. Increasing the concentration at the low flow performance (third performance) increased the efficiency, but not to a comparative level as could be reached with the higher flow.

Table 4.7 efficiency and pressure drop decrease Clean Operator applied at low and high flow

	RO1		RO2	
variable	Low flow		High flow	
First performance (100%)	53.4% (3 m3/h)	43.5 kPa	85.8% (11-10 m3/h)	70 kPa
Second performance (100%)	0.4% (3 m3/h)	0.3 kPa	2% (9 m3/h)	1.6 kPa
Third performance (200%)	7.9% (3 m3/h)	6.4 kPa	-	-
Overall	61.7%	50.2 kPa	87.8%	71.6 kPa

Because of the low efficiency of Clean Operator at a lower flow, Clean Operator is performed again with a 7 m^3/h flow and a 100% saturated solution on RO1. This increased the overall efficiency with 14% (11.4 kPa decrease of the pressure drop) towards a total of 75.7%.

4.4.   Effect of Clean Operator on membrane integrity

Most spiral wound membranes used in RO applications are composite membranes. The membrane is coated or cast on a support sheet, typically a non-woven polyester film, about 0.1 mm thick. On top of this layer, a thin UF support membrane, about 0.05 mm thick, made of polysulfone, is applied to the support fabric. The final RO membrane, only about 0.2 nm thick, is then coated on the top of the support membrane [TriSep]. Figure 4.5 shows an impression of the different layers.
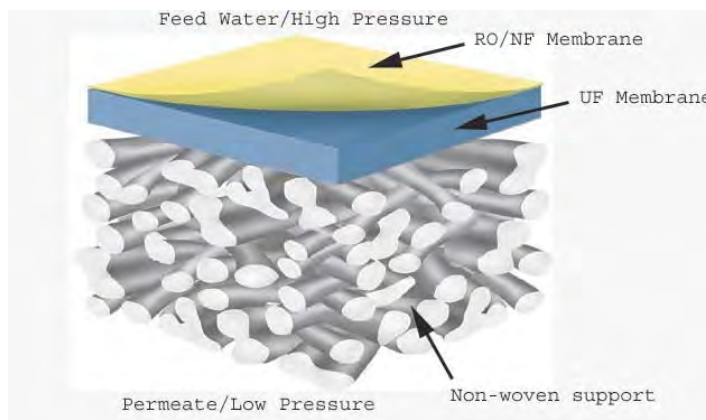
Figure 4.5 different layers of a RO membrane [TriSep]

An objective of the research was to determine the effect of Clean Operator on the integrity of the membrane. The integrity of the membrane is very important. RO membranes are applied to remove dissolved ions and/or bacteria, priority compounds, organic matter, etc. Damage of the membrane will decrease the permeate quality. Clean Operator aims at the nucleation of gas bubbles inside the membrane modules. The nucleation takes place were a pressure drop occurs. Throughout the entire feed channel the pressure will decrease due to hydraulic resistance. But the membrane layer, especially the RO membrane, creates a bigger pressure drop when water is passing the membrane. This means that if during a Clean Operator performance the saturated solution will pass through the RO membrane, nucleation of the gas bubbles will occur when the pressure is reduced. This can damage the coating of the RO membrane on his support layer. To avoid this phenomenon, the permeate valve is closed

during the Clean Operator performance. Then CO_2 can only pass through the membrane by forward diffusion. A closed permeate valve will result in a lower CO_2 passage through the membrane, and consequently, a lower gas formation in the membrane layer once the membranes are taken in operation again.

First research period

During the first research period, the permeate valve was closed during flushing with water and CO_2, and directly opened after the CO_2 dosage stopped. During the flush out of the water and CO_2 solution, no water or gas flow could be observed due to the low pressure drop over the membrane. As soon as the RO was taken in the production again, it was clearly visible that relatively big gas bubbles came along with the first permeate (visible through the flow meter).

After every Clean Operator cleaning, the retention based on conductivity measurements was temporary decreased. Figure 4.6 shows this temporary drop in retention after a Clean Operator cleaning. Also after every CIP, the retention is temporarily decreased. Until day 42 the retention of both RO lines was equal after a few days of permeate production. After the cleanings applied on day 42 the retention of RO line 2 is slightly deceased compared to RO line 1. After the dosage of a surplus of CO_2 at the end of the period (due to a malfunctioning flow controller), the retention of RO line 2 was about 1% lower compared to RO line 1 (data not shown in figure 4.6).
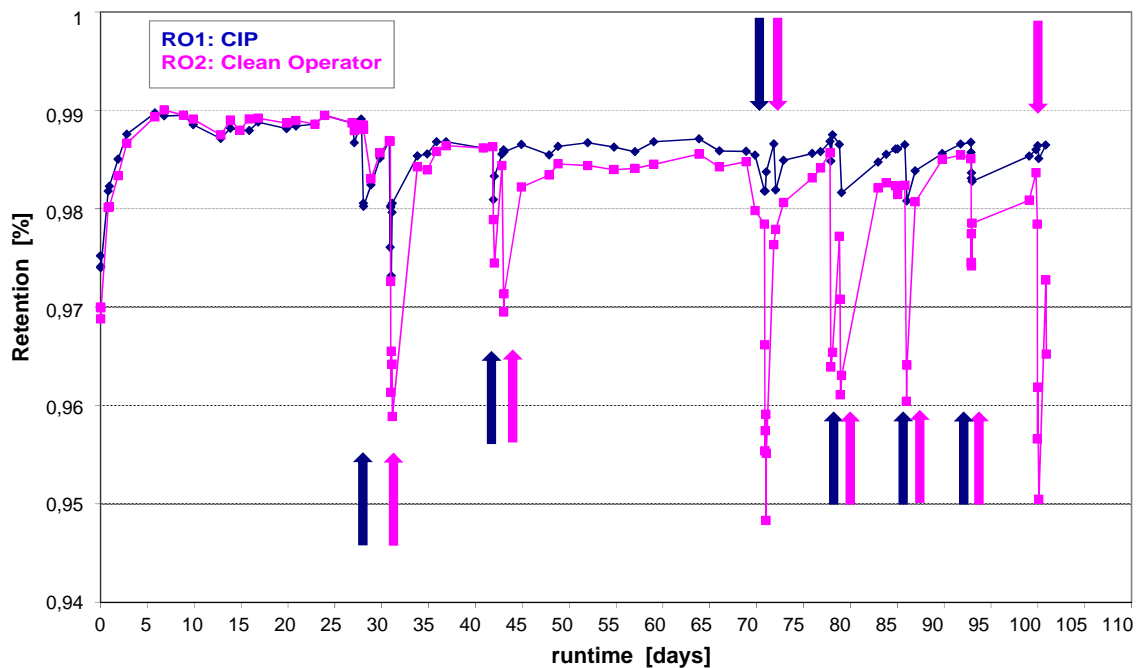
Figure 4.6 course of the retention during the first research period (arrows indicate cleaning events)

Second research period

The procedure for the Clean Operator cleaning was adapted before the start of the second research period in order to avoid CO_2 transport through the membrane as much as possible (see paragraph 4.3). Clean Operator was applied on the membranes with the highest retention, the duration of the flush out after the CO_2 dosage was extended, and the permeate valve was kept closed during the first phase of the flush out. At the end of this flush, when it is assumed that most of the CO_2 gas is flushed out, the permeate valve was opened again. Visually this had the desired effect as no large gas bubbles came out anymore with the first permeate produced after a cleaning. But with the increased concentration that was used (225% saturation by mistake) still some smaller gas bubbles came out. Application of Clean Operator cleaning with a 100% saturated solution decreased the quantity of gas bubbles in the permeate even further. In al cases, still a temporary decrease of the retention was observed measured as Electrical

Conductivity in the permeate (figure 4.7). After a Clean Operator performance the retention decreased with about 1%, but after one day the retention was restored.

A CIP has also some effect on the retention. After the first acid part of a CIP the retention is increased with about 0.3% and after the second base CIP the retention decreased with about 0.3% compared to the situation before the CIP.
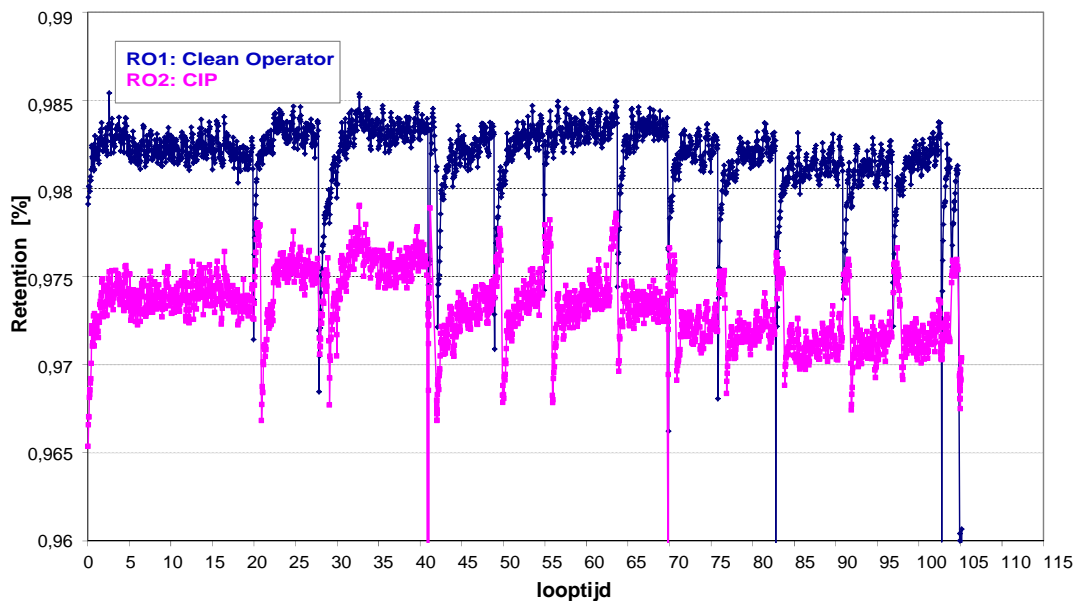
Figure 4.7 course of the retention during the second research period

Just before a Clean Operator cleaning, feed water and permeate was sampled (table 4.8). During the first and second Clean Operator cleaning in a row, a bulk sample is taken of the flushed out water (C.O.1 and C.O.2) during the period of Clean Operator that the saturated water and CO_2 solution entered the pressure vessel. The sample is taken directly at the pressure vessel before the degassing tower (in absence of air). Both samples (C.O.1 and C.O.2) give an impression of the chemical reactions during a Clean Operator cleaning. Finally, 15 and 60 minutes after the second Clean Operator cleaning, permeate was sampled and analysed. The results of the analysis are presented in table 4.8.

Table 4.8 analyse before, during and after a Clean Operator performance

		feed	permeate RO1	C.O. 1	C.O. 2	permeate RO1 15 min after C.O.	permeate RO1 60 min after C.O.
temperature		14	14	14	14	14	14
pH		7,9	6,1	4,15	4,12	5,49	6,19
E.C.	mS/m	52,7	1,1	6,2	5,8	2	1,7
HCO3	mg/l	132	5,3	0	0	8,4	6,4
FTE	mg/l	<0,1	<0,1	0,59	0,24	<0,1	<0,1
Cl	mg/l	105	<3	<3	<3	<3	<3
SO4	mg/l	4	<2	<2	<2	<2	<2
Al	ug/l	8,38	<2	274	88	<2	<2
Na	mg/l	48,7	1,96	0,682	<0,5	2,52	2,57
K	mg/l	2,8	0,1	<0,1	<0,1	0,1	0,1
Ca	mg/l	55,6	<0,5	0,894	<0,5	0,844	0,77
Mg	mg/l	10,7	<0,1	<0,1	<0,1	0,167	0,15
Fe	mg/l	<0,01	<0,01	1,28	0,183	<0,01	<0,01
Mn	mg/l	<0,005	<0,005	0,008	<0,005	<0,005	<0,005

The results in table 4.8 show that the dosage of CO_2 decreased the pH of the permeate with about 2 units. From chemical point of view Clean Operator removed aluminium, iron and a minor amount of calcium. Particles are also removed as indicated by an increase in turbidity in the flushed out water.

As soon as the RO was taken in operation again, a little increase of the HCO_3 concentration in the permeate was observed, together with an increase in Sodium, Magnesium, Calcium and EC. The pH of the permeate was significantly lower direct after a Clean Operator cleaning (pH ~5.49) compared to the pH of the permeate under steady operation (pH ~6.1).

5.   FULL SCALE DESIGN CLEAN OPERATOR

A Clean Operator system can easily be integrated in the CIP or flush system of an existing RO plant. In this chapter first a CIP system is described. Then the Clean Operator set up is described, including how it can be integrated in an existing CIP system. A full scale design is made for Vitens new drinking water treatment plant Vechterweerd.

5.1.   Basic CIP design

Most RO plants have their own Cleaning In Place (CIP) system installed on location. With this CIP system the membranes can be cleaned with a chemical solution at an elevated temperature. Figure 5.1 shows a schematic impression of a CIP system. Normally the cleaning tank is filled with permeate of the membrane installation and the required chemicals. Most membranes are cleaned at a maximum temperature of 40°C. The solution is circulated over the membrane installation alternated with periods of soaking. Normally there is a cartridge filter between the CIP pump and the membranes in order to prevent eventually removed particles from the membranes to be fed again to the membranes. The solution is circulated over one stage while the solution is soaking the other stage(s). At the end of the cleaning the solution is neutralized with chemicals before it can be discharged to the sewer. Finally the membranes are flushed with permeate to remove the last remaining cleaning solution before the stack can be in operation again. The process of one cleaning can take several hours, typically between three and five hours depending on the time that is needed to circulate and soak the membranes. To clean one stack the CIP procedure is performed twice, once using an acid cleaning and once using a base cleaning. This means that the time to clean one stack is between six and ten hours. Often this is spread over two days.
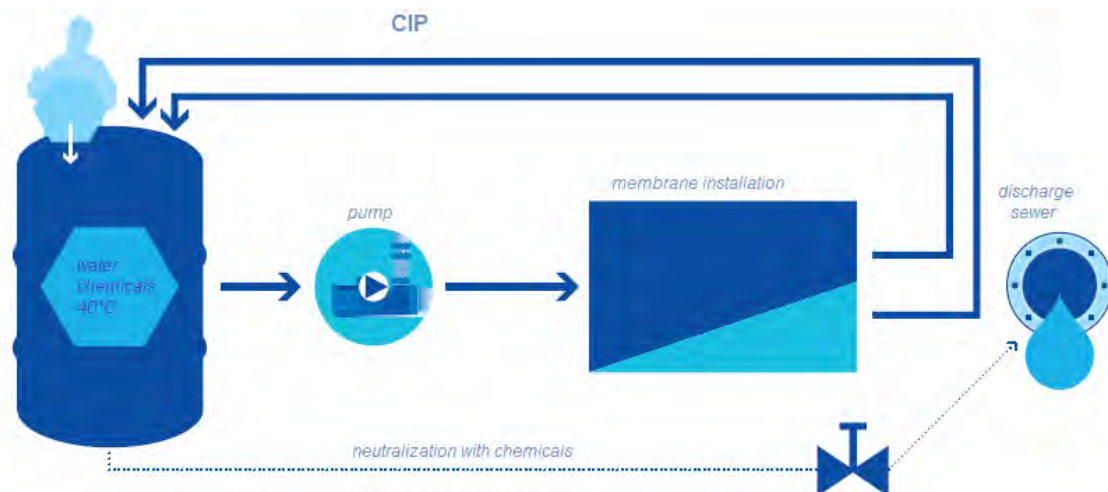
Figure 5.1 scheme of a CIP system

5.2.   Clean Operator design

The design of a Clean Operator installation is not very complicated. It is easily integrated in a CIP system. Figure 5.2 shows the schematic impression of a Clean Operator set-up. A Clean Operator performance needs water (preferably permeate) to feed the membrane installation (a). Before the water enters the membrane installation, the required amount of CO_2 is dosed (b). After the solution enters the first membrane the pressure is decreased automatically due to the hydraulic resistance of the (fouled) membranes. As a result continuously gas bubbles are formed. This release of gas bubbles takes place over the entire length of the pressure vessel (c). The gas bubbles detach and transport the fouling through the serial placed membrane modules and the flush water coming out of the system is then discharged without the need for neutralization (d). The flushed out water and free CO_2 gas needs to be treated safely to avoid personal accidents as carbon dioxide gas is toxic. It is a good idea to inject the flushed out water and CO_2 gas directly into the regular concentrate discharge pipe. It helps to prevent

scaling in this concentrate pipe and the concentrated ions in the concentrate react with the carbon dioxide gas.

To integrate Clean Operator in a CIP system, the only extra installations needed area CO_2 storage and an injection point for the CO_2 with an efficient static mixer. All the other equipment is already present in the CIP system. Another option can be to use a tank filled with saturated permeate that is used to flush a stack after a shutdown or before a start-up. In paragraph 5.2.1 the Clean Operator equipment is described.

Figure 5.2 scheme of a Clean Operator system

For the design it is important that the resistance form the membranes towards the discharge point is kept as low as possible. Any increase here will lead to an increase of the feed pressure during the Clean Operator performance and thus to unnecessary higher CO_2 consumption.

5.2.1. Clean Operator equipment

The CO_2 equipment can be subdivided in a storage part and a dosage/injection part. The difficulty in the system is the fact that not a continuously CO_2 flow is needed but a relatively high peak flow at in a short time.

Storage

For the storage of CO_2 several options are possible. Storage can be done with cylinders or as bulk in a tank. The choice depends on the quantity of CO_2 that will be yearly used and is more an economic optimization. The storage of CO_2 is located outside the building and on a safe distance. The CO_2 is stored as a liquid but will be dosed as a gas. Therefore the liquid CO_2 must be transformed to the gas phase. This can be done with electric heaters when it needs to be very quick. Because most of the time the CO_2 dosage is not needed also an atmospheric evaporator can be applied, which is slower compared to an electric heater.

Dosage/injection

For the dosage of the CO_2 (as a gas) a static mixer is used to mix CO_2 gas under pressure into the water or permeate. A mass flow meter and flow controller ensure the correct quantity of gas to be dosed. Finally the solution is fed to the fouled membranes.

5.2.2. Investment costs Clean Operator

The investment cost for the dosage system is between €48,500 and €60,000 depending on the quantity of CO_2 to be dosed, 750 – 7,500 kg CO_2 per hour [info Messer BV]. This cost calculation is based on an atmospheric evaporator. The system includes all the hardware from the storage of CO_2 up to the static mixer, which is also part of the investment. The storage is not part of the investment mentioned. This storage can be hired by the supplier of the gas. The yearly rental costs are between €3,250 and €11,000, depending on the quantity of CO_2 yearly used.

The P&ID of the CO_2 dosage system is given in appendix 4, the second last sheet.

The solution that leaves a stack after a Clean Operator cleaning must pass a degassing device to remove the excess of CO_2 before it is discharged. Another option is to dose this waste

stream directly into the regular concentrate discharge pipe. The investment for integrating Clean Operator in the RO system will be around €20,000. This includes all kind of connections and the degassing device. Another €25,000 is needed for automation costs.

5.3.   Integral assessment Clean Operator; case Vechterweerd

Vitens plans to build a new drinking water treatment plant, Vechterweerd. The water source of this new plant is a mix of (aerobic) riverbank filtrate and groundwater. It is located near the river "de Vecht" in the province Overijssel. Reverse Osmosis will be part of the treatment of this new plant. In the first phase of development, two RO stacks will be installed with 55 m^3/ feed water capacity each. The staging of the three stage stacks for Vechterweerd will be 6:3:2, each stage containing 3 elements in series (Optiflux design). Sustainability is an important topic for the design and construction of the Vechterweerd plant. Clean Operator, as a new innovative cleaning technology for the RO membranes, will be part of this design. A design for the Clean Operator part is made based on the following design criteria; an 8 m^3/h permeate flow for each pressure vessel and a 225% saturated CO_2 solution (~15 kg CO_2/m^3).

The goal of the assessment is to compare the situation with and without Clean Operator. The interval for the CIP is assumed once a year. For this design Clean Operator is assumed to be applied once a month, 5 minutes on both stacks. With this strategy the feed pressure will be kept as low as possible since the fouling is removed on a regular basis. With this approach the energy consumption will be lower compared to one CIP event each year. The integral effect of introducing Clean Operator in the design is elaborated, based on costs, energy consumption, chemical use and CO_2 footprint.

5.3.1.   Investment costs

The RO system of Vechterweerd won't have a CIP system. Vitens will use their mobile cleaning unit to clean both stacks. But the RO system will contain a permeate tank that will be used to flush the stacks at the start and shutdown of a stack. This tank with permeate will be used as the permeate storage for a Clean Operator cleaning. The flush pump will be used to perform Clean Operator. This will not increase the investment costs of Clean Operator. The extra investment of Clean Operator is about €95,000 (table 5.1). This is exclusive the storage of CO_2 but it includes the integrating in the RO design (degassing device, connection and automation). The situation without Clean Operator will not have any effect on the investment costs of the Vechterweerd design.

Table 5.1 investment costs Clean Operator design Vechterweerd

Investment Clean Operator		
electric heater		
pressure controller		
CO2 connection unit		
CO2 dosage unit		
static mixer		
CO2 gas detection		
subtotal	50000	€
connection costs (incl. degassing)	20000	€
process automation	25000	€
investment	95000	€

5.3.2. Variable costs

Two different situations are calculated; Clean Operator and the CIP. The Clean Operator is performed once a month on both stacks. The CIP interval is once a year on both stacks. But it needs to be performed twice each stack, with citric acid and with caustic soda. A 10 m^3 chemical solution is used and heated for each CIP. With the CIP also neutralization of the solution before discharge is included.

Because the CIP is performed with a mobile unit transport costs are part of a CIP and additional hours are needed to build up and break down the mobile system. Clean Operator is performed with a fixed system.

Table 5.2 yearly variable costs for Clean Operator and CIP

Costs			Clean Operator		CIP	
	€			€		€
energy	0,09	/kWh	2 kWh	0,2	625 kWh	56
citric acid	1,08	/kg	-	-	200 kg	430
caustic soda	0,14	/kg	-	-	20 kg	3
CO2	0,10	/kg	63 kg	6	-	-
hours	45	/hour	0,5 h	23	32 h	1440
transport	-	-	-	-	-	300
			per stack	29	per stack	2229
			total	58	total	4458
			frequency: Clean Operator 12*y and CIP 1*y			
			692	€/y	4458	€/y

One single Clean Operator performance for a stack is clearly cheaper compared to one single CIP (excluding the Rent and Depreciation costs of the extra CO_2 equipment). Still with a higher Clean Operator frequency the variable costs are higher for CIP performance.

5.3.3. Energy consumption

In figure 5.3 a theoretically increase course of the feed pressure is shown. Assumed is a linear increase of the feed pressure due to fouling of the feed channel mainly by biofouling or particle fouling. The feed pressure of a comparable plant within Vitens, Engelse Werk, shows about the same pattern. Pre-treated riverbank groundwater is also the water source at the Engelse Werk plant which makes the assumption reasonable. The efficiency of Clean Operator is set on 90% which is reasonable since within this research an efficiency of about 94% is determined.

With Clean Operator, applied each month, the level of the feed pressure is better controlled. Over a period of one year the feed pressure is increased with 0.26 bar till 7.26 bar. Without any cleaning the feed pressure is increased with 1.5 bar till about 8.5 bar. Assuming that the feed pressure increase is a linear line, the average increased feed pressure is 0.13 bar with Clean Operator and 0.75 bar with the CIP. Clean Operator performed every month will decrease the energy consumption on a yearly basis with 23,140 kWh (equal to 13,300 kg CO2 emission) and €2.083 (appendix 12).
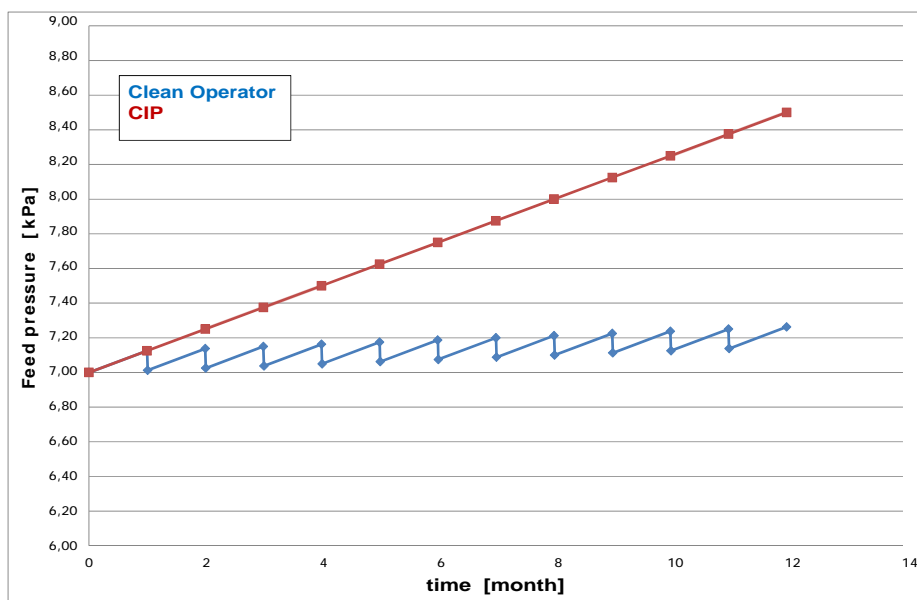
Figure 5.3 theoretical course of the feed pressure based on Clean Operator or CIP cleaning

5.3.4. Total cost of ownership

The total cost of ownership is divided in fixed (capital) costs and variable (operation) costs.

The fixed costs are the yearly depreciation and rent, and the rental cost for the CO_2 storage. The capital costs are calculated based on an annuity basis with 5% interest and a depreciation period of 15 years. For the situation without Clean Operator no extra investments are needed. The CIP unit is already planned and in the case of Vechterweerd an existing mobile cleaning unit will be used. The investment of this mobile cleaning unit, build in 2010, is divided over the five locations were it will be used. This includes Vechterweerd.

With the assumption that Clean Operator is performed every month and the CIP once a year the total costs are calculated and shown in table 5.3. Clean Operator will increase the yearly costs with about €3,560 (€11,062- €7,502), which is only about €0.002 per produced m^3 of drinking water at the Vechterweerd plant. This is an increase of only 0.2% for the total design.

Table 5.3 total cost of ownership for Clean Operator and CIP

Clean Operator			CIP		
investment	9153	€/y	investment	3044	€/y
rent CO2 storage	3300	€/y	-	-	-
variable costs	692	€/y	variable costs	4458	€/y
savings on energy (P feed)	-2083	€/y	-	-	-
total operational costs	11062	€/y	total operational costs	7502	€/y
per m3 drinking water	0,0067	€	per m3 drinking water	0,0045	€

Subsides, to implement green technologies, are not taken into account with the calculated investment costs based on an annuity basis.

5.3.5. CO_2 footprint

The CO_2 footprint of one single Clean Operator performance is a factor 8.4 lower compared to one single CIP (appendix 12). The CO_2 footprint for the use of CO_2 is assumed to be 1. But in fact the used CO_2 is recovered from waste, polluted air from chemical factories (info Messer). The CO_2 footprint for the production of citric acid could not be traced and is not part of the calculation. Based on the theoretical course of the feed pressure in figure 5.3 Clean Operator is performed 12 times and the CIP once. This would suggest that the yearly footprint for Clean Operator will be higher compared to the CIP, by a factor 1.5. But, because the average increased feed pressure is better controlled with Clean Operator (12x per year), the energy consumption can be decreased with 23,140 kWh. This leads to a total reduction of the CO_2 footprint of the RO system with 7.6%. For the Vechterweerd case this would lead to a decrease of the CO_2 emission with of 13.3 ton.

5.4.   Impact of frequent cleaning on large RO plants

The original plan for the development of Clean Operator is to apply the technology at RO plants suffering with biofouling. Clean Operator will increase the cleaning efficiency compared to CIP. In new plants, limitation of pre-treatment steps could be achieved when Clean Operator is applied. This would bring down the total costs significantly. Biofouling is an important type of membrane fouling when applying seawater desalination. Seawater desalination plants become bigger and bigger throughout the last decade. The largest plant in Israel, Hadera, has a 146 million m^3/year production capacity after an extension in January 2012, up to 456.000 m^3/day maximum!! This is more than 30 times Vitens biggest RO plant, Engelse Werk. The Hadera plant consists of about 53.000 membrane elements divided over four stages and the overall recovery is 42% [DOW]. With seven membrane elements in each pressure vessel, these are more than 7.500 pressure vessels. In figure 5.3 a photograph of the plant is shown.

Figure 5.3 photo of the Hadera SWRO plant (www.ide-tech.com)

Membrane fouling and cleaning has a huge impact on the operation of such a plant size. With a cleaning interval of once a year and every day cleaning, 21 pressure vessels have to be cleaned each day. The total number of cleaning events (CIP) in one day is practically limited. A CIP requires time, heated water, and manpower. If the cleaning interval will increase, one arrives quickly at a point that the cleaning facilities cannot handle the situation anymore. Then the operator has to decide to replace the fouled membrane modules by new modules. With Clean Operator, the plant operator has a new tool to clean the membrane modules within 15 minutes instead of the several hours needed for one single CIP. The frequency of the relatively expensive CIP can be decreased and the lifespan of the membrane modules can be extended. The potential of the application of Clean Operator therefore is significant.

6.   DISCUSSION

The discussion of the results is classified by the same paragraphs as in chapter 4 were the results are shown. In addition the content of chapter 5 is discussed.

6.1.   Reserch period 1

General

Clean Operator was able to remove biofouling and particle fouling from spiral wound membrane modules. Clean Operator was also able to transport the fouling, flushed out from the first element through the second and third serial placed modules, as can be concluded from the pressure drop development over each individual module and the visual particulates in the flush water leaving the pressure vessel. This shows that Clean Operator is capable of removing biofouling and particulate fouling in existing membrane plants, having several spiral wound membrane elements housed in series in horizontal pressure vessels.

Cleaning mechanism Clean Operator vs CIP

A clear difference was found in how the biofouling is removed with Chemical Cleaning (CIP) and Clean Operator. The flush water from the (acid) CIP turned yellowish without any particulates indicating that some attached iron dissolved. The pressure drop over the cartridge filter, installed within the CIP system, did not increased during all applied chemical cleanings. The flush water from the Clean Operator cleaning was not colored but contained particulate matter (up to ~ 1 mm). This indicates that the mechanism for removing biofouling is different for the two investigated methods: CIP and Clean Operator. With CIP, biofouling seems to be removed by destroying the cells and dissolving the inner cell fluids released. With Clean Operator, the cells in the biofilm are not destroyed. Instead, Clean Operator is able to detach and remove the major part of a biofilm as complete films. Removing biofilms without destroying cells is regarded positive, as destroying cells can cause spreading of released cell fluids and attachment of released cell fluids to the membrane surface. This will enhance further and new biomass development, and adsorption onto the membrane surface can have a direct negative effect on the MTC.

Cleaning Efficiency

The rate of the increase of the pressure drop due to biofouling was well comparable for both RO lines. This means that both lines faced the same biofouling intensity, and that differences in development of the normalized pressure drop over the feed spacers between both lines are mainly caused by the different cleaning technologies applied (CIP and Clean Operator). The fouling can be classified as extreme, as the pressure drop over the first module increased by a factor ~9-13. This means that, having such severe biofouling, the cleaning technologies are challenged to their maximum ability and that differences in efficiency between the two cleaning technologies should be enlarged. The results showed that, even with extremely fouled membranes, the Clean Operator cleaning had more or less the same cleaning effect as a CIP cleaning. The CIP cleaning however took about 8 hours, where the Clean Operator cleaning only took less than half an hour.

Because of the extreme increased pressure drop in this first research period channeling might have occurred during the different cleaning events. Due to channeling, part of the fouling may not have been reached well enough, by chemicals (CIP) or CO_2 (Clean Operator), so that the biofouling was not remove completely. Left behind biofilm after a cleaning, based on the pressure drop which was not completely restored, can stimulate further fouling development. This can worsen the channeling and even enhance scaling. There are some differences between CIP and Clean Operator that are important to keep in mind. The most important difference is the water temperature applied during cleaning. The water temperature is higher during a CIP (~40 °C) compared to Clean Operator (~15 °C). A higher temperature is positive for CIP as it increases the viscosity of the water, will cause expansion of the membrane matrix and will fasten chemical reactions. The higher temperature is needed during a CIP to reach every corner of the membrane element with the chemicals used in order to prevent channeling to occur.

A Clean Operator cleaning has a quite different working principle. At lower temperatures more CO_2 can be dissolved in water, which is more positive for Clean Operator. And, even more important is the fact that dissolved CO_2 is much more mobile in water compared to chemicals used during a CIP, even at lower temperatures. This gives ground to the expectation that, with the application of Clean Operator, channeling would be less of a problem. Membrane autopsy can provide more evidence to strengthen this hypothesis, but at the time of reporting, membrane autopsy was not yet performed. The fact that, at the end of the first research period, scaling of the membranes took place is not regarded as a clear indication that channeling has occurred, because the last element did not suffer any biofouling or particulate fouling. The variation of the pH value in the feed water was between 7.8 and 8.6. Together with a recovery of 50% and the absent of an antiscalant dosage probably caused the scaling. Clean Operator was not able to remove ($CaCO_3$) scaling from the membranes. With a normal CIP ($CaCO_3$) scaling could be removed successfully. The pH during a Clean Operator cleaning is about 4-4.5. This pH is too high, and the cleaning time is too short for an efficient removal of (a lot of) $CaCO_3$ scaling. Although some $CaCO_3$ can actually be removed as the analysis of flush out water (table 4.8. research period 2) clearly proved. A CIP at pH ~2 was applied with a few hours contact time.

After a CIP cleaning, still some more fouling could be removed with a Clean Operator cleaning. And also, after a Clean Operator cleaning, some more fouling could be removed with a CIP. This is an indication that both cleaning technologies can have additional value to each other. It seems effective to use Clean Operator alone for a number of cleanings as it can be performed much faster and proved to be very effective, and then to have a CIP after a Clean Operator for additional disinfection and cleaning (removal of adsorbed material).

A co current and counter current permeate flush on RO line 1 and 2 at day 93 with an increased flow (8.5 m^3/h) removed a about 35% of the pressure drop over the lead elements. This was also observed at the Proof of Principle were an efficiency of 40% was achieved with a permeate flush.

At the end of research period 1, the normalized pressure drop over both RO lines was increased compared to the initial pressure drop of the clean membranes. One should keep in mind however, that the fouling was exceptionally high due to the high Sodium Acetate dosing.

Turbidity measurement did not provide added value to determine the length of a Clean Operator performance. The data was not distinctive enough because it flushed out water was mixed in the degasifying tower. The values were flattened by this. From the experiences with Clean Operator in the first research period, it became clear that Clean Operator only needs to be performed for a few minutes. This is in line with earlier research regarding hydraulic cleaning with a water and air flush (Cornelissen et.al 2007).

As Clean Operator is well able to remove biofouling, this technology should also be very effective in removing particulate fouling. In order to prevent particulate fouling, advanced particulate removal technologies, such as ultrafiltration or microfiltration, are currently advised as a pre-treatment for spiral wound membranes. When particulate fouling can be removed faster and more easily by using Clean Operator technology, then this will provide other options for pre-treatment. Related to this issue, it is interesting that in the Evides Botlek demiwater plant a combination has been made between hydraulic cleaning of the spiral wound membranes (AiRO) and a moderate pre-treatment without the use of membranes: coagulation followed by flotation/mediafiltration and cation exchange to improve recovery. The Botlek plant is successful in operation since 2010, treating surface water from the Brielse Maas (mainly fed by river Rhine).

Volume of gas released

The gas formation in the individual membranes during Clean Operator largely depends on the flow direction, flow rate and amount of CO_2 dissolved (% saturation).

The volume of gas formation is depending on the amount of gas that is transferred from liquid (dissolved) to gas bubbles and the pressure at the location. At a higher pressure, the same amount of gas (grams) takes less volume ($P*V=R*T$, and $R*T$ = constant). Consequently, during a Clean Operator cleaning, the highest volume of gas is present in the last module. This indicates that counter current cleaning is the best way, because then most of the gas is formed in the most fouled module. Counter current cleaning has another theoretical advantage: the most fouled module is cleaned last, meaning that a minimum of washed out solids need to pass other feed spacers of other membranes.

Clean Operator was applied with a 100% saturation at the pressure before the first module to be cleaned. This means, that gas formation starts directly in the first module, proceeding in the second and the third module. The formation of gas in the first module causes free CO_2 gas leaving that first module. This free gas needs to be transported through the second module, in which extra free gas is formed, which has to be transported through the third module. At least the second and third membranes will receive a feed containing water and CO_2 dissolved in it, and free CO_2 gas. This can have negative effects as we should expect that gas is collected in the upper part of the pressure vessel between two individual modules and is predominantly fed to the upper part of the downstream membrane module. Looking at the development of the pressure drop over the feed spacers in the second and third module, this effect is minimal since the second and third modules were not very much fouled at all. However, it is imaginable that in full scale membrane plants not just the first membrane module is fouled. Then it would be a good idea to fill a complete membrane system with water and CO_2 completely dissolved in it, at a higher pressure. And then releasing that pressure while flushing, assuring gas formation in the entire system at the same moment. Another option would be to start the Clean Operator cleaning with CO_2 saturated water at a pressure equal to the pressure at the outlet of the pressure vessel, and then gradually increase the CO_2 amount that is dissolved. Doing so, the gas formation starts in the last module and shifts slowly towards the first module.

Composition and concentration of the used gas

Using less CO_2 gas and some N_2 gas instead, decreased the cleaning efficiency significantly in terms of a restored pressure drop. Actually the Clean Operator cleaning is then performed with a gas composition which is more equal to the composition of air from the outside. The higher effectiveness of pure CO_2 above using N_2 gas was also proven in the Proof of Principle (Ngene et al, 2010).

With normal CO_2 dosages (max. 100-200% saturation), the integrity of the membrane was not affected. Only during the first day after a Clean Operator performance the retention is temporarily decreased with 1-1.5%. This is further discussed in paragraph 6.4. Dosage of a huge amount of CO_2 (done by mistake, because of a malfunctioning control valve) improved the cleaning efficiency significantly, but had a negative effect on the integrity of the membrane. After this incident the retention was stayed decreased with 0.5%.

6.2.   Research period 2

The second research period started with the same membranes as were used in the first research period. In the membranes some fouling was left from the first research period, as was observed based on the increased normalised pressure drop. The pressure drop over both third modules was more or less equal to the start of research period 1. The modules that were first and third in the first research period were switched in the second research period. First the effects of the adjustments to research installation are discussed followed by other remarkable results.

Impact adjustments

During research period 2 no scaling occurred as did happen in research period 1. This is concluded based on the development of the MTC, which shows a stable MTC over the entire period (appendix 9). The dosage of anti-scalant and the decreased recovery were clearly effective.

The Sodium Acetate dosage of 10 μg C/l was enough to increase the normalised pressure drop over RO1 and RO2 between 50% and 100% in about a week.

The implementation of the modified CO_2 dosage has not been tested. At the end of the second research period it was found that the CO_2 was based on a fixed setpoint.

The extended flush, with only permeate at the end of a Clean Operator cleaning, was able to flush out more CO_2 compared to research period 1. No large CO_2 gas bubbles were observed after Clean Operator as it was the case during research period 1, despite the higher CO_2 concentration that was used. The temporary decrease of the retention based on the conductivity however, continued to occur. The effect on the membrane integrity is further discussed in paragraph 6.4.

General

The general observations in research period 1 are confirmed in research period 2. Clean Operator was again able to transport the fouling, flushed out from the first element through the second and third serial placed modules.

Again, as measured in the first research period, both cleaning strategies were not able to restore the normalised pressure drop to their initial value in research period 2. The percentage removed pressure drop by both cleaning strategies was comparable, ~92% for the RO2 (CIP) and ~94% for RO1 (Clean Operator). The Clean Operator cleanings did not result in completely the same efficiency as during the Proof of Principle where the measured efficiency for Clean Operator was ~100%. However, the Proof of Principle is performed with one single flow cell of 2*17 cm. In such a small cell fouling is probably more easily removed. Moreover, in the Proof of Principle, the efficiency was measured after only one Clean Operator cleaning, whereas in the research installation in period 2, thirteen Clean Operator cleanings were performed in a period of 105 days, resulting in a total cleaning efficiency of ~94%. The scale up from such a small flow cell towards a full scale situation with three eight inch spiral wound membrane modules in serial likely had some effect on the efficiency. This can be explained by the construction of a spiral wound module: it is questionable if one will have an equal uniform flow pattern through a spiral wound module as one will have through the small and flat flow cell. Consequently, if the flow pattern is not fully uniform, some parts of the spiral wound module would be not or less effectively be cleaned with a Clean Operator cleaning and a CIP. Another explanation is that the (synthetic) membrane fouling was different in both cases. It is unfortunate that a CIP was not part of the Proof of Principle in order to see what the effect of a CIP is compared to Clean Operator at those circumstances. Nevertheless, an efficiency of 94% can be considered as a good efficiency and even quite comparable to the Proof of Principle. Clean Operator again proved to be an effective method the control membrane fouling and that Clean Operator is able to reduce the frequency of a CIP significantly.

Efficiency

RO1 (Clean Operator line) started with a heavier fouled membranes compared to RO2 (CIP line). Also the retention of the membranes was higher. Clean Operator cleanings appeared to be able to remove fouling in an efficient way. Secondly, Clean Operator was able to outperform the CIP cleaned line starting with more fouled membranes.

At day 42 RO1 was temporarily fed with water having an increased turbidity, up to 5 NTU for twelve hours. An extra Clean Operator cleaning was able to restore the increased pressure drop due to this event indicating that Clean Operator is able to remove particle fouling in an efficient way. This is also a known phenomenon in hydraulic cleaning with air and water (Cornelissen et.al., 2010). The CIP line (RO2) was automatically shut down during the high turbidity peak on day 42. Therefore no extra CIP was needed on this line. This also explains why the Clean Operator line was 13 times cleaned against the CIP line, which was 12 times cleaned.

On the long run however, the pressure drop in the Clean Operator line exceeded the pressure drop of the CIP line. It is questionable to what extend the fouling in both lines is comparable as the rate of fouling was different for both lines at the start of the research period. RO1 (Clean Operator line) had a quick win at the start but then got behind more and more. One explanation for this could be that a Clean Operator cleaning only took 30 minutes and a CIP about 8 hours. In between the low and high pH CIP, RO2 was in production. This means that the Clean Operator line had about 89.5 hours more operation compared to the CIP line (12 CIP cleaning x 8 hours downtime − 13 Clean Operator cleanings x 0.5 hours = 282). This is about 3.7 days extra (~ 3.5% of total production time) operation compared to the CIP line. Mentioned should be, that during and between the CIP of RO2, the Sodium Acetate dosing was stopped. Still, during this first day of the run without the Sodium Acetate dosage the residual biomass was able to develop again based on the development of the pressure drop. Taking into account, the extra production time, the Clean Operator line certainly did not perform less. More likely, the Clean Operator line performed better compared to the CIP line.

Overall, the conclusion is justified that, with Clean Operator the CIP frequency can be reduced significantly. The increase of the pressure drop can be controlled by a frequent Clean Operator cleaning till a point that the pressure drop after Clean Operator will stay too high. Then, a CIP must be applied. In fact this was done at RO1, at the end of research period 2, where thirteen Clean Operator events were performed. After the last Clean Operator performance, directly a CIP was applied. The efficiency of this CIP event was extremely high. The mutual additional value of CIP and Clean Operator was already observed in research period 1. The high efficiency of a Clean Operator cleaning directly followed by a CIP cleaning, can be explained as follows: first the Clean Operator cleaning removes the bulk of the biofouling, leaving behind a teared biofilm which might be less strong attached and other types of (adsorbed) fouling. This remain fouling is also less protected against the influence of chemicals used in the additional CIP. This causes the CIP to be very effective. The chemicals are not 'wasted' on a thick biofilm, but very optimal used on the thin remains of the biofilm and the other fouling. Doing so, less biomass needs to be destroyed and dissolved.

The adverse approach, first several CIP performances and then followed by a Clean Operator cleaning, was less efficient. A possible explanation for the lower efficiency is that during CIP a lot of biomass is destroyed and internal cell fluids may have attached to the membranes, leaving a lot of nutrients for new biofouling to grow. The structure and properties of the fouling might have changed also due to the CIP events, which made it more difficult to remove the remaining fouling with a Clean Operator cleaning. In figure 4.4, the outcome between these two strategies can be seen. The overall pressure drop increase during research period 2 was only 2-5 kPa on RO line 1 and 12-15 kPa on RO line 2. In percentage terms this represents an increase of 2.7-6.3% on RO line 1 and 24.2-30.2% on RO line 2.

Analyses of the out coming flush water during Clean Operator cleaning showed that a significant amount of iron and aluminum, but also some magnesium and calcium was removed. These parameters were probably for a major part entrapped in de biomass which was flush out as a whole.

6.3. Parameters of major influence

During research period 2 the Sodium Acetate dosage is increased from 10 µg C/l to 20 µg C/l. This had an impact on the increase of the pressure drop between two cleaning events as can be seen in the development of the pressure drop (appendix 11). The intent was that with a higher increase of the pressure drop the differences in efficiency in each experiment could be better observed. The normalised pressure drop over a RO line increased with about 20-30 kPa during the second research period. During the experiments with the changed variables the pressure drop increased only 18.4-18.8 kPa during the first run and 68.4-56 kPa respectively 81.4-81.6 kPa during the next runs (RO1-RO2). The first run was directly after the double cleaning event at the end of research period 2.

All observations are based on one single experiment which makes it difficult to draw solid conclusions. The results however will give an indication whether the specific parameter can increase or decrease the efficiency of Clean Operator.

Influence of CO_2 concentration

An increase of the CO_2 concentration above the 100% saturation seems beneficial for the efficiency of the Clean Operator performance, as the cleaning efficiency measured was ~50% at 100% CO_2 saturation and ~66% at 225% CO_2 saturation. Based on the decrease of the pressure drop the difference is limited, 9.1 kPa vs 12.4 kPa (table 4.5). This experiment however, was performed directly after the second research period. At the end of this period, both RO lines were cleaned with Clean Operator and with an additional CIP resulting in a best possible cleaning. The pressure drop was only about 18 kPa increased despite the increased Sodium Acetate dosage.

The moderate fouling influenced the accuracy of the measurement of cleaning effect, consequently reducing the meaning of this one measurement. This can also be conclude from the low efficiency after the first performance (co-current) measured on RO1 with 100% CO_2 saturation (~52% efficiency) compared to the first performances of other cleaning experiments with the comparable settings, ~75% efficiency at RO1 (co- vs counter current) and ~53% efficiency at RO1 (low vs high flow). As well as the results of the second research period (~94% efficiency after 13 Clean Operator cleanings) with comparable CO2 saturation levels (200%-225%) and increase of the pressure drop between two cleaning events compared to the result of RO2(~66% efficiency).

It is not exactly clear what is to be expected as most optimal regarding the application of Clean Operator at higher/lower CO_2 saturation levels. With Clean Operator using a 225% CO_2 saturated solution the upper surface of the membranes may be flushed with mainly CO_2 gas because gas is already formed before the lead module is entered. This should not be expected as optimal. However, at the start of the cleaning, the feed spacers are filled with water, which still ensures some water/gas mixing. With Clean Operator at a 100% CO_2 saturated solution, total membrane surface of the lead module will receive water. The second membrane however will also receive gas and water at the feed side. Another aspect, evidently, is the economic and environmental optimum CO_2 dosage. A higher CO_2 dosage means higher costs and a higher CO_2 emission.

During the experiment with low and high flow (paragraph 4.3.3), the low flow variant is performed three times. The first two performances were applied with a 100% saturated solution. The second attempt removed almost no fouling. The third performance, with a 200% saturated solution however, did remove additional fouling (7.9% extra above 53.4%). This is an indication that saturation above 100% can be beneficial.

Overall it is estimated that the increase of CO_2 saturation has a limited positive effect on the cleaning efficiency. It is not known if the effect is proportional to the higher CO_2 consumption and therefore in terms of costs and carbon footprint.

Co-current vs counter-current

The normalised pressure drop during this experiment was increased with 68.4 – 56 kPa (RO1 – RO2). The co-current performance had a slightly higher cleaning efficiency during this experiment (~ 79% compared to ~73%). Based on the decrease of the normalised pressure drop the difference is 54.3 kPa vs 41.1 kPa (table 4.6). This clearly indicates that co-current application of Clean Operator on eight inch membranes housed in series in horizontal pressure vessels is an effective way of the application of Clean Operator. However, the results are somewhat influenced by the previous experiment (influence of CO_2 concentration). The co-current cleaning was applied on the RO line which was cleaned less efficient, making it easier to have a better cleaning efficiency in the co-current versus counter current cleaning experiment.

That a co-current cleaning was as effective as a counter current cleaning was not expected in advance. This result cannot be explained alone by the fact that the membranes in RO1 (which were co-current cleaned) were less efficiently cleaned in the experiment with different CO2 concentrations. In the counter-current cleaning "old" gas bubbles flow through the lead module. Based on calculations (paragraph 4.1.3) in the co-current mode and with a 7 m^3/h water flow, about 1.7 m^3/h CO_2 gas is formed in the lead module, which is most fouled (table 4.3). In the counter-current mode, 2.4 m^3/h CO_2 gas is formed in the lead module. With the difference in gas formation in mind, one would expect a better cleaning efficiency with the counter-current mode. However, this was not the case. An explanation might be that the volume of the already formed CO_2 gas is blocking the access of the saturated solution towards the fouling in (the upper part of) the lead module during counter current cleaning. In that way the nucleation cannot completely take place on the entire feed spacer surface, were the biofouling is attached on. If this hypothesis is correct then the height of the CO_2 saturation to perform Clean Operator is also limited.

Another hypothesis is that co-current Clean Operator cleaning might benefit from the contribution of particulate matter. Most particulate matter is released from the lead element and needs to be transported through the second and third membrane element. This particulate matter might have increased the turbidity and thereby contributed to the cleaning effect in the second and third element. On the other hand, the CO_2 gas formation is lower in the most fouled membrane module compared to counter current cleaning. This is because the pressure is the highest in the lead module and CO_2 gas formed fills a smaller volume at higher pressures. However, whether smaller gas bubbles are better or worse is also unknown at the moment.

Counter current Clean Operator cleaning might benefit from the fact that the most fouled membrane receives the most CO_2 gas and most of the particulate matter released is directly flushed out of the system. On the other hand, the last module (which is the most fouled) will be fed with water and a lot of CO_2 as a gas. This might be less optimal when the upper part of the lead membrane is dominantly being fed with CO_2 as a gas.

Low flow vs high flow

Applying Clean Operator at higher flows clearly increased the cleaning efficiency (~54% efficiency at 3 m^3/h compared to ~88% efficiency at 11 m^3/h) after two performances. Based on the absolute decrease of the pressure drop the difference is 50.2 kPa vs 71.6 kPa (table 4.7).

Not only is the effect of a higher flow positive. At a higher flow, the pressure drop is also higher, which will cause a higher CO_2 consumption. At a higher flow the pressure drop over the module will be higher; consequently more gas will be released. In paragraph 4.1.3 the amount of gas is calculated. With this outcome (table 4.3) also the gas to water ratio (RQ) is calculated (table 6.1).

Table 5.1 calculated RQ value at different setting

RQ ratio (co current and cummulative calculated gas volume			
flow	module 1	module 2	module 3	outflow
2	0,102	0,173	0,278	1,572
3	0,127	0,236	0,401	1,731
4,1	0,175	0,316	0,560	1,948
5	0,207	0,386	0,686	2,124
6,1	0,233	0,439	0,822	2,363
6,9	0,243	0,458	0,884	2,509
8	0,246	0,479	0,989	2,794

This RQ value will also be a variable. In fact this can also be influenced by the level of the saturation. With a higher RQ value there is more surface of gas bubbles available to create more shear stress. Obviously, there will be an optimum. This needs to be determined in future research.

The effect of a lower flow is contrary to a higher flow: less CO_2 needs to be dosed and the flow velocity is lower, thus less mechanical cleaning. The result is a poorer cleaning. In fact the flow (3 m^3/h) is even lower compared to the flow during production (4.5 m^3/h) together with a lower RQ value. The cleaning efficiency is worse. However, a cleaning efficiency of ~50-60% with only 3 m^3/h water saturated with CO_2 can be considered as quite good. The major advantage of a lower flow is the fact that much less CO_2 is needed. But the consumption of CO_2 has limited effect on the total costs to perform Clean Operator and won't affect the CO_2 footprint too much either. Due to the lower efficiency, the frequency needs to be increased to reach the same performance as with Clean Operator with a high flow. It may well be that in the end, CO_2 consumption is even worse.

The increased CO_2 concentration at a low flow performance increased the cleaning efficiency. This could suggest that consumption of CO_2 could be saved by performing Clean Operator at low flow with an increased concentration of CO_2. On the other hand the Clean Operator performance at higher flow and 100% saturation increased the efficiency significantly at the end of the experiment. This suggests that the dominant factor is the higher velocity of the water together with the gas instead of the concentration alone. The CO_2 consumption is directly dependent of the flow velocity and the concentration.

6.4. Membrane integrity

Overall, Clean Operator did not had a negative effect on the retention based on the online conductivity (EC) measurements using normal (<225% saturation) quantities of CO_2. After every Clean Operator cleaning the EC retention was temporarily decreased, but this is also the case after every CIP cleaning (although to a less extend).

Research period 1

During the first period the retention of the Clean Operator line (RO2) decreased with about 0.5% at day 42 as a result of the CIP cleaning. After each Clean Operator performance the retention is decreased by 1-1.5%. This was a temporary effect, within one day the retention restored to the level from before the Clean Operator cleaning.

At the end of the period the retention is affected due to an unknown overdose of CO_2. The pressure in the gas cylinders was about 40 bars and the flow controller was malfunctioning. Based on the 40 bar pressure in the cylinders, the overdoses must have been huge, although the exact dose could not be quantified. In the beginning the effect of the dosage of a huge amount of CO_2 was a drop in retention of 3%. This was later stabilized at a remaining level of 0.5% decrease.

Research period 2

During the second period Clean Operator was applied on RO1 which was not affected by the overdoses of CO_2 and did not show a reduction in EC retention in the first research period. During this period of 105 days no significant decrease could be observed, despite the high concentration of CO_2 dosed compared to research period 1 (225% compared to 100% saturation), and despite the larger number of Clean Operator cleanings (13 compared to 5) . Again there was the temporary effect after each Clean Operator cleaning, despite the better flush out of CO_2 gas with a closed permeate valve during this period. Again the retention dropped about 1-1.5% after each performance and after one day the retention was restored. Based on laboratory analyses, it is confirmed that the CO_2 that passes the membrane reacts with water under the formation of HCO_3 (table 4.8). This slightly increases the permeate conductivity until the CO_2 is consumed. The formation of HCO_3 is regarded as a solid explanation for the temporary decrease of the retention, and its natural restoration.

The temporary decrease of the retention can be small disadvantageous if the permeate is used for purposes where the permeate quality is critical, for instance if it is used for boiler water. In that case, some extra attention must be given to the downstream ion exchange. For drinking water production this temporary effect is not critical at all.

Each CIP also affected the retention. Whereas an acid CIP increased the retention with about 0.3%, the base CIP decrease it with about 0.6% after the acid CIP. Overall the retention decreased with about 0.3% and was restored within one day. The affect on the permeate quality is not determined.

6.5. Full scale design

The investment for only the hardware to implement Clean Operator is between €48,500 and €60,000. With this hardware between 750 and 7,500 kg CO_2/h can be dosed at 50 to 500 m^3/h water. This is based on a concentration of 15 kg/m^3 which was needed in this research to get a 225% saturated solution. Based on the outcome of this research it is quite questionable if this is the optimum concentration since the optimum concentration is not determined. With a water flow of 8 m^3/h per pressure vessel one can feed between 6 (~50 m^3/h flush) and 60 (~500 m^3/h) pressure vessels with these CO_2 dosing systems.

A full scale design is made for a new drinking water treatment plant, called Vechterweerd. In fact this is a relatively small plant with limited membrane fouling to expect. It is to expect that the membranes only needs one CIP a year. With such a low cleaning interval the (financial and environmental) savings are low and the investment is relatively high. For the Vechterweerd case it is chosen to apply Clean Operator at a higher frequency in order to remove the membrane fouling relatively fast and prevent the feed pressure to increase too much. With this approach the energy consumption and CO_2 footprint is reduced compared to the situation with one CIP a year.

This makes the case not optimal in terms of financial and environmental benefits which can be achieved with Clean Operator especially at bigger installation suffering with more severe (bio) fouling.

Vechterweerd case

Since Vechterweerd is a new not existing treatment plant an assumption had to be made about the degree of the membrane fouling. This assumption is based on the Engelse Werk plant, which is a plant with a comparable water source and treatment. The monthly increase of the feed pressure is at Engelse Werk is about 0.05 - 0.1 kPa each month. But at Engelse Werk the stacks are frequently out of operation and flushed with permeate with an increased pH (pH=9) during the shutdown. At Vechterweerd the stacks will be continuously in operation and therefore a slightly higher monthly increase of the feed pressure is assumed, 0.125 kPa each month.

With a Clean Operator cleaning each month the increase of feed pressure is limited. The CO2 footprint will decrease by 13,300 kg (23,140 kWh) based on the assumption of the increase of the feed pressure of the RO unit.

The investment costs for Clean Operator are off course higher, but the variable costs are significantly lower. Even with this approach, a Clean Operator frequency of 12/year compared to a CIP frequency of 1/year.

The total cost of ownership for the Vechterweerd case is shown in table 5.2. To implement Clean Operator in the Vechterweerd plant the total cost of ownership will increase by €0.0022/m^3 (difference between Clean Operator and CIP). This is an increase of only 0.2% compared to the total cost of ownership of Vechterweerd without Clean Operator.

Any increase of the CIP frequency will already increase the total cost of ownership for the CIP situation to a higher lever compared to the Clean Operator situation since the variable costs are based on one CIP and twelve Clean Operator cleanings.

Table 5.2 total cost of ownership Vechterweerd

Clean Operator			CIP		
investment	0,0055	€/m3	investment	0,0018	€/m3
rent CO2 storage	0,0020	€/m3	-	-	-
variable costs	0,0004	€/m3	variable costs	0,0027	€/m3
savings on energy (P feed)	-0,0013	€/m3	-	-	-
total cost of ownership	**0,0067**	**€/m3**	**total cost of ownership**	**0,0045**	**€/m3**

Large installations

The potential of Clean Operator on large installations is huge. One of the benefits of Clean Operator is that it is applied in a twinkling, within 15 minutes. In large installations the CIP unit can clean a certain part of the RO unit. If the efficiency of the CIP cleaning becomes worse the frequency needs to be increased until the point is reached that the frequency cannot be increased anymore because of the capacity of the CIP: more CIP units will be needed as one CIP unit will be in operation 100% of the time. With Clean Operator one can significantly decrease the CIP frequency. Instead, the fast and efficient Clean Operator cleaning can be performed. This will reduce the CO_2 footprint because the feed pressure is better controlled. Due to a higher CIP frequency (f.i. 4/y) compared to Vechterweerd (1/y) the variable costs will increase for the situation without Clean Operator even more (6*0.0027=0.0108 €/m^3). The major benefit will be the saving on operational costs (man hours) with in the variable costs and the potential to increase the lifetime of the membranes. The lifetime of the membranes is not taken into account in the Vechterweerd case.

7. CONCLUSIONS & RECOMMENDATIONS

This research leads to the following conclusions;

1. Clean Operator is able to efficiently remove and control biofouling and particulate fouling from spiral wound membrane modules within 5 minutes. Even if these spiral wound modules are serial and horizontal housed in a pressure vessel.

2. Clean Operator is able to transport the fouling released from the lead module, which is most fouled, through the downstream placed modules without leaving significant quantities of the fouling behind in these modules.

3. With Clean Operator a CIP cannot be omitted. The CIP frequency however can be decreased significantly. In this research the efficiency of 12 applied CIP events was more or less the same as 13 applied Clean Operator events. One extra Clean Operator cleaning was needed because this RO line was fed with feed water with an increased turbidity (up to 5 NTU) for twelve hours. The other RO line was shut down during this incident.

4. With Clean Operator a RO unit is back in operation within 15 minutes. With a double performed CIP (acid and base CIP) the shutdown time will be hours, typically between 8 to 10 hours.

5. Because of this reduced shut down time the RO line with Clean Operator had about 3.7 days extra production time, an increase of 3.5% compared tot the CIP RO line.

6. Increasing the CO_2 concentration has a positive but limited effect on the cleaning efficiency. The optimum CO_2 concentration is not determined.

7. No significant difference is observed between the performance Clean Operator in a co-current or counter-current mode.

8. Clean Operator applied at a high flow (8-10 m^3/h per lead element) had a significant higher efficiency compared to a low flow (3 m^3/h per lead element).

9. The integrity of the membranes was not affected by Clean Operator in this research, using normal (<225% saturation) quantities of CO_2. There is however a temporary decrease of 1% in EC retention which is caused by CO_2 present in the permeate that reacts to HCO_3^-. This reduced retention is restored within one day. After a CIP the retention also temporary decreased with about 0.3% and restored in about one day.

10. The total cleaning efficiency is maximized with a Clean Operator cleaning first, followed by a CIP compared to a CIP eventual followed by Clean Operator.

11. The CO_2 footprint for a full scale RO with Clean Operator and only moderate potential for membrane fouling will decrease. For the elaborated design of Vechterweerd the reduction is 7.6%.

12. The total cost of ownership is only 0.2% (€0.0022/m^3) increased for the Vechterweerd plant, using two stacks with a capacity of 55 m^3/h each. When Clean Operator is applied on a bigger scale and with more severe (bio) fouling the total cost of ownership for Clean Operator will be significantly lower compared to the situation without Clean Operator.

Recommendations;

1. This research showed that some variables affect the efficiency of Clean Operator. The most optimal setting of Clean Operator is not determined yet. With the applied setting already an efficiency of ~94% is observed over a period of 105 days. This can be even further optimized if the different variables are optimized. Future research is recommended to determine the optimum CO_2 dose (CO_2 dose versus efficiency and costs) when applying Clean Operator.

2. Remaining research questions are;
   - What is the optimal size of the bubble?
   - What is the effect of the decrease of the pH during Clean Operator?
   - Will dosing additives (for example particulates or coagulants) during Clean Operator improve the efficiency?

3. This research is performed with synthetic fouled membrane modules. Next step is to determine the effect of Clean Operator on natural fouled membranes for instance urface water with a minimum pre-treatment.

8. LITERATURE

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APPENDIX 1 CALCULATIONS MEMBRANE MODULE

Calculation of volumes of one membrane module

by	Peter Knappe	(TriSep)					
date	17-1-2013	(by email)					

Calculations feed spacer (tricot) and permeate spacer (netting)

		Length	Width	Thickness	Volume	Displacement	Porosity
		(cm)	(cm)	(cm)	(cm3)	(cm3)	(%)
	10 mil Tricot	30,48	30,48	0,0254	23,59737	8	66,1%
	31 mil netting	30,48	30,48	0,07874	73,15185	9	87,7%

Calculation module

		# leaves	Length	Width	Thickness	Total Volume	Spacer Volume	Water Volume
			(cm)	(cm)	(cm)	(lites)	(lites)	(lites)
	8040-ACM5-TSAN							
	31 mil netting	22	93,98	96,52	0,07874	15,7	1,9	13,8
	10 mil Tricot	22	85,09	83,82	0,0254	4,0	1,4	2,6
	8040-ACM5-UWAN							
	28 mil netting	24	91,44	96,52	0,07112	15,1	1,9	13,2
	10 mil Tricot	24	81,28	83,82	0,0254	4,2	1,4	2,7

APPENDIX 2 HENRY'S CONSTANT FOR CO$_2$

The graph shows: $y = 0,0024x^2 + 0,3064x + 7,1821$, $R^2 = 0,9999$
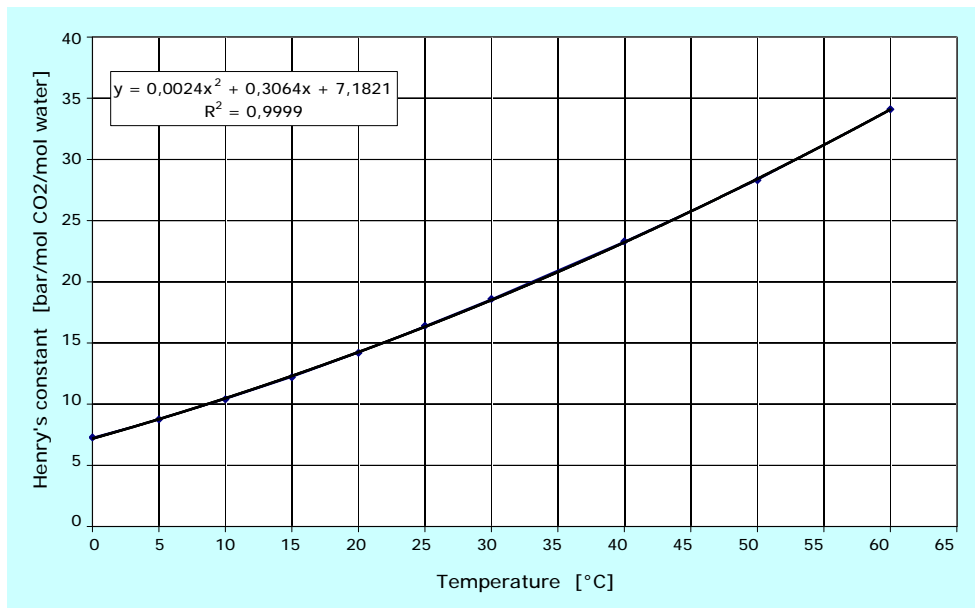
Figure A5.1 Henry's constant for carbon dioxide in water at different temperatures.

The Solubility of CO$_2$ in water depends on pressure and temperature. The relation between the solubility and temperature at atmospheric pressure can be calculated with the polynomial given in figure A5.1. This polynomial is determined with the data from Binas.

The graph shows: $y = -1E\text{-}05x^3 + 0,002x^2 - 0,1176x + 3,3474$, $R^2 = 0,9998$

Figure A5.2 Solubility of CO$_2$ in water at different temperatures.

With the polynomial from figure A5.2 the solubility of carbon dioxide can be calculated at every temperature occurring in the process.

APPENDIX 3 QUANTITY OF CO2 THAT WILL RELEASE

Temperature	12 °C						

Quantity of CO2 [kg/h]to get a saturated solution at different pressures and water flows

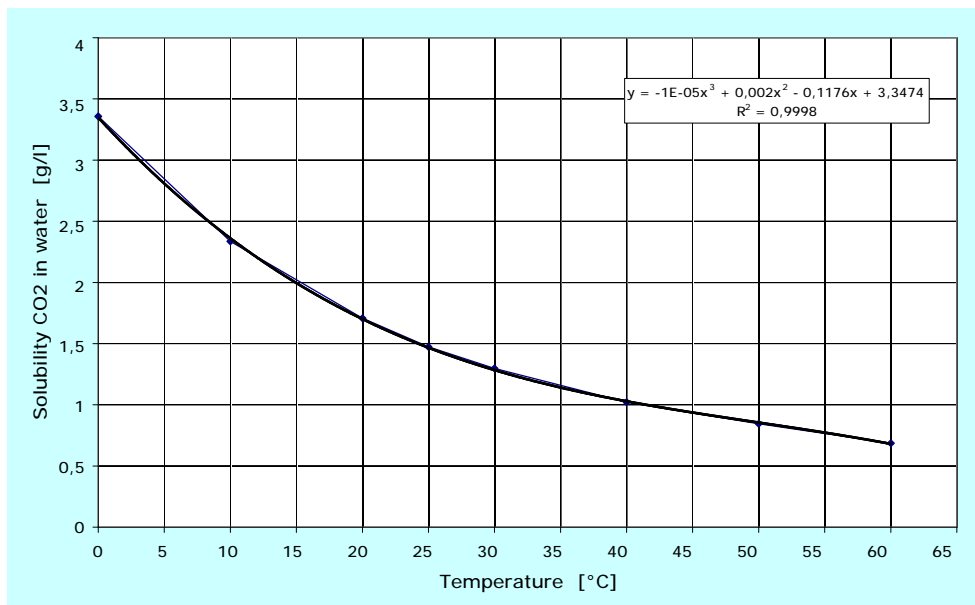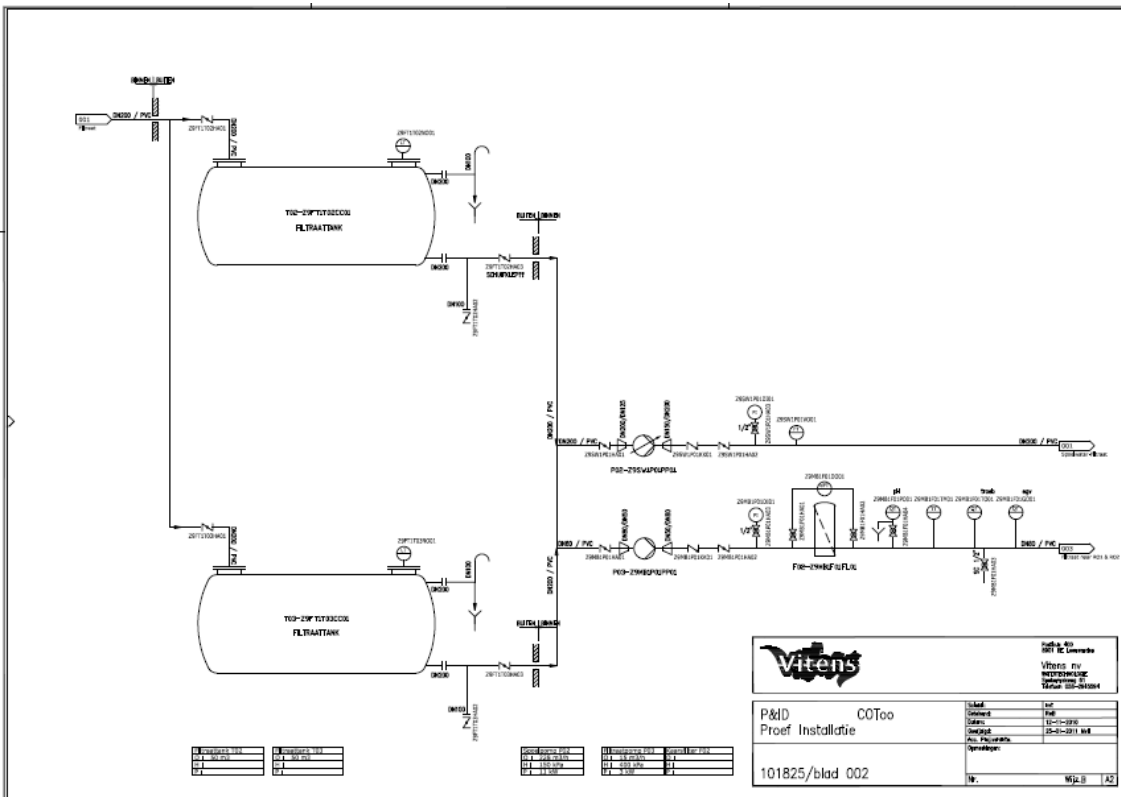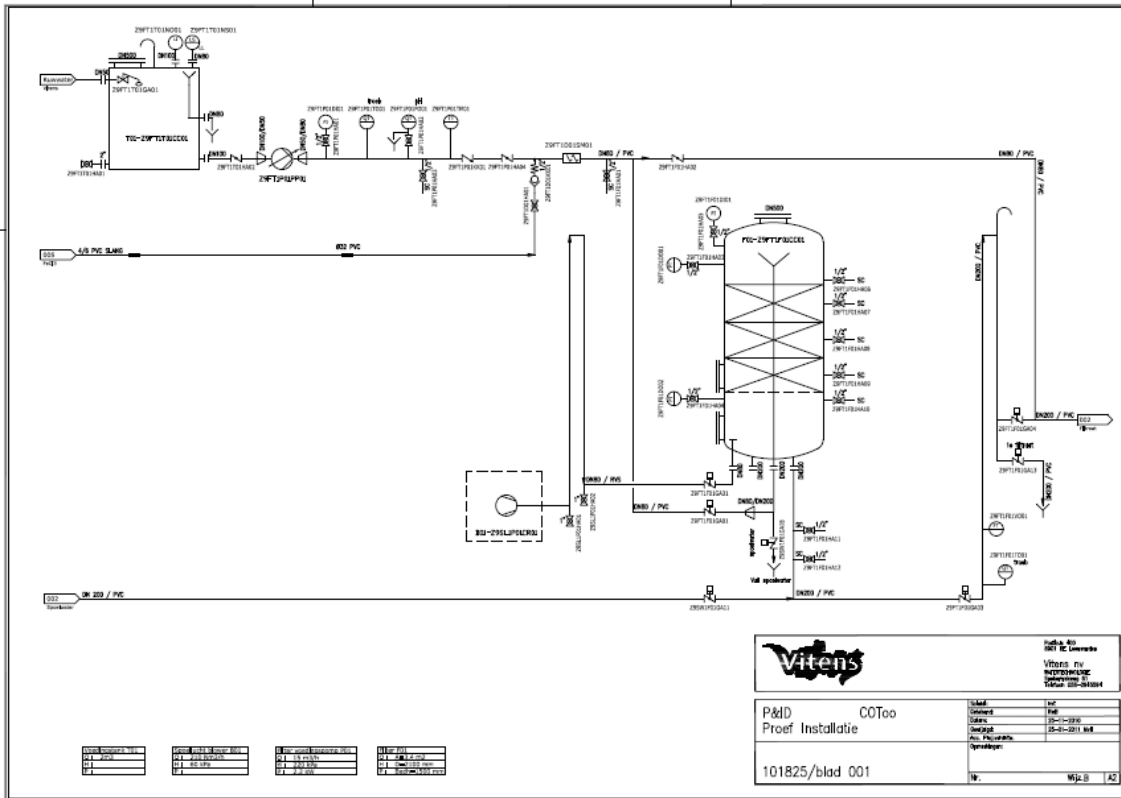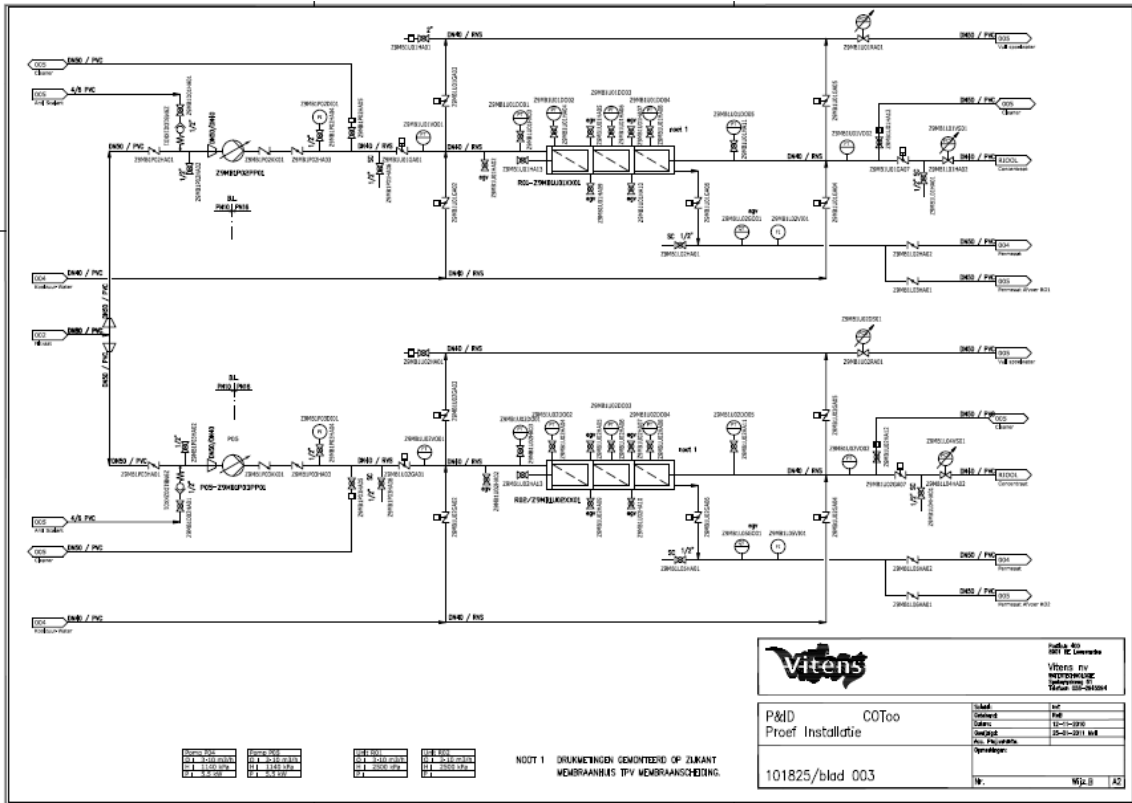| pressure		Water flow [m3/h]						
barg	bara	2	3	4	5	6	7	8
0	1	4,41	6,6	8,8	11,0	13,2	15,4	17,7
0,1	1,1	4,86	7,3	9,7	12,1	14,6	17,0	19,4
0,2	1,2	5,30	7,9	10,6	13,2	15,9	18,5	21,2
0,3	1,3	5,74	8,6	11,5	14,3	17,2	20,1	23,0
0,4	1,4	6,18	9,3	12,4	15,4	18,5	21,6	24,7
0,5	1,5	6,62	9,9	13,2	16,6	19,9	23,2	26,5
0,6	1,6	7,06	10,6	14,1	17,7	21,2	24,7	28,2
0,7	1,7	7,50	11,3	15,0	18,8	22,5	26,3	30,0
0,8	1,8	7,94	11,9	15,9	19,9	23,8	27,8	31,8
0,9	1,9	8,39	12,6	16,8	21,0	25,2	29,4	33,5
1	2	8,83	13,2	17,7	22,1	26,5	30,9	35,3
1,1	2,1	9,27	13,9	18,5	23,2	27,8	32,4	37,1
1,2	2,2	9,71	14,6	19,4	24,3	29,1	34,0	38,8
1,3	2,3	10,15	15,2	20,3	25,4	30,5	35,5	40,6
1,4	2,4	10,59	15,9	21,2	26,5	31,8	37,1	42,4
1,5	2,5	11,03	16,6	22,1	27,6	33,1	38,6	44,1
1,6	2,6	11,48	17,2	23,0	28,7	34,4	40,2	45,9
1,7	2,7	11,92	17,9	23,8	29,8	35,8	41,7	47,7
1,8	2,8	12,36	18,5	24,7	30,9	37,1	43,3	49,4
1,9	2,9	12,80	19,2	25,6	32,0	38,4	44,8	51,2
2	3	13,24	19,9	26,5	33,1	39,7	46,3	53,0
2,1	3,1	13,68	20,5	27,4	34,2	41,0	47,9	54,7
2,2	3,2	14,12	21,2	28,2	35,3	42,4	49,4	56,5
2,3	3,3	14,57	21,8	29,1	36,4	43,7	51,0	58,3
2,4	3,4	15,01	22,5	30,0	37,5	45,0	52,5	60,0

differences per step of 0,1 bar in kg/h CO2

		0,44	0,66	0,88	1,10	1,32	1,54	1,77

this means that this quantity will release per 0.1 bar decline of the pressure

Quantity of CO2 [kg/m3]to get a saturated solution at different pressures and water flows

pressure		Water flow [m3/h]						
barg	bara	2	3	4	5	6	7	8
0	1	2,2	2,2	2,2	2,2	2,2	2,2	2,2
0,1	1,1	2,4	2,4	2,4	2,4	2,4	2,4	2,4
0,2	1,2	2,6	2,6	2,6	2,6	2,6	2,6	2,6
0,3	1,3	2,9	2,9	2,9	2,9	2,9	2,9	2,9
0,4	1,4	3,1	3,1	3,1	3,1	3,1	3,1	3,1
0,5	1,5	3,3	3,3	3,3	3,3	3,3	3,3	3,3
0,6	1,6	3,5	3,5	3,5	3,5	3,5	3,5	3,5
0,7	1,7	3,8	3,8	3,8	3,8	3,8	3,8	3,8
0,8	1,8	4,0	4,0	4,0	4,0	4,0	4,0	4,0
0,9	1,9	4,2	4,2	4,2	4,2	4,2	4,2	4,2
1	2	4,4	4,4	4,4	4,4	4,4	4,4	4,4
1,1	2,1	4,6	4,6	4,6	4,6	4,6	4,6	4,6
1,2	2,2	4,9	4,9	4,9	4,9	4,9	4,9	4,9
1,3	2,3	5,1	5,1	5,1	5,1	5,1	5,1	5,1
1,4	2,4	5,3	5,3	5,3	5,3	5,3	5,3	5,3
1,5	2,5	5,5	5,5	5,5	5,5	5,5	5,5	5,5
1,6	2,6	5,7	5,7	5,7	5,7	5,7	5,7	5,7
1,7	2,7	6,0	6,0	6,0	6,0	6,0	6,0	6,0
1,8	2,8	6,2	6,2	6,2	6,2	6,2	6,2	6,2
1,9	2,9	6,4	6,4	6,4	6,4	6,4	6,4	6,4
2	3	6,6	6,6	6,6	6,6	6,6	6,6	6,6
2,1	3,1	6,8	6,8	6,8	6,8	6,8	6,8	6,8
2,2	3,2	7,1	7,1	7,1	7,1	7,1	7,1	7,1
2,3	3,3	7,3	7,3	7,3	7,3	7,3	7,3	7,3
2,4	3,4	7,5	7,5	7,5	7,5	7,5	7,5	7,5

differences per step of 0,1 bar in kg/m3 CO2

		0,221	0,221	0,221	0,221	0,221	0,221	0,221

this means that this quantity will release per 0.1 bar decline of the pressure

APPENDIX 4 P&ID RESEARCH INSTALLATION

NOOT 1 DRUKMETINGEN GEMONTEERD OP ZIJKANT
MEMBRAANHUIS TPV MEMBRAANSCHEIDING.

Container

Locatie + aantal nader te bepalen.

Deze tekening is eigendom van Messer NV en mag niet gekopieerd of doorgegeven worden aan derden zonder geschreven toelating.

RWB Vitens

P&ID CO2 installatie

MESSER

Nieuwe Weg 1 - Haven 1053
2070 Zwijndrecht
Tel.: 03/561.61.11 - Fax: 03/561.61.01

Alle rechten tot verandering voorbehouden,
Tous droits de modifications reservés

TEK.	DATUM	GOEDK.	SCHAAL	PLANNR.	REV.
JS	17/02/11		nvt	1001384	

Vitens

Postbus 400
8901 BE Leeuwarden

Vitens nv

P&ID   COToo
Proef installatie

101825/blad 005
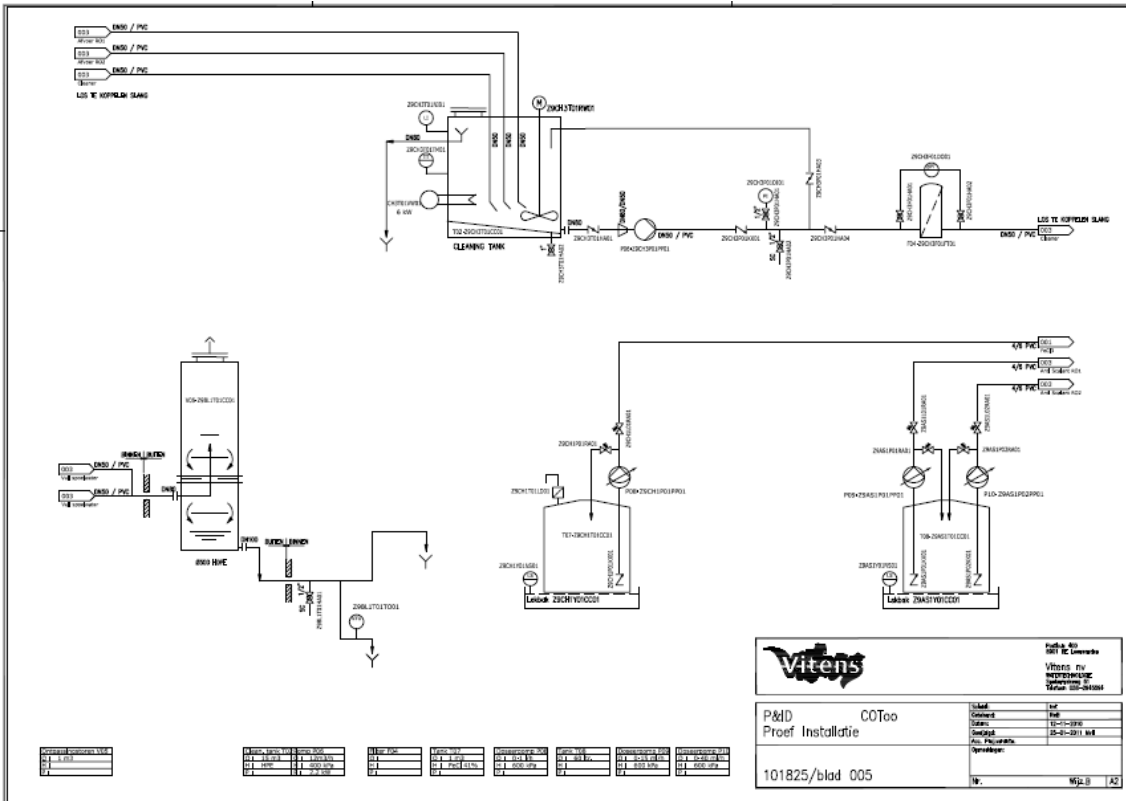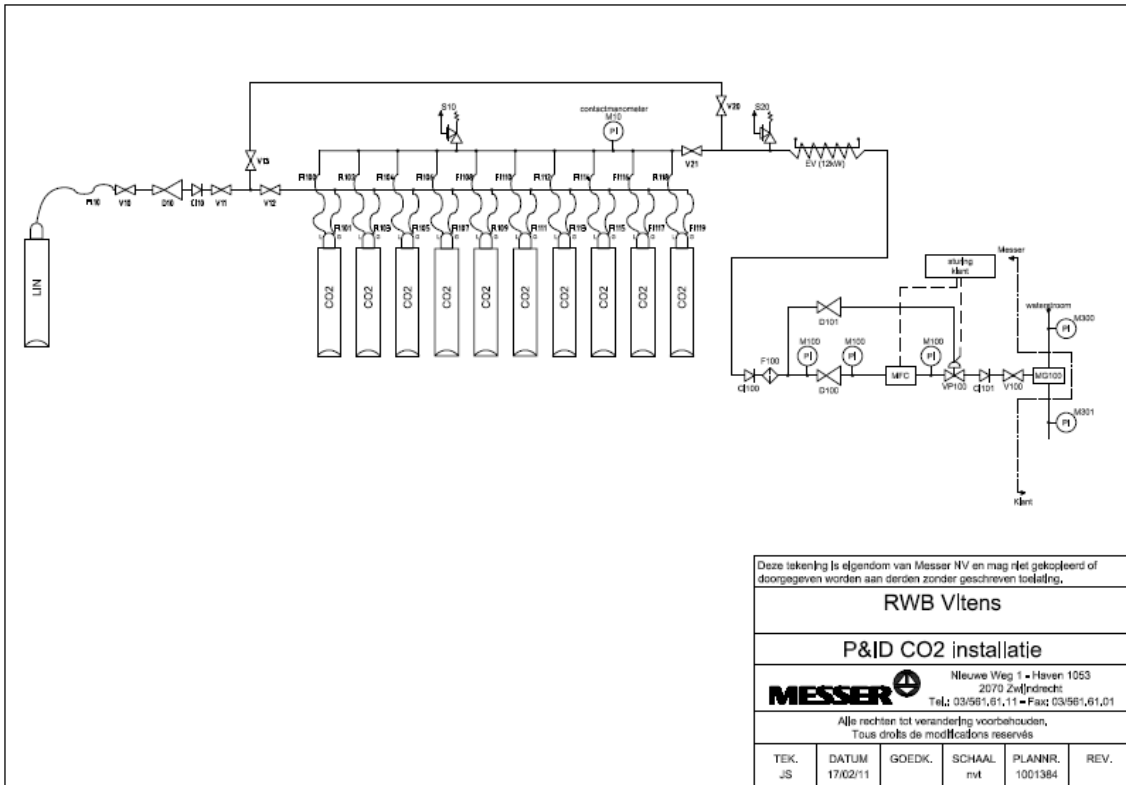
APPENDIX 5 SPEC SHEET MEMBRANE

PRODUCT SPECIFICATION

8" ACM-LP Low Pressure RO Element Series

Model	Permeate flow GPD (m3/day)*	Average Salt Rejection (%)	Minimum Salt Rejection (%)
8040-ACM5-TSA	11,900 (45.0)	98.50	97.50

Performance is based on the following test conditions: 2,000.0 ppm NaCl, 150.0 psi, 25°C, 15% recovery, pH 8.0, 30 minutes operation.

OPERATIONAL AND DESIGN DATA

Membrane Type..	ACM-LP Fully Aromatic Polyamide Low Pressure Advanced Composite
Configuration...	Spiral Wound,Fiberglass Outer Wrap
Active Membrane Area.................................	365 ft² (33.5 m²)
Recommended Applied Pressure...................	50 - 300 psi (3 - 21 bar)
Maximum Applied Pressure...........................	600 psi (41 bar)
Recommended Operating Temperature........	35 - 113°F (2 - 45°C)
Feedwater pH Range.....................................	2 - 11 continuous
Chlorine Tolerance.......................................	<0.1 ppm
Maximum Feed Flow......................................	80 GPM (18 m3/hr)
Minimum Brine Flow/Permeate Flow Ratio.....	5:1
Maximum SDI (15 minutes)	5.0
Maximum Turbidity...	1 NTU

Element Weight :   45 (20)
Length (A) :   40.0 (1,016)   Diameter (B) :   7.9 (200)   Permeate Tube (C) :   1.50 (38.1)
Units in pounds and inches, units in paranthesis in kilograms and millimetes.
Mechanical Configuration: TriSep Style Core Tube
Feed Spacer: 0.031" thick diamond spacer

* Permeate flow is clean water flux at standard conditions above. Not applicable for all feedwater conditions. Individual element's permeate flow may vary +/- 15%.

Engineered Membrane SOLUTIONS

APPENDIX 6 NORMALISATION PROCESS DATA

In order to review the performance of the installations in time the process data is normalised [Huiting, 1999]. In this way, the process data can be compared in time despite variations in temperature or flow rates.

Normalised pressure drop (feed – concentrate), NPD

$$NPD = \Delta P_a * \frac{Q_r^{1,6}}{\left(\frac{Q_v + Q_c}{2}\right)^{1,6}} * (1,03^{t_v - t_r})^{0,4} \quad [kPa]$$

ΔP_a = actual pressure drop (= feed pressure - concentrate pressure) [kPa]

Q_v = feed flow [m^3/h]

Q_c = concentrate flow [m^3/h]

Q_r = reference flow [= 10 m^3/h]

t_v = temperature feed water [°C]

t_r = reference temperature feed water [= 10 °C]

Normalised flux, Mass Transport Coefficient, MTC

$$MTC = \frac{Q_p * TCF}{\left(\left(\frac{P_v + P_c}{2}\right) - \left(\frac{\pi_v + \pi_c}{2}\right) - P_p\right) * A * 3600} \quad [*10^{-8} \text{ m/s.kPa} *10^{-8} \text{ at } 10 \text{ °C}]$$

Q_p = permeate flow [m^3/h]

P_v = feed pressure [kPa]

P_c = concentrate pressure [kPa]

P_p = permeate pressure [kPa]

π_v = osmotic feed pressure [kPa]

π_c = osmotic concentrate pressure [kPa]

A = membrane area [m^2]

TCF = e^x = temperature correction factor

$$x = U * \left(\frac{1}{t_v + 273} - \frac{1}{t_r + 273}\right)$$

U = membrane constant (depend on membrane type)

t_v = actual temperature feed water [°C]

t_r = reference temperature feed water [= 10 °C]

APPENDIX 7 DIFFERENT FIGURES WITH PROCESS DATA FIRST PERIOD

RO1: CIP
RO2: Clean Operator

RO1: CIP
RO2: Clean Operator

RO1: CIP
RO2: Clean Operator

MTC [*10 -8 m/s.kPa bij 10°C]

runtime [days]

MTC RO1   MTC RO2

RO1: CIP
RO2: Clean Operator

Retention [%]

runtime [days]

ret RO1   ret RO2
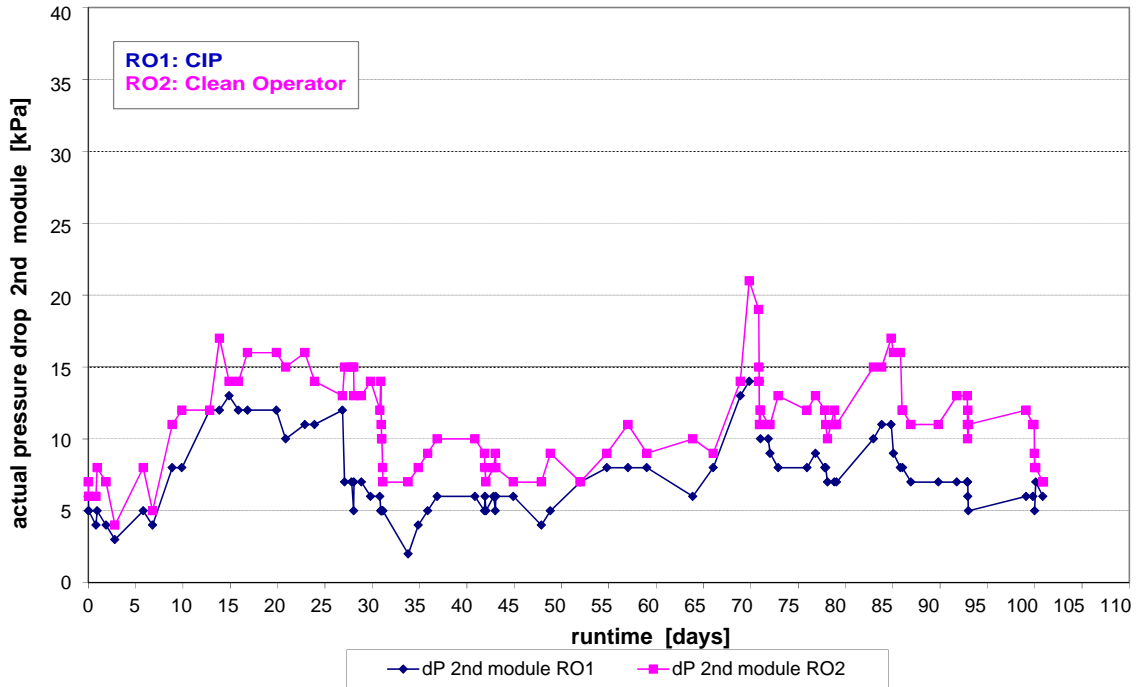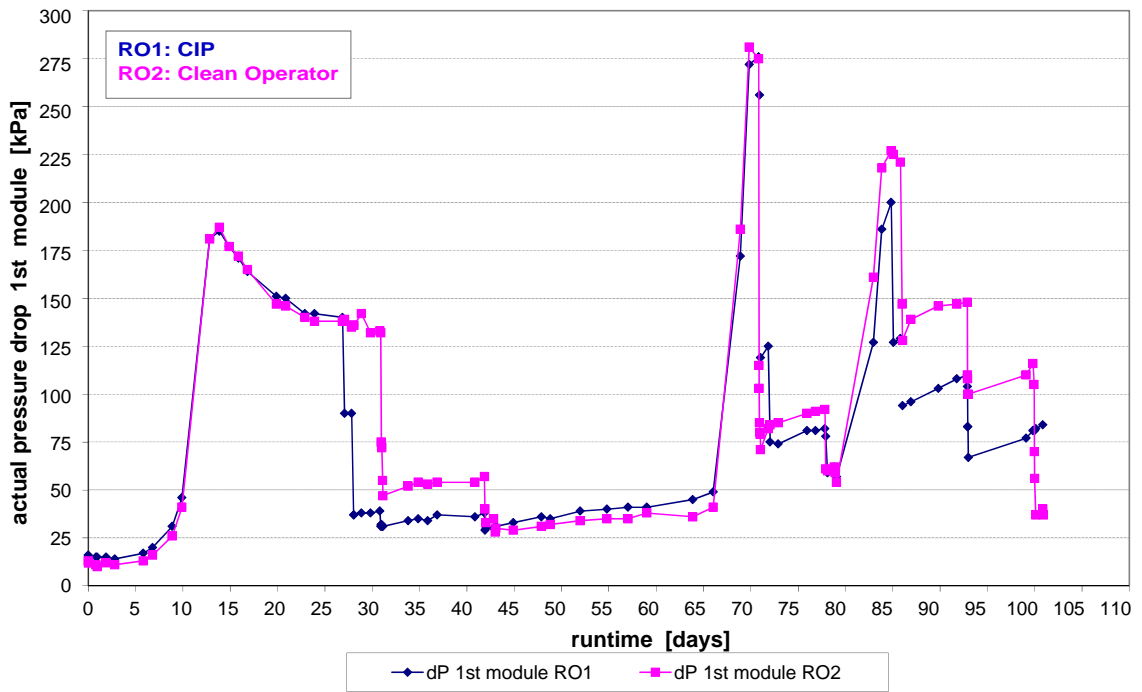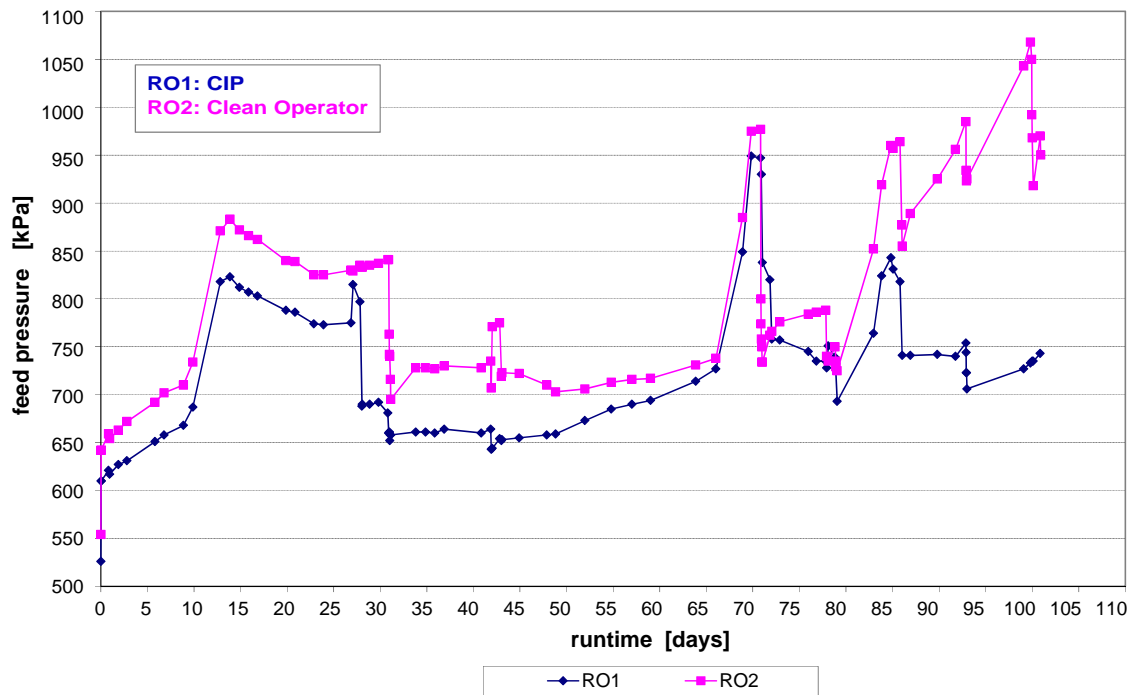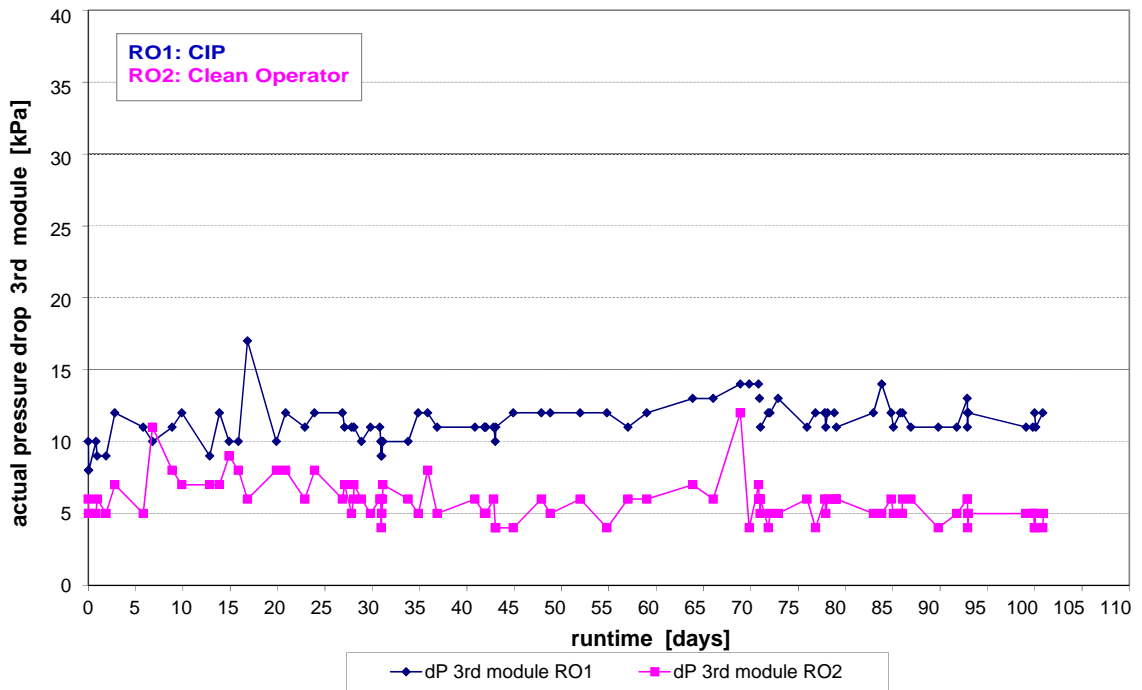
APPENDIX 8 CALCULATION VOLUME CO_2 TE BE RELEASED

differential pressure per module and outflow

dP 1	dP 2	dP 3	outflow	flow
14	8	11	27	2
19	13	17	28	3
29	17	25	29	4,1
37	22	30	30	5
47	27	40	35	6,1
53	30	47	41	6,9
63	38	63	54	8

Quantity of CO2 te be released [kg/m3] per module

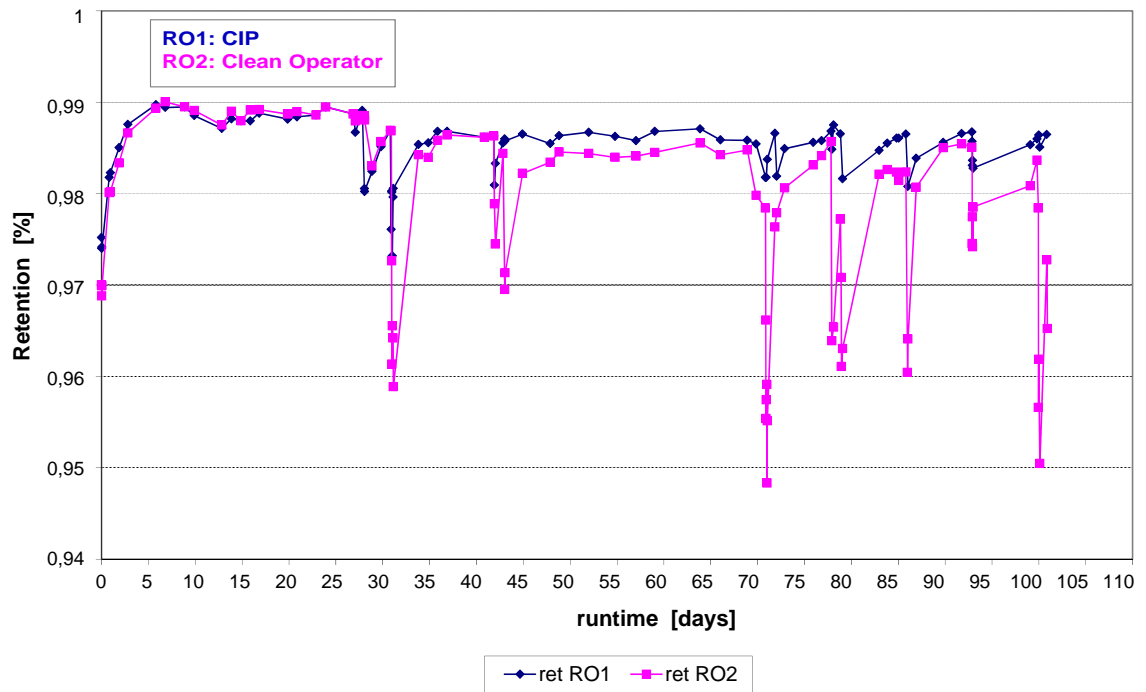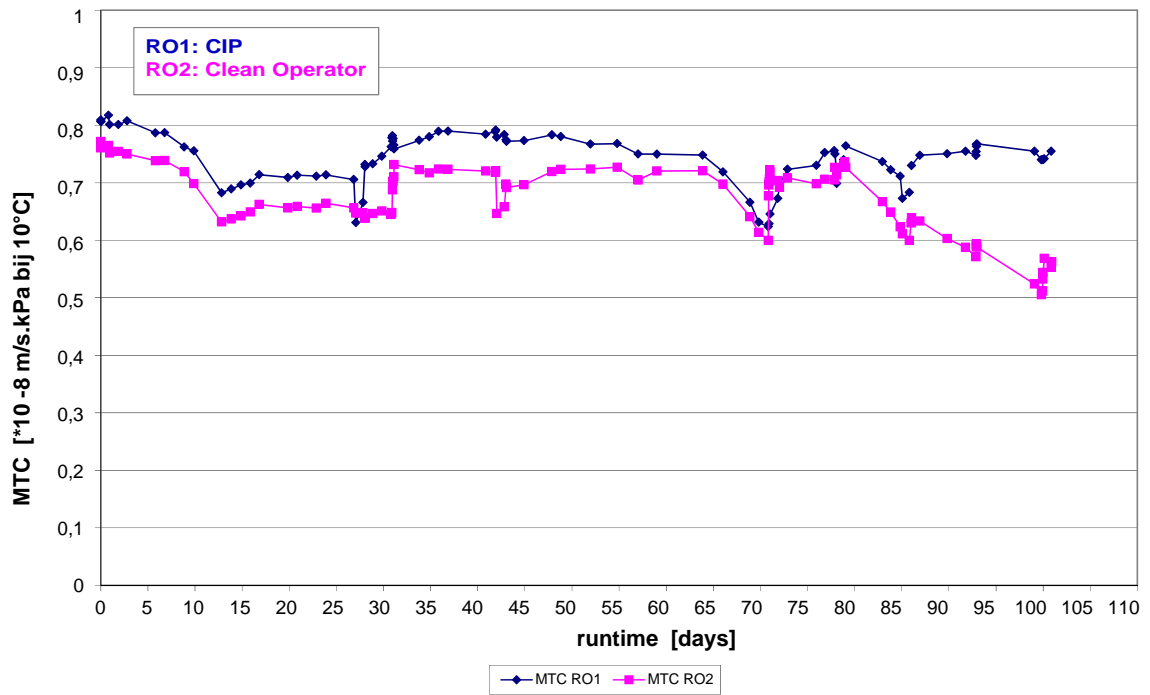| dP1	dP2	dP3	outflow	flow
0,299	0,171	0,235	2,711	2
0,406	0,278	0,363	2,732	3
0,619	0,363	0,534	2,754	4,1
0,790	0,470	0,640	2,775	5
1,003	0,576	0,854	2,882	6,1
1,131	0,640	1,003	3,010	6,9
1,345	0,811	1,345	3,287	8

Cumulative quantity of CO2 te be released [kg/m3]

dP1	dP2	dP3	outflow
0,299	0,470	0,704	3,415
0,406	0,683	1,046	3,778
0,619	0,982	1,516	4,269
0,790	1,259	1,900	4,675
1,003	1,580	2,433	5,315
1,131	1,772	2,775	5,785
1,345	2,156	3,501	6,788

Quantity in kmol/m3 per module

				flow
0,007	0,004	0,005	0,062	2
0,009	0,006	0,008	0,062	3
0,014	0,008	0,012	0,063	4,1
0,018	0,011	0,015	0,063	5
0,023	0,013	0,019	0,065	6,1
0,026	0,015	0,023	0,068	6,9
0,031	0,018	0,031	0,075	8

cumulative quantity in kmol/m3

0,007	0,011	0,016	0,078
0,009	0,016	0,024	0,086
0,014	0,022	0,034	0,097
0,018	0,029	0,043	0,106
0,023	0,036	0,055	0,121
0,026	0,040	0,063	0,131
0,031	0,049	0,080	0,154

Quantity in m3 CO2 /m3 water per module

				flow
0,102	0,063	0,093	1,248	2
0,127	0,096	0,139	1,252	3
0,175	0,117	0,197	1,256	4,1
0,207	0,144	0,231	1,261	5
0,233	0,160	0,286	1,281	6,1
0,243	0,165	0,319	1,305	6,9
0,246	0,180	0,380	1,353	8

cumulative quantity in m3 CO2 / m3 water

0,102	0,173	0,278	1,572
0,127	0,236	0,401	1,731
0,175	0,316	0,560	1,948
0,207	0,366	0,666	2,124
0,233	0,439	0,822	2,363
0,243	0,456	0,884	2,509
0,246	0,479	0,969	2,794

Quantity in m3 CO2/h per module

				flow
0,205	0,126	0,185	2,495	2
0,380	0,288	0,417	3,756	3
0,717	0,479	0,809	5,151	4,1
1,033	0,719	1,156	6,303	5
1,424	0,978	1,759	7,817	6,1
1,676	1,141	2,204	9,007	6,9
1,972	1,443	3,040	10,826	8

cumulative quantity in m3 CO2/h

0,205	0,346	0,556	3,144
0,380	0,708	1,203	5,194
0,717	1,297	2,299	7,986
1,033	1,929	3,428	10,618
1,424	2,679	5,014	14,417
1,676	3,158	6,096	17,311
1,972	3,835	7,913	22,355

Step 1: pressure drop * 0.213 kg CO_2/m^3 water

Step 2: conversion from kg towards kmol (divided by 44)

Step 3: conversion from kmol towards volume (m3) based on average pressure
n*8.315*285/((100 +(Pv+Pc)/2) * 1000)

Step 4: multiplied by the water flow to get m^3 CO_2/h

Calculated release CO₂ based on reversed pressure data

differential pressure per module and outflow

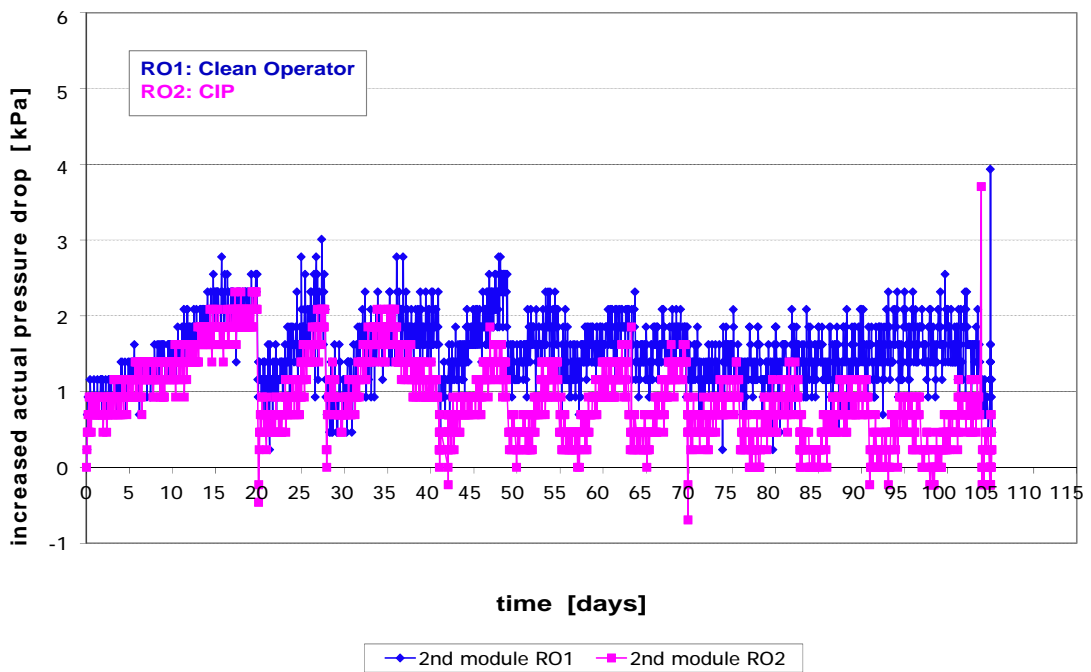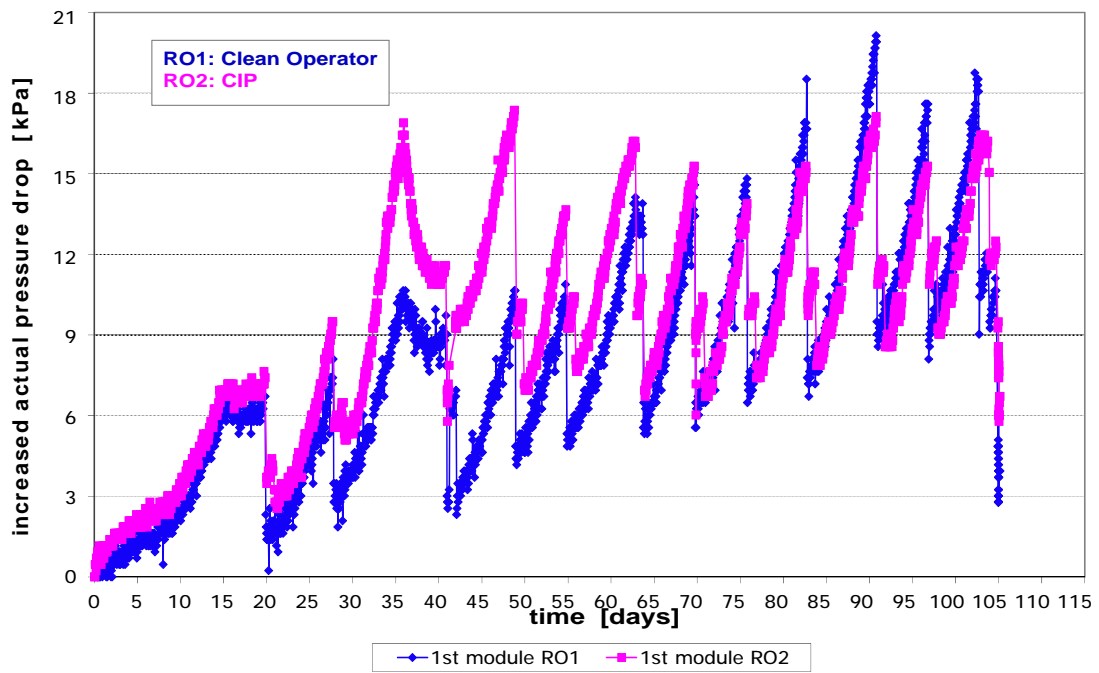| dP 1	dP 2	dP 3	outflow		flow
14	8	10	128		2
19	13	15	130		3
29	17	22	132		4,1
37	22	28	132		5
47	27	37	138		6,1
53	30	44	144		6,9
63	38	59	158		8

Quantity of CO2 te be released [kg/m3] per module — **Cumulative quantity of CO2 te be released [kg/m3]**

dP1	dP2	dP3	outflow	flow	dP1	dP2	dP3	outflow
0,299	0,171	0,213	2,732	2	0,299	0,470	0,683	3,415
0,406	0,278	0,320	2,775	3	0,406	0,683	1,003	3,778
0,619	0,363	0,470	2,818	4,1	0,619	0,982	1,452	4,269
0,790	0,470	0,598	2,818	5	0,790	1,259	1,857	4,675
1,003	0,576	0,790	2,946	6,1	1,003	1,580	2,369	5,315
1,131	0,640	0,939	3,074	6,9	1,131	1,772	2,711	5,785
1,345	0,811	1,259	3,373	8	1,345	2,156	3,415	6,788

Quantity in kmol/m3 per module — **cumulative quantity in kmol/m3**

dP1	dP2	dP3	outflow	flow	dP1	dP2	dP3	outflow
0,007	0,004	0,005	0,062	2	0,016	0,009	0,005	0,078
0,009	0,006	0,007	0,063	3	0,023	0,014	0,007	0,086
0,014	0,008	0,011	0,064	4,1	0,033	0,019	0,011	0,097
0,018	0,011	0,014	0,064	5	0,042	0,024	0,014	0,106
0,023	0,013	0,018	0,067	6,1	0,054	0,031	0,018	0,121
0,026	0,015	0,021	0,070	6,9	0,062	0,036	0,021	0,131
0,031	0,018	0,029	0,077	8	0,078	0,047	0,029	0,154

Quantity in m3 CO2 /m3 water per module — **cumulative quantity in m3 CO2 / m3 water**

dP1	dP2	dP3	outflow	flow	dP1	dP2	dP3	outflow
0,116	0,061	0,072	1,257	2	0,266	0,138	0,072	1,572
0,152	0,093	0,099	1,272	3	0,379	0,201	0,099	1,731
0,221	0,112	0,130	1,285	4,1	0,524	0,257	0,130	1,946
0,275	0,137	0,153	1,280	5	0,650	0,311	0,153	2,124
0,325	0,152	0,180	1,310	6,1	0,775	0,361	0,180	2,363
0,346	0,156	0,198	1,333	6,9	0,840	0,391	0,198	2,509
0,372	0,177	0,229	1,388	8	0,955	0,453	0,229	2,794

Quantity in m3 CO2/h per module — **cumulative quantity in m3 CO2/h**

dP1	dP2	dP3	outflow	flow	dP1	dP2	dP3	outflow
0,232	0,122	0,144	2,515	2	0,531	0,275	0,144	3,144
0,456	0,260	0,297	3,815	3	1,137	0,604	0,297	5,194
0,907	0,460	0,534	5,270	4,1	2,148	1,055	0,534	7,986
1,374	0,684	0,764	6,400	5	3,251	1,554	0,764	10,618
1,984	0,929	1,097	7,990	6,1	4,730	2,201	1,097	14,417
2,398	1,093	1,366	9,198	6,9	5,798	2,696	1,366	17,311
2,976	1,419	1,834	11,107	8	7,638	3,622	1,834	22,355

APPENDIX 9 DIFFERENT FIGURES WITH PROCESS DATA SECOND PERIOD

Figure: Top — increased actual pressure drop [kPa] vs time [days]; RO1: Clean Operator, RO2: CIP; 3rd module RO1, 3rd module RO2. Bottom — Feed pressure [kPa] vs runtime [days]; RO1: Clean Operator, RO2: CIP; MTC RO1, MTC RO2.

RO1: Clean Operator
RO2: CIP

MTC [*10 -8 m/s.kPa bij 10°C]

runtime [days[

→ MTC RO1   → MTC RO2

RO1: Clean Operator
RO2: CIP

Retention [%]

looptijd

→ ret RO1   → ret RO2
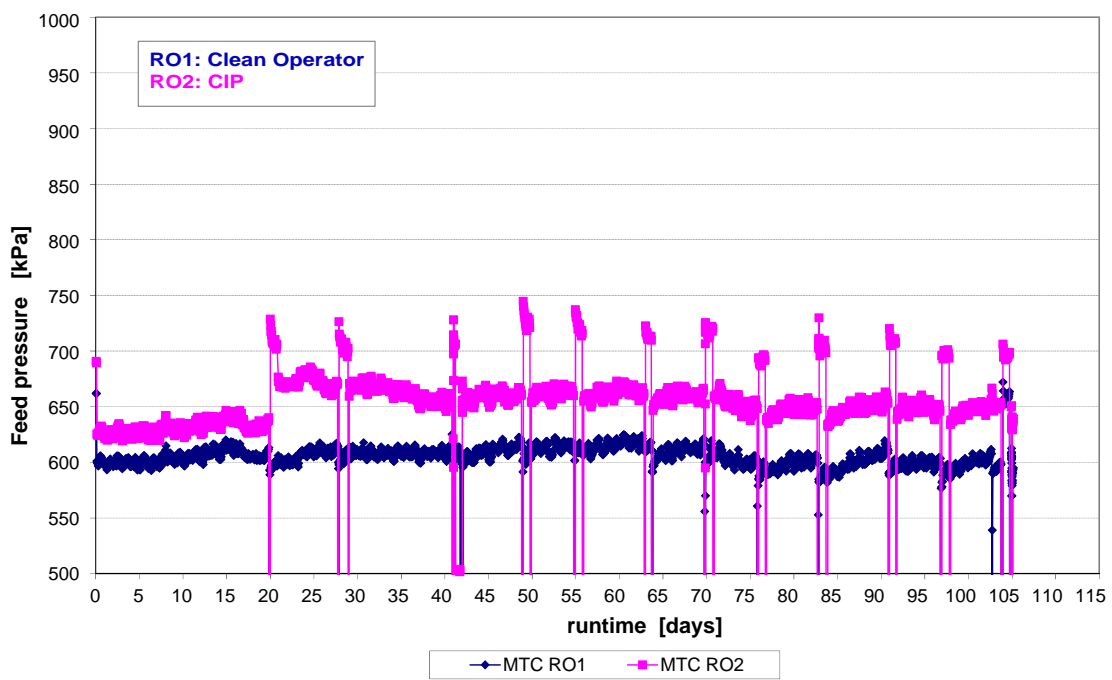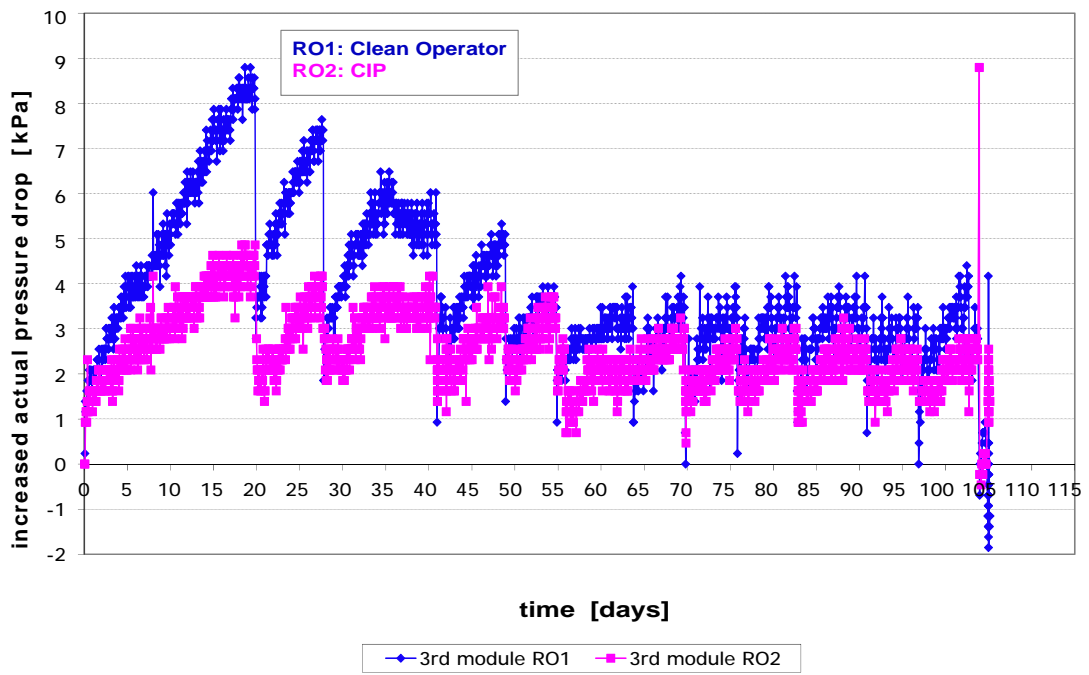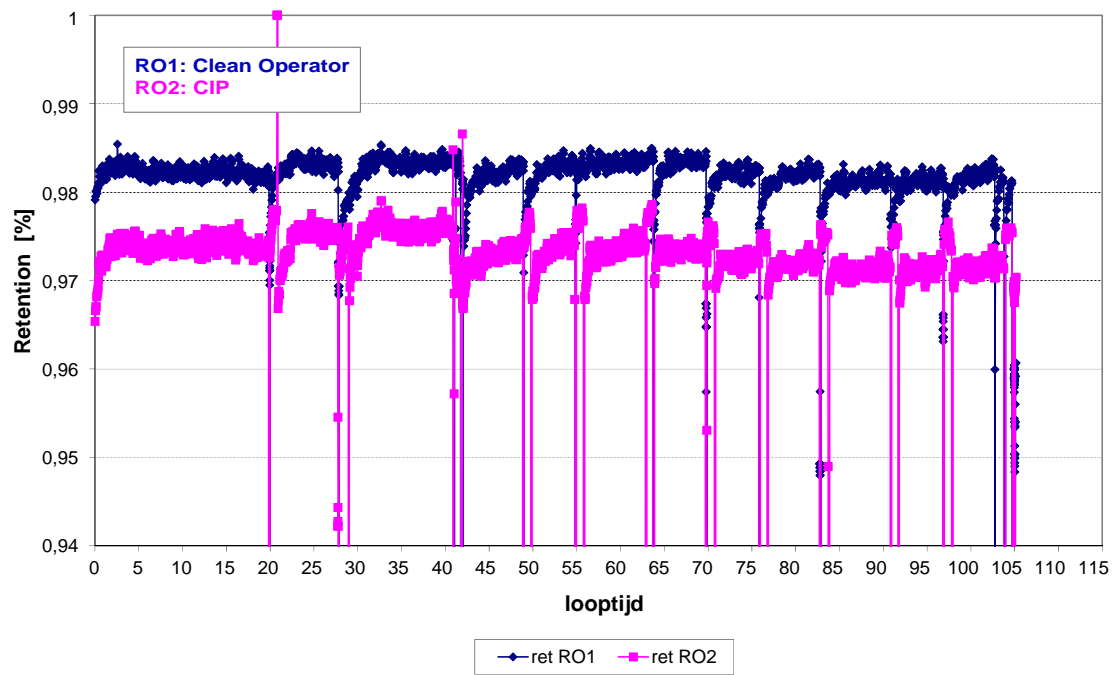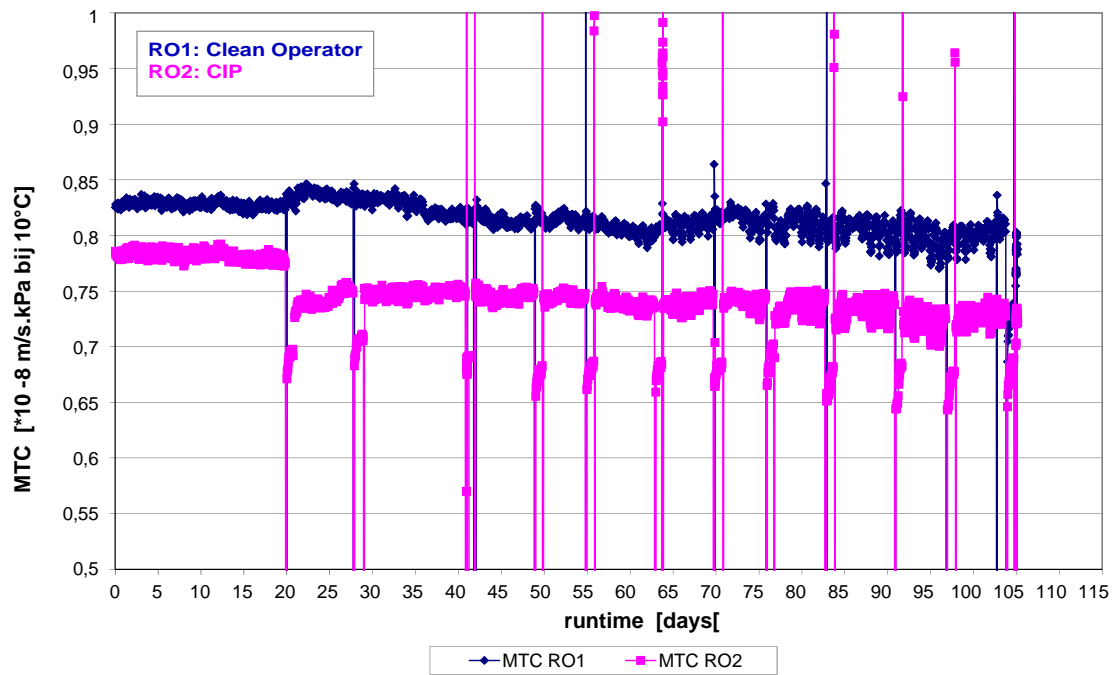
APPENDIX 10 INCREASE PRESSURE DROP OVER 1ST MODULE AT SECOND PERIOD

increased pressure drop over 1st module with 10 ug C/l dosage

RO1: Clean Operator
RO2: CIP
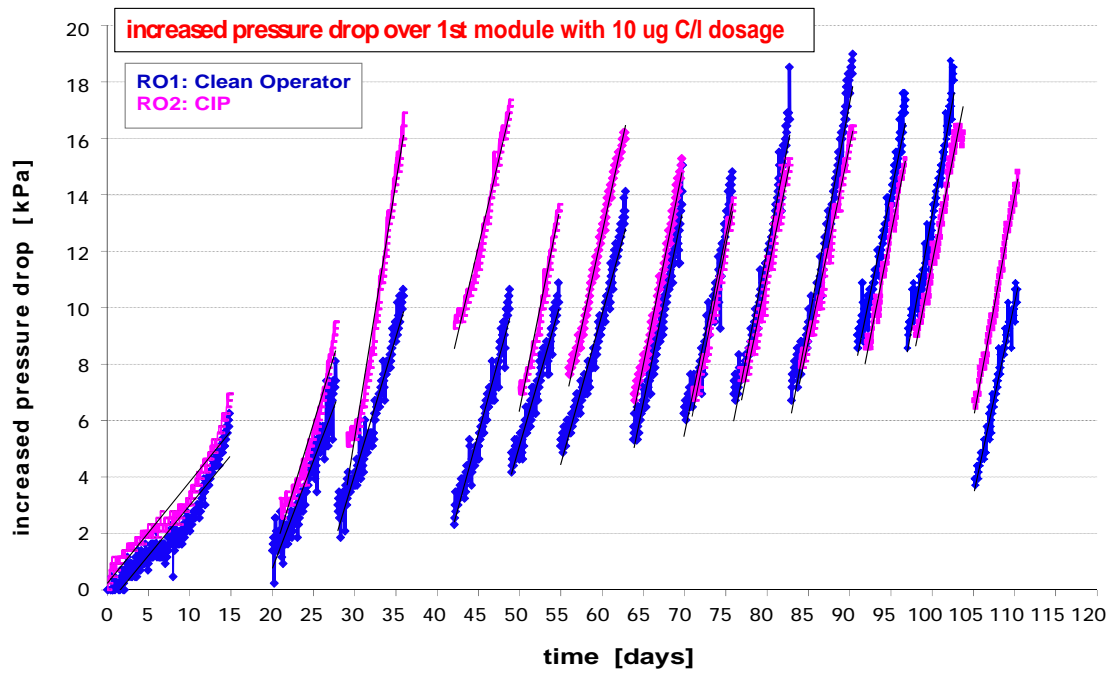
	RO1			RO2	
	equation	R^2		equation	R^2
1	0,35587x - 0,5615	0,8975		0,3606x - 0,2258	0,9158
2	0,7669x - 14,59	0,9106		0,933x - 18,188	0,9444
3	0,9736x - 25,115	0,9563		1,8106x - 48,929	0,9757
4	1,0734x - 42,762	0,9571		1,2438x - 43,791	0,9722
5	1,0156x - 45,659	0,9518		1,456x - 66,408	0,9748
6	1,0601x - 53,821	0,9653		1,3423x - 67,888	0,9914
7	1,4226x - 85,819	0,972		1,4535x - 86,485	0,9837
8	1,4008x - 92,497	0,9426		1,4842x - 99,094	0,978
9	1,4897x - 107,16	0,959		1,4363x - 103,74	0,9733
10	1,5572x - 122,91	0,9654		1,3824x - 108,69	0,9797
11	1,4183x - 120,69	0,9628		1,4693x 126,97	0,9736
12	1,6186x -148,56	0,9622		1,4733x - 135,73	0,9784
13	1,368x -140,29	0,9764		1,5778x - 159,6	0,9899
average inclination angle					
run 1-13	1,194			1,341	
run 7-13	1,468			1,470	

APPENDIX 11 NORMALISED PRESSURE DROP INFLUENCED BY MAJOR PARAMETERS
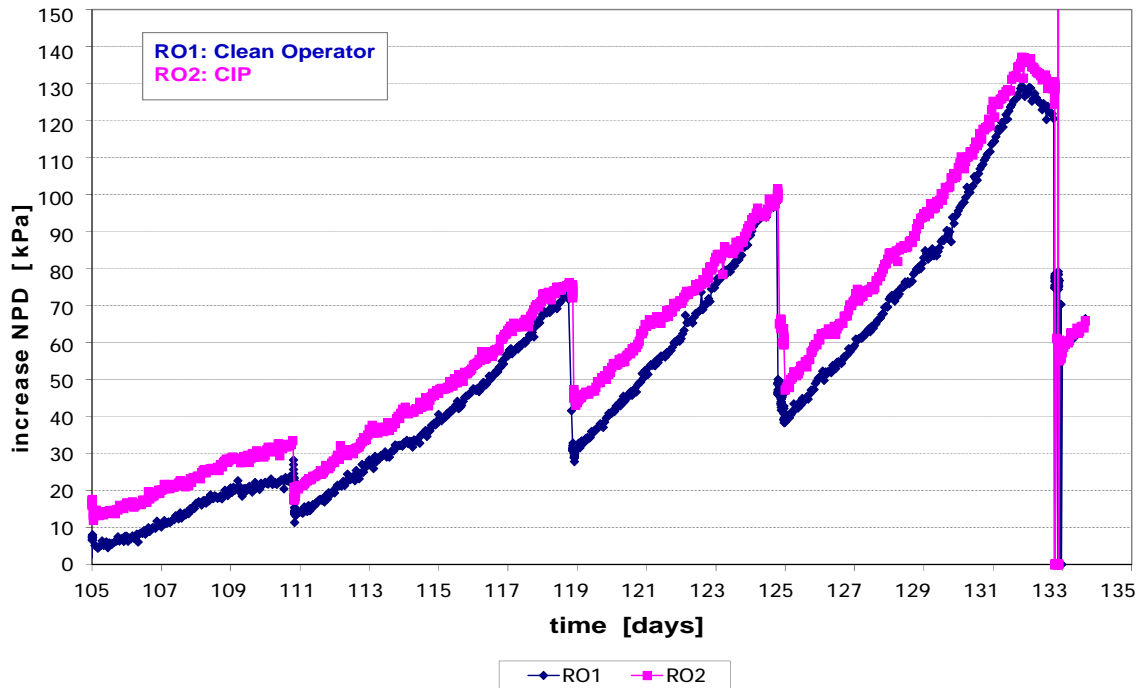
At the end of each experiment additional Clean Operator cleanings are performed in order to remove as much fouling as possible before starting next experiment. This allows the shape of the lines to be some how misleading.
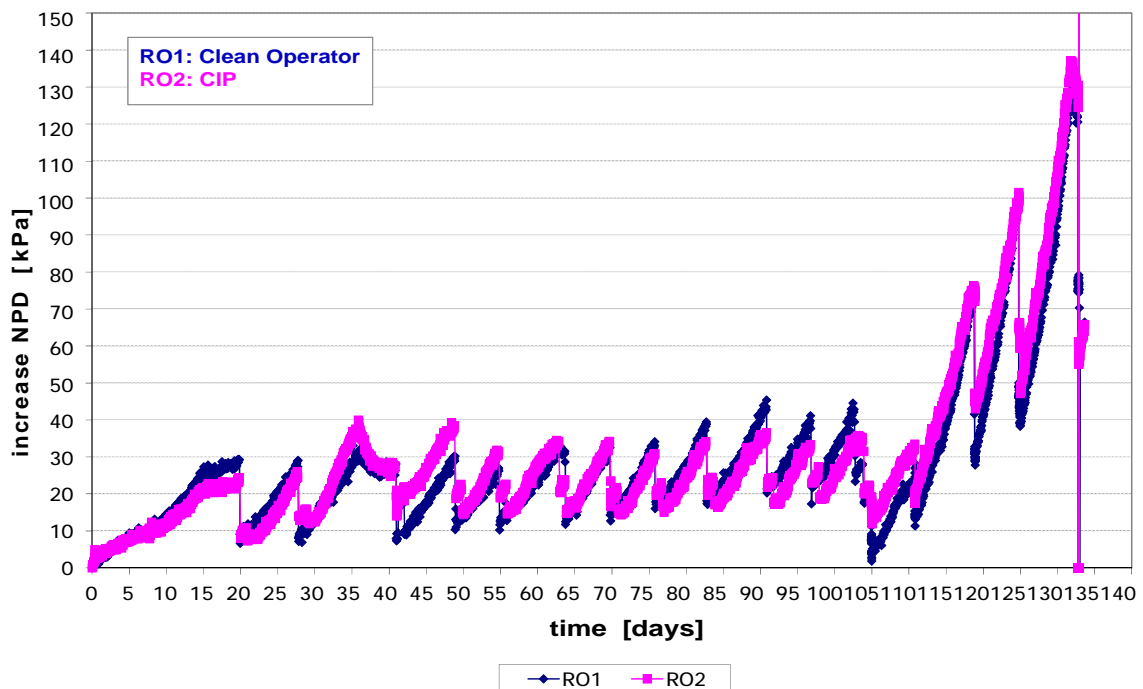
Sodium acetate dosage was 10 µg C/l till day 105. At day 15-20 and 35-41 the acetate dosage was stopped because of the increase of the normalised pressure drop. From day 105 – 133 the sodium acetate dosage was 20 µg C/l. At day 132 the acetate dosage was stopped because of the increase of the normalised pressure drop.

APPENDIX 12 DESIGN CALCULATIONS; CASE VECHTERWEERD

Vechterweerd						
110	m3/h RO					
935000	m3/y					
		CIP	Clean Operator			
increase P feed		1,5	0,2625			
average increase		0,75	0,13125			

Energy costs [€/ year] = 4 * delta H * P_{kWh} * Q_{jaar} * 10^{-3}

delta H	: head [mWk]		
P_{kWh}	: energy price [0,09 €/kWh]		
Q_{jaar}	: yearly water flow [m^3/y]		

energy consumption based on average feed pressure

CIP		Clean Operator		CIP - Clean Operator	
289850	kWh	266709	kWh	23141,3	kWh
26087	€	24004	€	2083	€

CO2 footprint Clean Operator versus CIP

Indicators CO2 footprint [kg CO2]

- citric acid (production)	0	per kg citric acid (not known)	
- citric acid (use)	1,375	per kg citric acid	
- cautic soda (production	0,55	per kg caustic soda	
- caustic soda (use)	0	per kg caustic soda	
- CO2 (production)	0,1425	per kg CO2	inclusief transport
- CO2 (use)	0,1	per kg CO2	
- energy	0,44	per kWh	(natural gas)
	0,6	per kWh	(average)
	1	per kWh	(coal)
heating	1,15	kWh/m3	
increase temperature	25	°C	

CIP

volume CIP tank	20	m3 (2 events of 10 m3)
capacity CIP pump	60	m3/h
head pump	3	bar
pumping time	4	h (2 times 2 hours)

Clean Operator

number to execute	1	Clean Operator events
capacity pump	50	m3/h
dosage time CO2	5	min
dosage CO2	750	kg CO2/h (200% saturated)
head pump	1,5	bar during water flush
head pump	5	bar during Clean Operator
time pump	6	min of water flush (before and after)
	5	min Clean Operator
Evaportor	0	kWh (atmospheric)

CO2 berekeningen

Chemical Cleaning In Place (CIP)

pump energy	50	kWh	30	kg CO2	
Citric acid (100%)	200	kg	0	kg CO2	production
			275	kg CO2	use
Caustic soda	20	kg	11	kg CO2	production
			0	kg CO2	use
energy heating	575	kWh	345	kg CO2	
consumption CO2			661	kg CO2	(average)

Clean Operator

pompenergie	2	kWh	1,2	kg CO2	
dosering CO2		kg CO2	77,7	kg CO2	
consumption CO2			78,9	kg CO2	
CO2 foot print reduction factor			8,4		