



report

IVL Swedish Environmental Research Institute

Eco-Efficient Technologies for
Improved Removal of Particulates
from Surfaces
Results of the European Union project
REPART

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| Sammanfattning/Summary Industrial cleaning and rinsing procedures are often resource demanding and money consuming processes. Through closing up systems and minimising the water and chemicals used, economy as well as quality and environmental aspects can be improved in many cases. This report is a summary of studies made within the EU project REPART. In one part of the project different methods for separation of particles are compared technically and economically. Also cleaning formulations are tested regarding their treatment possibilities on membrane filtration. Calcium has been identified as a trouble causing parameters in membrane filtration of rinse water and investigations have been made to show how to avoid the problems. A small study for determination of the desired rinse water quality was made. There are often large profits to gain through closing up processes, but since almost each process is complex and unique, studies have to be made on-site before installing the new technique. | |
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Table of content

| | |
|--|----|
| 1. Introduction | 1 |
| 2. Description of work | 2 |
| 2.1 Separation of particles | 2 |
| 2.2 Recovery of cleaners | 3 |
| 2.3 Definition of rinsing requirements | 4 |
| 2.4 Recovery of the chemicals and water from the rinsing system..... | 4 |
| | |
| Appendix 1. Comparison of different methods for removing particles from a cleaning process..... | 8 |
| Appendix 2. Membrane filtration of degreasing bath - multivariate evaluation of experiments in laboratory scale | 20 |
| Appendix 3. Evaluation of different parameters of cleaning formulations in correlation with membrane filtration..... | 30 |
| Appendix 4. Rinsing requirement - a small test in lab scale | 36 |
| Appendix 5. Membrane filtration of rinse water after degreasing - How to attain a successful process | 44 |

1. Introduction

Within the frames of the European union project Report (Improved REmoval of PARTiculate from surfaces to increase functionality and appearance of products) a series of studies on eco-efficient processes has been performed. The studies are compiled here, but also presented in separate reports, found as appendixes to this report.

A main objective of the project was to increase eco-efficiency of particle removal processes by closing up cleaning and rinsing systems, saving water and chemicals and also testing the compatibility of process chemicals and separation technologies.

A large number of pilot-scale membrane filtration tests have been performed.

- Separation of particles – comparison of techniques
- Ultra filtration for recycling of cleaners. Are the cleaners well compatible with the separation methods available? Some different parameters are studied.
- Rinsing requirements – the cleanliness of the rinse water contra quality of the goods.
- Nanofiltration for recovery of chemicals and reuse of water from the rinsing system.

The tests have lead to valuable knowledge about what parameters causing trouble while installing recycle techniques on cleaning and rinsing systems.

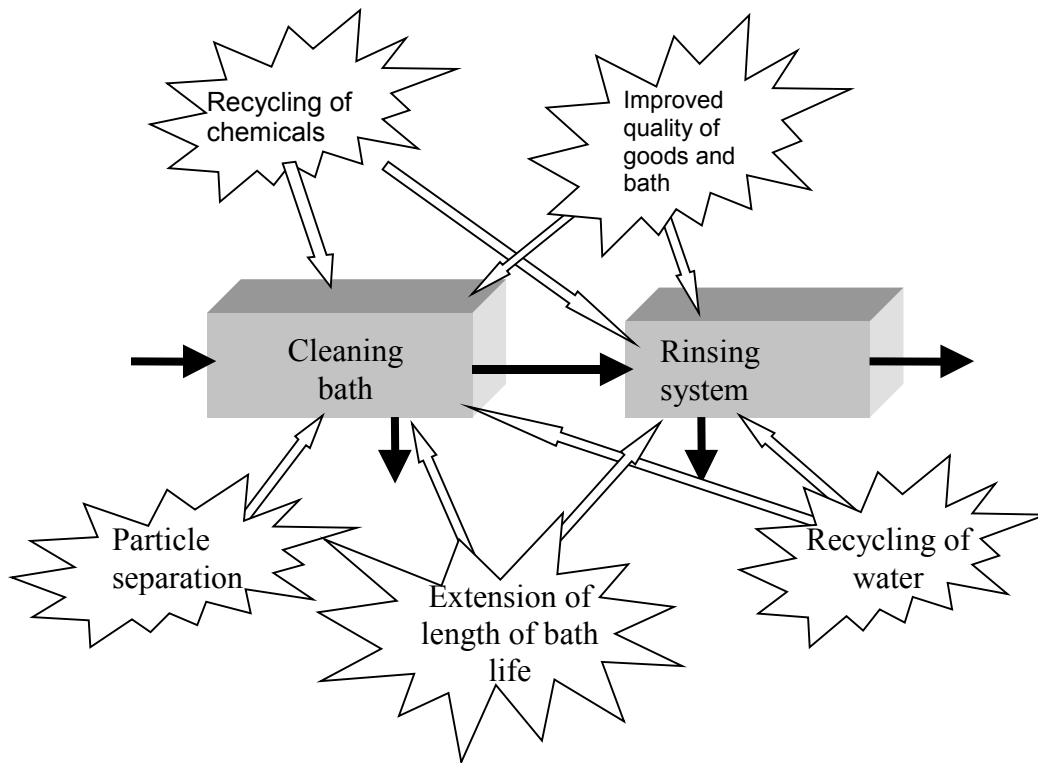


Figure 1. Illustration of the objectives for the project.

2. Work description and results

2.1 Separation of particles

Four different techniques for separation of particles from a cleaning process were tested. The techniques were evaluated in terms of efficiency, maintenance and economics. The techniques tested were:

- Microfiltration
- Bag filter
- Hydrocyclone
- Centrifugation / separation

The tests were performed on site at a cleaning process, where the particles were represented by silica carbide (SiC), aluminium and iron.

Microfiltration showed the best separation ability in the test. A ceramic membrane with 0,2µm cut off was used. Membrane technique, though, demands some maintenance and produces a liquid concentrate.

The **bag filter** tested had a pore size of 1µm. The method is very simple, but in this test the separation of particles were almost none. Advantages for the techniques are, besides the simplicity, the price, the ease of exchanging filters and also that the particles separated are gathered in the bag so that the waste comes in a solid form. The technique is however restricted to processes with rather low concentration of particles, since the bags otherwise gets full and needs frequent exchanging.

The **hydrocyclone** separated particles larger than 250µm and was easy to maintain. The particles were separated in a sludge container, easy to remove and empty.

Centrifugation showed a fairly good separation in the test, but the equipment needed manual cleaning and was rather expensive for this purpose. The technique is more suitable if the three phases oil, water and particles have to be separated.

More information about the experiments and results are to be found in Appendix 1.

2.2 Recovery of cleaners

In order to minimise the chemicals and water used in cleaning processes, closed loop systems are being introduced in many processes. Membrane filtration is a commonly used technique for this purpose, providing the right membrane is chosen and the cleaning formulation is compatible with the membrane process. Problems could however occur, fouling of the membranes causes lower flow rates, but also depletion of certain chemicals from the cleaning solution.

A series of tests on membrane filtration of cleaning solutions was made, where a number of different parameters were studied with respect to the membrane filtration compatibility.

- A hydrophilic membrane surface is preferable for attaining a high capacity of the membrane, a good recovery of chemicals and a good separation of oil and dirt.
- Silicates in the solution showed no negative effects of the membrane filtration. On the contrary silicates seemed to contribute to higher flux and better recovery. Earlier studies have, though, pointed out silicates as troublemakers in membrane filtration processes.
- Low concentrations of surfactants in the cleaning agent showed a positive effect on flux and recovery rate.
- High pH correlated with good recovery and high flux through the membrane.

- Antifoaming agent showed no significant impact on the filtration, when using hydrophilic membranes.

It should however also be noted that membrane processes as well as cleaning solutions are complex, and each case ought to be tested and evaluated specifically before installation of new techniques.

The work is described more in detail in Appendix 2 and 3, respectively.

2.3 Definition of rinsing requirements

A small test was made in order to study how the cleanliness of the rinse water affects the quality of the goods. Although rinsing is an important stage in many processes, little research is made in the area. Important questions are: how clean has the rinse water to be for a satisfactory result? Can it be too clean? These questions are important both while installing closed loop systems in order to minimise the water consumption, and also for optimisation of the quality of the rinsed goods.

In the test clean iron sheets were exposed to simulated rinse water with varying pH, amounts of CaCO₃-particles, oil, surfactants and salt. Quality of the goods were measured as corrosion and the results were evaluated with multivariate analysis in order to find most significant parameters:

- A high amount of particles in the rinse solution contributed to a higher degree of corrosion of the goods.
- Low amounts of surfactants in the solution, though, contributed to a larger quantity of particles on the goods surface.
- A neutral pH gave more corrosion on the goods than a rinse water with pH 11.

More information about the experiments and results are to be found in Appendix 4.

2.4 Recovery of the chemicals and water from the rinsing system

Rinsing procedures are often consuming significant amounts of water. Installation of closed loop systems and recycling of rinse water could give large profits in many ways:

- Economy – through saving of large quantities of water and also recycling of cleaning chemicals.
- Quality – in a continuous closed loop system, a stable high level of the water quality could be attained. In many processes where no such system is used, the rinse water

is dumped at a certain time, and replaced with new fresh water. By this method the quality of the water – and of the goods produced varies significantly.

- Environmentally – savings of resources - minimisation of water and chemicals used in the process.

Recycling of rinse water is however a complex process and problems with fouling of membranes often occur. Through a series of experiments in lab scale and pilot scale some trouble-causing parameters have been identified.

The membranes used in the tests were spiral wound nano-filtration membranes and the chemicals used were fatty alcohol polyetoxylate, sodium zylolsulphonat and potassium tetraborate.

Parameters that were varied and studied through the test were:

- Ageing of the cleaning bath
- Air exposure of the bath
- Tap water contra using de-ionised water
- Content of calcium
- content of oil
- pH
- Addition of complexing agent

All experiments were performed at 40°C and at a pressure of 15 Bar. The membrane filtration is driven step-wise up to VRF 10 (volume reduction factor 10) i. e. one tenth of the solution is left in the concentrate.

In this solution, calcium in the water showed out to have a devastating effect on the membrane filtration ability. Such low concentrations as 20mg/l drastically decreased the flux through the membrane.

Tap water showed a very low flux compared to using de-ionised water. The most probable reason might be the content of calcium, since the tap water used contains 20-30mg/l Ca.

The other parameters tested showed out to have little or no negative effect on the flux. Addition of the complexing agent NTA to the solution containing calcium (tap water) counteracted the flux decline.

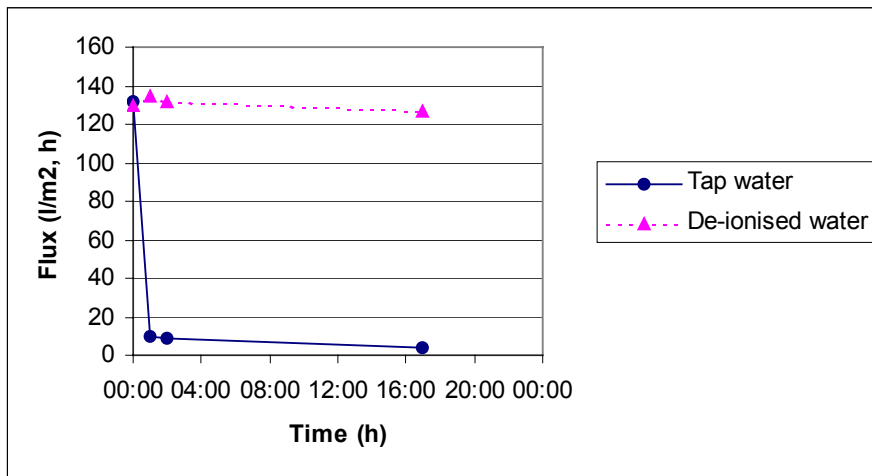


Figure 2. Differences in flux between experiment made with tap water and de-ionised water. When using de-ionised water the flux is stable throughout the separation cycle, but with tap water the flux drops drastically already after short time.

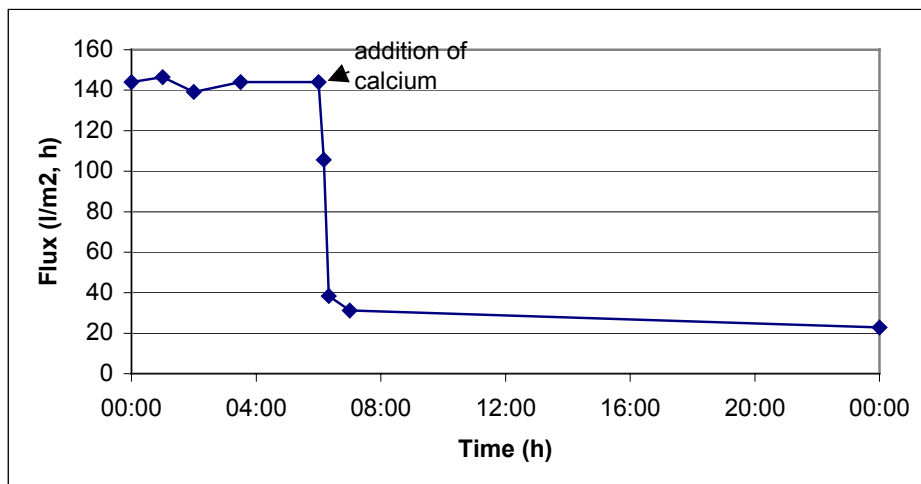


Figure 3. Addition of calcium 30mg/l after 6 hours of filtration of a solution based on de-ionised water. The flux drops drastically within a few minutes after the addition.

Using de-ionised water could therefore highly enhance the process. Since the installation of a closed loop system means a large reduction in water consumption, the possibilities for using de-ionised water increases significantly.

Addition of complexing agents, such as NTA or EDTA, could also eliminate the calcium problems.

More information about the experiments and results are to be found in Appendix 5.

3. Conclusions

The studies show large possibilities for savings of water and chemicals within cleaning as well as rinsing processes. It is however important that each process is studied separately, since no system is exactly like another. Membrane filtration is a good separation method for many applications, but which membrane to choose is also strictly bound to the specific process of question. It is also important to state the demands of the process – how clean must the rinse water be in order to reach a proper quality?

Through closing up systems, there are many profits to make; economical and environmental through minimisation of water and chemicals, but also in terms of quality. Installation of a closed loop system mean a more stable process bath, since the momentary exchanges of whole baths are replaced by a continuous drag out of polluting agents.

For extending the life length of a process bath, it is in many cases necessary to keep the bath free from particles, but also keeping it free from oil and other impurities. The removal of particles can be made by a number of different techniques depending on what quality is demanded on the process. Micro filtration is a well-defined process for high demands, while a simple bag filter may be sufficient where the level of particles is low and the quality demands are lower.

Appendix 1. Comparison of different methods for removing particles from a cleaning process

1. Introduction

Within the frames of the European Union project Report, a minor investigation has been made in order to evaluate different methods for removing particles from a cleaning process in a metal industry. The different methods tested are compared in terms of cleanliness of the outgoing water from each technique and the parameters analysed are particle size, suspended solids, dry weight (dw) and ignition residue.

The techniques tested and compared are:

- **Microfiltration**
- **Bag filtration**
- **Hydrocyclone**
- **Centrifugation/separation**

Each technique was tested in situ and run constantly for 14 days and between each test period was a time lag of minimum 14 days in order to obtain the same conditions for each test. The rinse water was new from the start of each technique. Unfortunately the cleaning solution was exchanged only once during the total experimental time, in the time lag between the third and the fourth (between hydrocyclone and centrifugation) technique tested. Therefore the solution is more heavily contaminated during the test of the hydrocyclone, than during the microfiltration.

Since the different equipment is of different scale, it is hard to draw any conclusions from looking at the quality of the bulk water. More relevant in this case is to look at the data on the outgoing water; the permeate or filtrate from each technique.

Other factors to take under consideration while comparing the different techniques are for example investment costs of the equipment, energy consumption and management of the equipment. In the evaluation of the techniques, an interview with process manager on site has been made, in order to get a better idea of the general impressions and the management of the equipment.

The goods cleaned in the process consist of iron and aluminium and have undergone lapping with silica carbide (SiC), and such particles are likely to be left on the goods and released in the cleaning procedure.

2. Technique/Equipment

2.1 Microfiltration

Membrane filtration involves a solution being forced under pressure through a semi-permeable membrane. A low-molecular fraction passes through the membrane during this process, the so-called permeate, while high-molecular compounds are recovered in a concentrate. Unlike ordinary filtration the flow direction of the fluid is parallel with the membrane surface. The principle is called cross-flow filtration. When the velocity of the fluid is high enough a turbulent flow is attained, that is important to avoid fouling of the membrane (see figure 2:1 below).

The separation properties of the membrane are indicated as its cut-off. The term ‘cut-off’ denotes the molecular weight of the least sized molecule which is held back by the membrane. In practice, a different cut-off from that specified is often achieved, which is due to the value being determined under idealised conditions. Membrane filtration is subdivided into various types of filtration depending on the imperviousness of the membrane:

- Microfiltration (MF)
- Nanofiltration (NF)
- Ultrafiltration (UF)
- Reverse osmosis filtration (RO)

Microfiltration has a cut-off between 0,05-2 μ m. The working pressure is often 0.1 - 0.5 MPa (IVL).

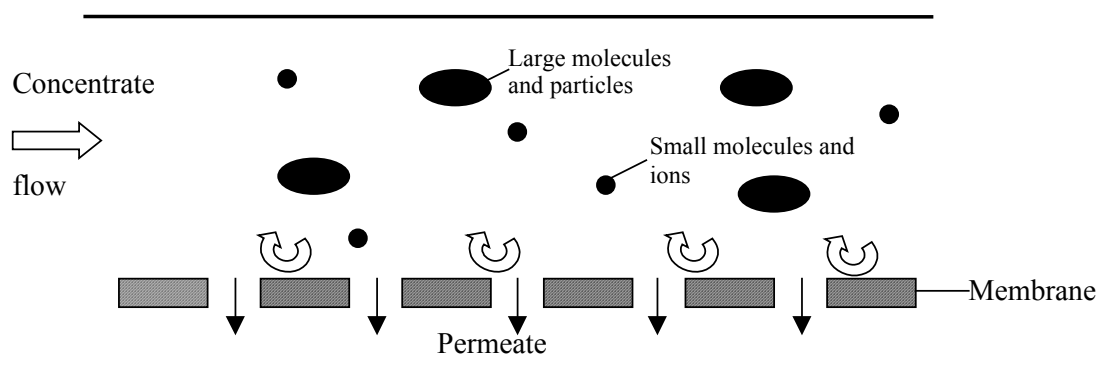


Figure 2.1 The membrane principle, where a cross-flow mechanism is illustrated.

In this test a ceramic membrane with 0,2 μ m cut-off was used. The unit used was manually controlled test equipment with 0,2 sqm membrane surface. Investment cost for a simple microfiltration unit would be around 5000 €. With automatic functions such as start, stop, alarms, washing etc the prize could be the double.

2.2 Bagfilter

Particles can be removed from the cleaning liquid by filtering through pressure filters designed as cartridge filters or bag filters and are placed in filter housings, figure 2.2. The filter inserts are replaced if they are saturated. Measuring the pressure drop across the filter controls the replacement interval. A high particle load means relatively rapid fouling and calls for frequent filter changes.

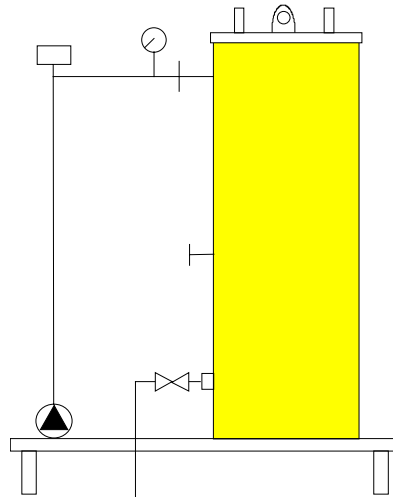


Figure 2.2 Cartridge- and bag filter principle.

Normally, filters are connected in parallel in order to cope with shutdowns for servicing and filter changes during operation. Filters can also be connected in series with a relatively coarse mesh size in the first filter housing and then with more fine-meshed filters. Common mesh sizes range between 50 and 150 μm (IVL 1998).

In this case a polypropylene filter from IFAB with 1 μm pore size was used (BPONG 001 P2S filterbag). Filter price is around 100 €. Equipment in this case is included in the cleaning process, otherwise a simple equipment cost may be about 2000 €.

2.3 Hydrocyclone

The practical range of classification for cyclones is 40-400 (1000) μm . During operation, the feed slurry enters the cyclone under pressure through the feed pipe into the top of the cylindrical feed chamber. As the feed enters the chamber, a rotation of the slurry inside of the cyclone begins, causing centrifugal forces to accelerate the movement of the particles towards the outer wall. The particles migrate downward in a spiral pattern through the cylindrical section and into the conical section. At this point the smaller mass particles migrate toward the centre and spiral upward and out through the vortex finder, discharging through the overflow pipe (see figure 2.3).

This product, which contains the finer particles and the majority of the water, is termed the overflow and should be discharged at or near atmospheric pressure. The higher mass particles remain in a downward spiral path along the walls of the conical section and gradually exit through the apex orifice. This product is termed the underflow and also should be discharged at or near atmospheric pressure (Arterburn R.A).

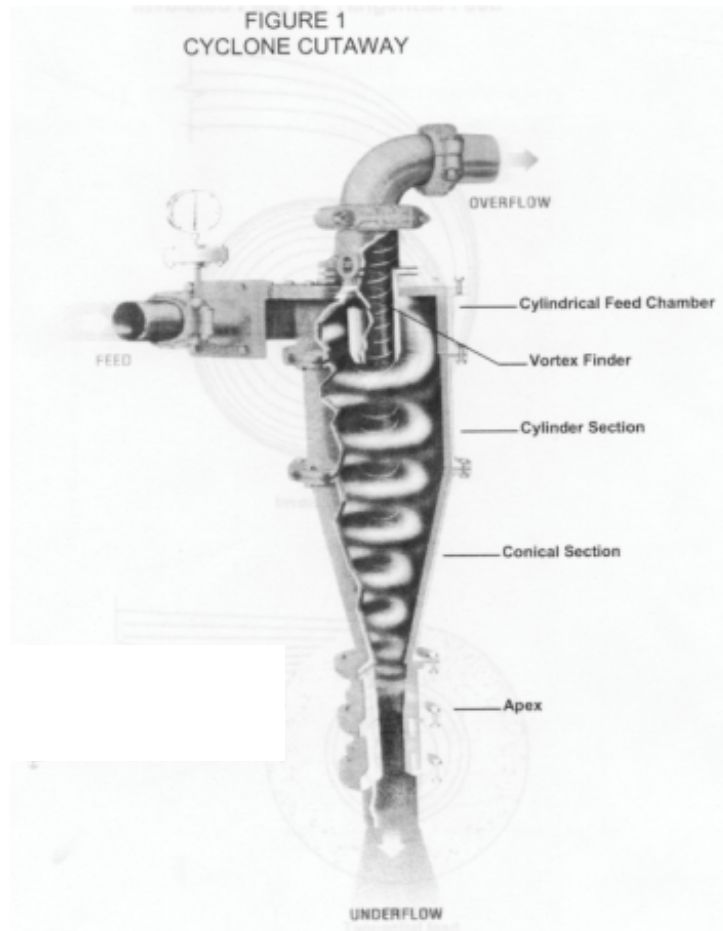


Figure 2.3 The figure shows the principle of a hydrocyclone (Arterburn R. A).

In this experimental set-up, a Mercatus hydrocyclone model F 60 with a capacity of around 5400 L/h was used. This capacity well covers the needs for this application and the investment costs is around 1600 €.

2.4 Centrifugation / separation

Centrifugal separation is like the hydrocyclone a gravimetric separating method. The separating properties of the components in the solution are reinforced by the influence of centrifugal force. Pollutants or substances with higher density than the ambient solution are pressed towards the side, where it is separated through a valve. The rest of

the solution is taken out in the middle of the centrifuge. Centrifugal separation often works on separation of 3 phases; liquid (water, cleaning solution for example), liquid (oil or grease) and particles. High G-forces (5-8000g) make the separation of particles effective (Alfa Laval).

The equipment used in this test was an Alfa Laval model Alfie 400 with a flow rate of around 400 L/h. Prize approximately 9000 €.

3. Results

Looking at suspended solids, microfiltration shows the largest separation of around 84%. The centrifuge shows a slight separation of 32%. The two other techniques tested, bag filter and hydrocyclone do not show any separation at all (see table 3:1).

The parameters dry weight and ignition residues show no separation for any of the techniques tested (see table 3:2 and 3:3).

Iron, silica and aluminium were analysed in order to see if there were some particles separated that thereafter had dissolved into the solution. Iron has about the same concentration in the tank solutions as in the filtrates for all techniques tested. (A separation of 6% for microfiltration). Silica shows a separation of 17% for microfiltration and no separation at all for the rest of the samples. For aluminium no separation at all is seen for any of the four techniques tested (see table 3:4, 3:5 and 3:6).

The particle size analyses made by YKI show, when studying the charts, a missing peak of particles $>250\mu\text{m}$ in the filtrate from the hydrocyclone sample. This indicates a separation of larger particles with the hydrocyclone technique. No such difference in particle size distribution is seen for the samples from microfiltration and bag filter. Looking at the table, there are not enough particles to get a value for the microfiltration permeate. This indicates a separation of particles with the microfiltration technique (see appendix 1). The last technique tested, centrifugation, was not analysed with this method.

The samples from the different techniques had different colours; the samples from the first technique tested, micro filtration, had the lightest colour. The samples from the third technique tested, hydrocyclone, has the darkest colour and also the highest turbidity together with the bagfilter samples. This colour difference is likely an effect of the age of the bath, since micro filtration was the first technique tested and the bath was exchanged before the centrifugation was started.



Figure 3.1 Samples from ingoing (tank solution) and outgoing (permeate) solution from each technique tested. From right; micro filtration, bag filter, hydrocyclone and centrifugation. The bath solution was changed between running of the hydrocyclone and the centrifuge. There is a visual difference in turbidity between the tank solution and permeate on the micro filtration but not on the other samples. There is also a difference in turbidity between the centrifugation and the other samples.

Table 3:1 Suspended solids

| Suspended solids, mg/L | In (tank solution) | Out (permeate) |
|------------------------|--------------------|----------------|
| Micro filtration | 79,5 | 13 |
| Bag filter | 96 | 91,5 |
| Hydro cyclone | 414,5 | 440 |
| Centrifuge | 104 | 71 |

Table 3:2 Dry weight

| Dry weight, g/L | In (tank solution) | Out (permeate) |
|------------------|--------------------|----------------|
| Micro filtration | 18,82 | 18,56 |
| Bag filter | 19,66 | 20,40 |
| Hydro cyclone | 18,39 | 20,06 |
| Centrifuge | 27,45 | 28,19 |

Table 3:3 Ignition residue

| Ignition residue, % of dry weight | In (tank solution) | Out (permeate) |
|-----------------------------------|--------------------|----------------|
| Micro filtration | 14,9 | 16,4 |
| Bag filter | 16,3 | 15,5 |
| Hydro cyclone | 17,6 | 16,9 |
| Centrifuge | 16,0 | 15,4 |

Table 3:4 Iron

| Iron, mg/L | In (tank solution) | Out (permeate) |
|------------------|--------------------|----------------|
| Micro filtration | 248 | 234 |
| Bag filter | 419 | 422 |
| Hydro cyclone | 488 | 497 |
| Centrifuge | 581 | 582 |

Table 3:5 Silica

| Silica, mg/L | In (tank solution) | Out (permeate) |
|------------------|--------------------|----------------|
| Micro filtration | 16,6 | 13,8 |
| Bag filter | 19,8 | 19,8 |
| Hydro cyclone | 22,8 | 23,3 |
| Centrifuge | 26,9 | 26,6 |

Table 3:6 Aluminium

| Aluminium, mg/L | In (tank solution) | Out (permeate) |
|------------------------|--------------------|----------------|
| Micro filtration | 126 | 135 |
| Bag filter | 133 | 133 |
| Hydro cyclone | 143 | 145 |
| Centrifuge | 183 | 185 |

3.1 Comment on the results

The most likely reason for why the analyses show almost no separation is that the samples could be incorrectly taken. Looking at the samples, only microfiltration shows

a visual difference between the in- and out-sample (see figure 3.1). The process engineer on site visually saw differences of the bath before and after every one of the different cleaning techniques tested.

4. Evaluation and comparison of the different techniques

The different techniques tested have been evaluated and compared in terms of costs, efficiency and other advantages and disadvantages of the different techniques. In order to catch the basic impressions of working with the different techniques an interview with the operator on site at Volvo Eskilstuna has also been made.

4.1 Microfiltration

- + Well defined separation ability
- + Reliable and robust technique
- + Good at low levels of particles and small particles
- + Good at applications with high demands on cleanliness
- Needs sometimes cleaning with chemicals
- High investment costs
- Produces a liquid concentrated waste
- The pump consumes energy

The impressions of the microfiltration by the operator is that it is a well functioning technique, perhaps better suited for laboratory applications though, since it demands a lot of maintenance. The equipment tested on site, however, was a manual test equipment, not at all automated.

4.2 Bagfilter

- + Easy to handle
- + Simple and cheap investment
- + Produces a solid waste
- + Good at low levels of particles
- Needs frequent replacement in heavy particle loaded applications
- A simple technique not suitable for applications with high demands on cleanliness

Operator's comment: A simple technique already existing in the tested installation. Easy to handle, but needs change when it gets clogged.

4.3 Hydrocyclone

- + Easy management – emptying of the sludge once in a while
- + Small volumes of waste (sludge)
- + Good at high concentrations of particles
- + Low investment costs
- +/- Gravimetric method that separates particles with a certain density and size
- The pump consumes energy

The operator on site appointed the hydrocyclone to the best of the four equipments tested since it showed a good (visual) separation and was easy to handle.

4.4 Centrifuge

- + Good for separation of 3 phases; liquid – liquid – particles.
- +/- Gravimetric method that separates particles with a certain density and size
- Require time for maintenance of the equipment.
- The pump consumes energy

According to the operator on site, this technique had several disadvantages. It demands a lot of service and cleaning management and is time consuming.

5. Acknowledgements

IVL and the Report project would like to thank Mats Björkman, operator at Volvo Eskilstuna, for valuable practical help and comments on the different techniques.

The project would also like to thank Mercatus and Alfa Laval for letting us use their equipment.

6. References

IVL – Internal information and course material

Arterburn R. A. “The sizing and selection of hydrocyclones” www.krebs.com
www.alfalaval.com + information

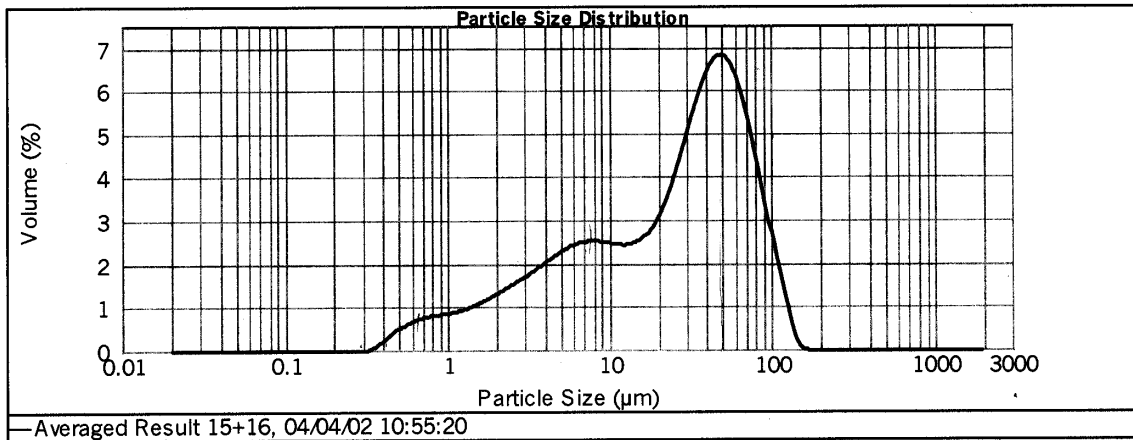
Appendix 1:1 YKI analysis of particle sizes

| Sample | Average Diameter (μm) | Median diameter (μm) | 90% of particles smaller than: |
|--------------------------------------|------------------------------------|-----------------------------------|--------------------------------|
| Bagfilter before (A) | 30,902 | 21,469 | 75,130 |
| Bagfilter before (B) | 36,393 | 33,335 | 76,600 |
| Bagfilter before (av.) | 33,648 | 27,402 | 75,865 |
| Bagfilter after (A) | 40,308 | 23,207 | 102,291 |
| Bagfilter after (B) | 36,919 | 19,004 | 97,981 |
| Bagfilter after (av.) | 38,614 | 21,106 | 100,136 |
| μF after, sample 1 | * | * | * |
| μF before, sample 1 (A) | 14,013 | 10,116 | 31,388 |
| μF before, sample 1 (B) | 11,751 | 9,191 | 26,530 |
| μF before, sample 1 (av.) | 12,882 | 9,654 | 28,959 |
| μF after, sample 2 | * | * | * |
| μF before, sample 2 | 6,326 | 4,091 | 14,390 |
| Cyclone, before (A) | 37,401 | 7,523 | 124,964 |
| Cyclone, before (B) | 16,179 | 6,962 | 49,820 |
| Cyclone, before (C) | 10,615 | 6,377 | 21,565 |
| Cyclone, before (av.) | 21,398 | 6,954 | 65,450 |
| Cyclone after (A) | 12,967 | 7,980 | 25,649 |
| Cyclone after (B) | 10,633 | 7,591 | 21,882 |
| Cyclone after (C) | 15,391 | 8,029 | 27,473 |
| Cyclone after (av.) | 12,997 | 7,867 | 25,001 |

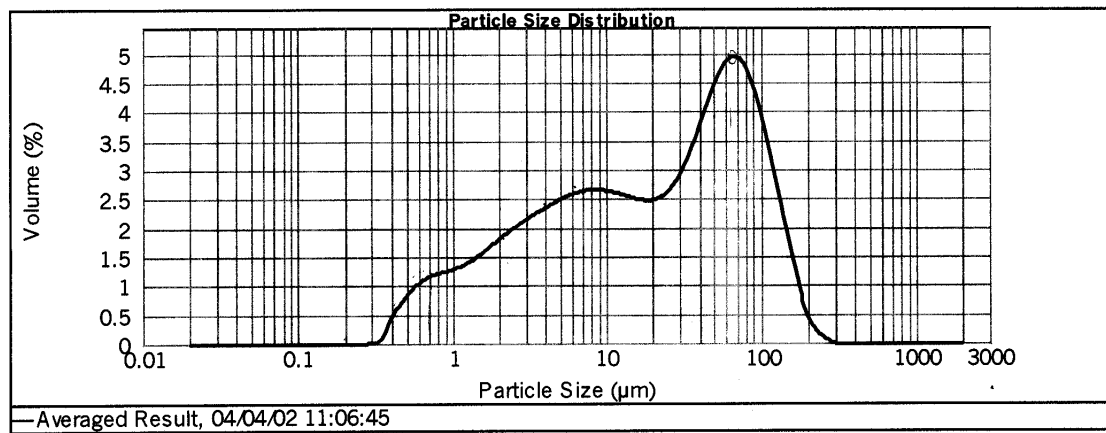
* No sufficient amount of particles for analysis.

The figures below show the particle size distributions for the different tests, where each filtrate/permeate (named “after”) is compared to the tank solution (named “before”) at that particular time.

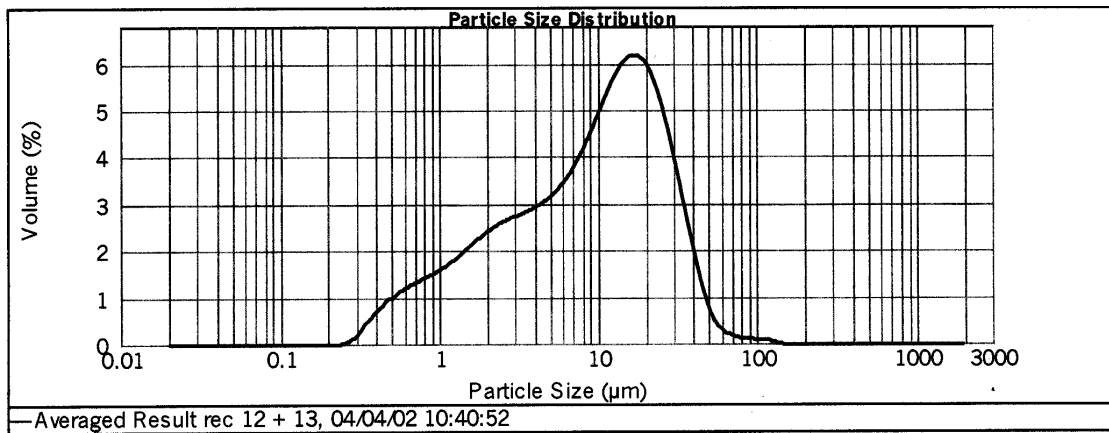
Before bagfilter:



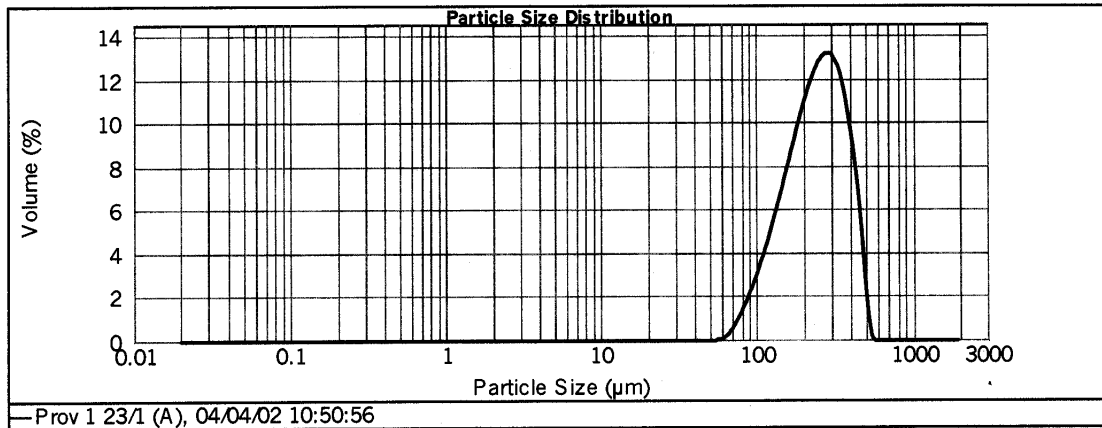
After bagfilter:



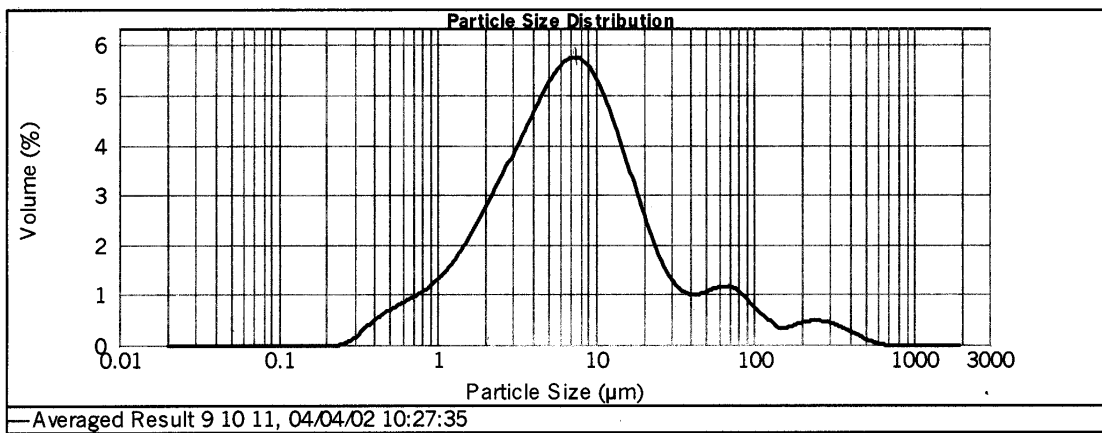
Before microfiltration:



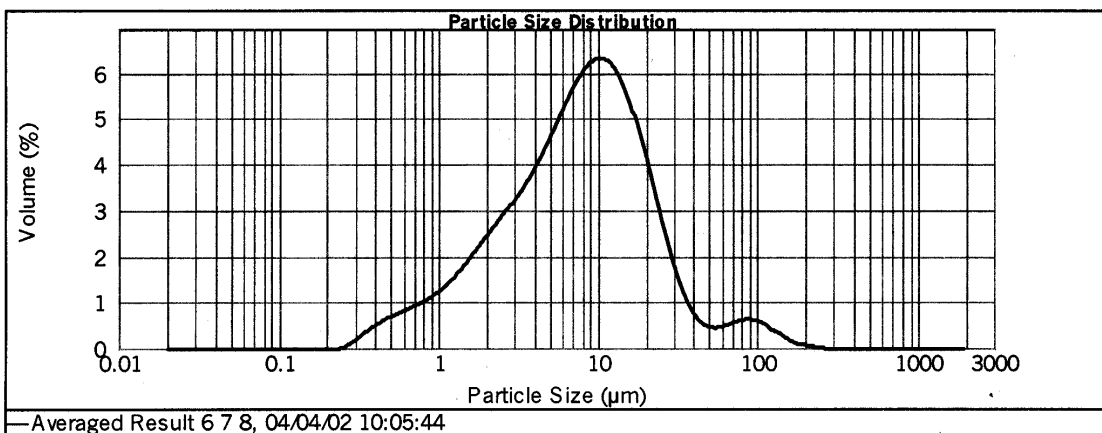
After microfiltration:



Before cyclone:



After cyclone:



Appendix 2. Membrane filtration of degreasing bath - multivariate evaluation of experiments in laboratory scale

1. Background

Cleaning and rinsing are common processes in the industry today and since no completely closed systems exist yet, different kinds of waste products are produced by these processes. Membrane filtration is a technique to reduce the quantity of waste and to minimize the resource consumption from the rinsing and cleaning processes through recycling of both process water and the chemicals used in the processes.

Membrane filtration is used in many different applications and is widely used in the engineering industry. The most common cleaning chemicals used today are based on surfactants and there is a growing need for developing closed systems, where oil and particles can be removed from the system in order to reuse surfactant chemicals with good quality. For this purpose membrane filtration could be a good choice.

To motivate the investment of membrane filtration equipment economically and technically, certain parameters are decisive:

- The degree of removal of oil and particles
- The degree of surfactants returned to the system
- The flux through the membrane

All these parameters have big influences on the treatment costs and the environmental impacts of the process. An optimal membrane filtration process results in high reduction of oil, low reduction of surfactants and a high flux through the membrane. A low reduction of surfactants results in minimized use of chemicals, which is favourable both in economical and environmental aspects.

The investment cost for a membrane filtration application is high. Therefore it is desirable to maintain a high flux through the membrane. Membrane filtration is also an energy consuming process and it is important to counteract fouling of the membrane.

Membrane filtration is a complex process that is influenced by many parameters such as the properties of the membrane, the structure and composition of the surfactant, content of polluting agents in the solution and interactions between these and other process parameters. This complexity makes it difficult to maintain a high degree of recycling of the surfactants and a high flux through the membrane.

More knowledge and understanding are needed to get a well-functioning technique for closing up industrial cleaning systems. This study is an attempt to highlight the importance of different parameters in the process.

2. Purpose

The purpose of this study is to understand the complexity of membrane filtration processes better. The influence of certain parameters and interactions between them are studied and evaluated through multivariate methods. An optimized process could mean both lower costs and environmental improvements.

3. Methodology

To achieve a maximum of information about how certain process parameters and interaction effects influence the filtration result, a selection of parameters are studied in an experimental set-up in factorial design. Properties of membranes, surfactants and process parameters are studied. First a number of parameters were chosen, the experiments were performed and the results were evaluated with multivariate methods.

The test solutions, simulated cleaning baths, were prepared at IVL's laboratory through addition of oil and surfactants to water.

3.1 Experiments

To get a maximum of information out of the project, the experiments were planned with a factorial design.

3.1.1.1 Parameters

The independent parameters chosen for this study have all in previous studies been identified to have big influence on the cleaning systems.

Salt

The concentration of electrolyte in the solution has a big influence for colloidal systems. The electrolyte destabilizes the systems since it minimizes the so-called energy barrier. The electrolyte neutralizes the repulsive electrostatic double layer. This destabilization makes the micelles easier fall apart. A secondary effect of this destabilization could be that the micelles to a higher degree could pass through a membrane. In these experiments sodium chloride is used as electrolyte. The concentration varies at two levels and the levels have been chosen on the basis of information from industries having degreasing bath in their processes. The conductivity in the test solution varies

between 16-21,5 mS/cm due to the concentration added. The concentration added is respectively 3 and 8,75 g/l.

Silica

It is not an established fact that silica effects the flux of the membrane. The complex binder sodium meta-silicate is varied in the experiments to investigate its influence on the flux. The compound has also got alkali and surface hydrophilic properties. The concentration added to the experimental solution is 1 and 2 g/l respectively.

Surfactant

The concentration of surfactant in the solution have been varied to investigate its effect on the separation and flux capacities on the membranes. The surfactant used in the experiments is a blend of non-ionic and cationic surfactants for waterborne degreasing and has a good cleaning and degreasing capacity on hard surfaces. The product has been diluted according to the instructions for use in industrial cleaning processes. The concentrations used in the experiments are respectively 2,5 and 4,5 g/l.

Temperature

Temperature is an important factor to take into account in a cleaning process and the optimal temperature is individual for every cleaning product. The cloud point is very sensitive for the content of tetra potassium pyrophosphate. In the experiments have temperatures below the cloud point been used and recommended quantity of tetra potassium pyrophosphate been added. The temperatures used in the experiments are 35 and 55°C respectively.

Membrane

Both membranes used in the experiments come from the same supplier and have the same cut-off; 25 000 Daltons. They differ in which material they are made of and therefor the hydrophilicity also differs for the two membranes. Facts about the two membranes are put together in table 1.

Table 1 Comparison of the two membranes used in the experiments

| Membrane: | Material: | Max. range: | pH | Max. pressure (bar) | Max temp. (°C) | Apparent retention character: | Hydrophilicity: | Solvent resistant: |
|------------|-------------------|-------------|----|---------------------|----------------|-------------------------------|-----------------|--------------------|
| AN 620 (1) | Polyacrylonitrile | 2-10 | | 10 | 60 | 25 000 MW | 5 | +++ |
| ES 625 (2) | Polyetharsulphone | 1,5-12 | | 15 | 80 | 25 000 MW | 2 | ++ |

Samples from the membranes used in all experiments were characterized in terms of zeta-potential in milliVolts. They are all negatively charged, although the charge is

higher for the AN 620 membrane (average -58mV for membrane AN 620 and -39mV for membrane ES 625).

Parameters that are held constant throughout the experiments

Another complex binding compound that is included in the cleaning formulation is tetra potassium pyrophosphate. Since no effects on the flux due to this compound has been indicated earlier, its level is held constant throughout the experiments. Tetra potassium pyrophosphate has a buffering effect. To every experiment 3 g/l is added to the solution.

pH is not controlled in the experiments, though it is measured continually. This is due to the buffering effect of tetra potassium pyrophosphate described above. Regulating of the pH in a buffering system demands large quantities of acid or base and could thereby rise the conductivity significantly. pH at start varied between 11,57 and 12,15 and at the end of the experiments between 9,72 and 11,14.

The stirring of the solution is enough since the total volume is pumped through the system in a minute. Industrially this is a very important factor to take into consideration.

The content of oil in the solution is based on the contents in a typical metal cleaning bath; i.e. approximately 2 % weight oil. In these experiments the mineral oil Quacker MP-2 is used. The oil was emulsified into the solution and the sizes of the particles were measured. Mean particle size was between 1-100 µm in diameter.

The pressure is held constant at 8 bar at the entrance of the system.

3.2 Evaluation of the experiments

The experiments were performed under similar conditions and many parameters were measured; permeate flux at certain times, foam magnitude, pH, flux of pure water before and after each experiment, conductivity, surface charge, concentration of oil in the permeate and COD. Surfactant concentration in the permeates are calculated from the amount of total extracted alifates subtracted by the amount of non-polar alifates (oil).

The results of the experiments were analyzed through multivariate methods to evaluate which parameters have most influence on the process and which interaction effects exist.

4. Results

The most important single parameter in this study showed out to be which membrane that was used. The flux was over all very much higher in the experiments made with

membrane 1 (the more hydrophilic one) than with membrane 2. Therefore the results of the multivariate evaluation are focused on the evaluations of each membrane separately.

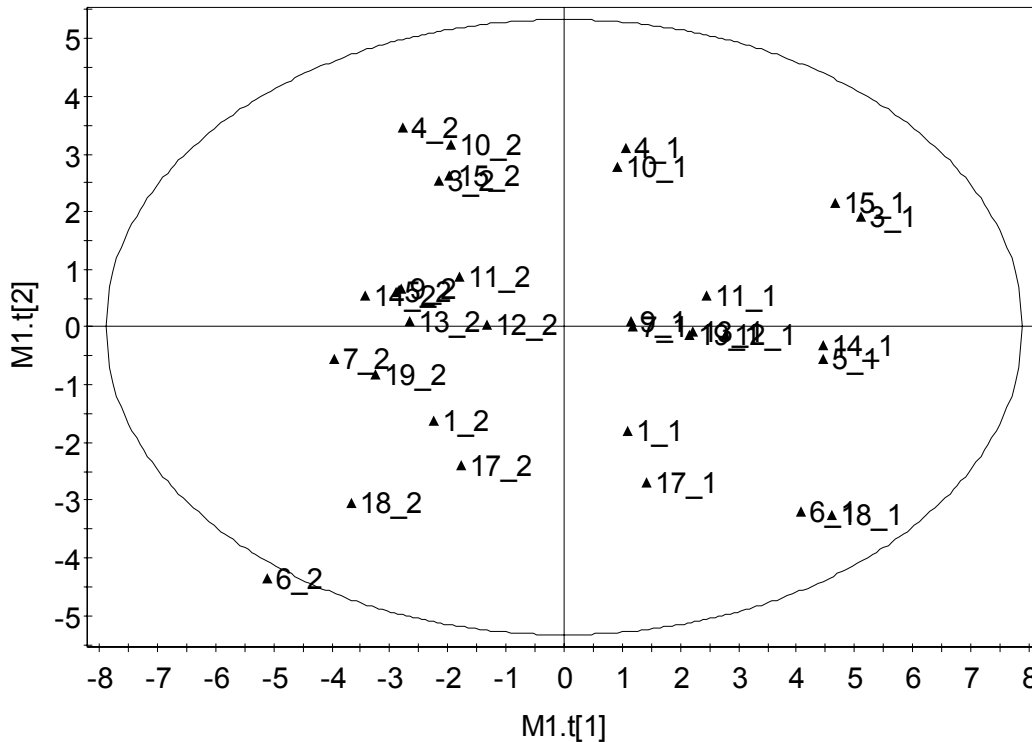


Figure 1 PCA for the entire study shows that the experiments made with membrane 1 ("_1") are separated from those made with membrane 2 ("_2").

PLSs are plotted to show the connections and correlation between the different parameters. Factors that are evaluated as Y-parameters are:

- Surfactants in the permeate
- Oil in the permeate
- Flux increase during the experiment
- Flux reduction of pure water
- Flux after 24 hours

These parameters are evaluated and correlated to all the measured and calculated values. Figure 2 and 3 shows the PLS model for the Y-parameter oil in the permeate for the two different membranes.

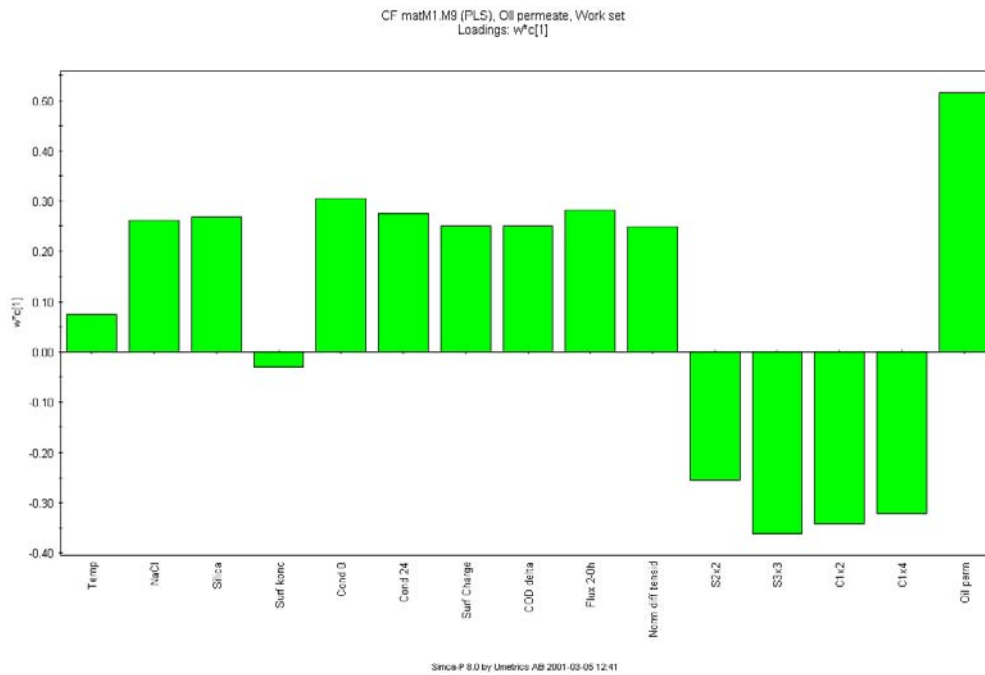


Figure 2 PLS describing how the concentration of oil in the permeate (Y-parameter) correlates and anti-correlates with different parameters (X-parameters) in the part of the experiments made with membrane 1.

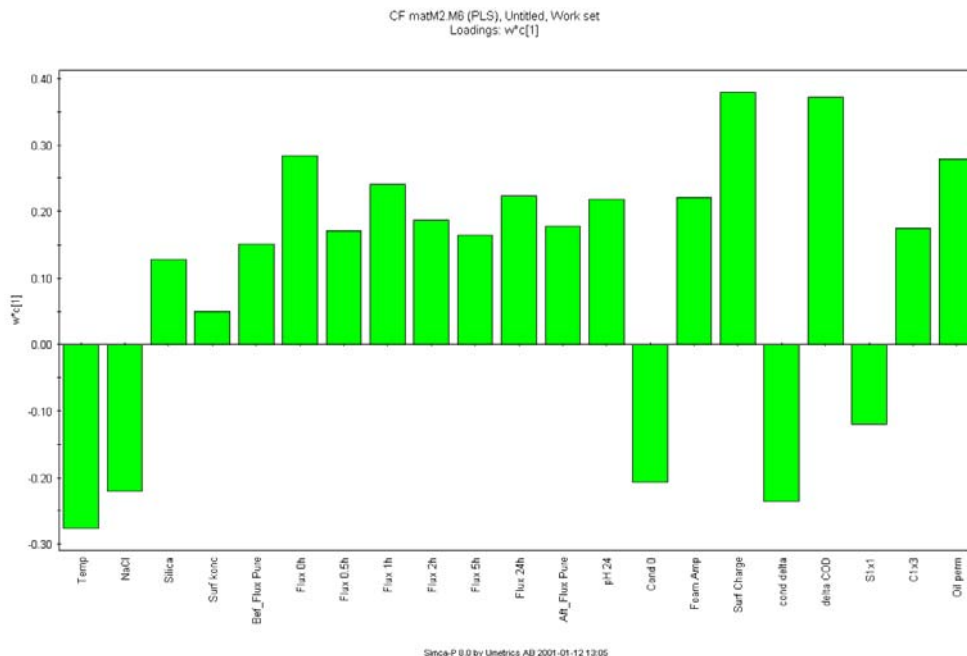


Figure 3 PLS describing how the concentration of oil in the permeate (Y-parameter) correlates and anti-correlates with different parameters (X-parameters) in the part of the experiments made with membrane 2.

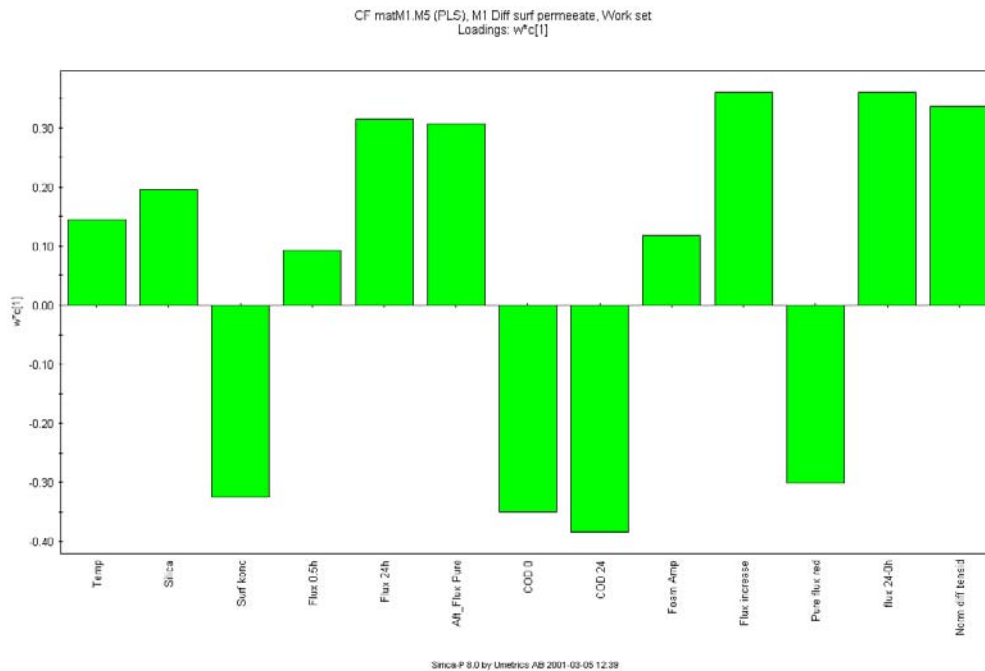


Figure 4 PLS describing how the concentration of surfactants in the permeate (Y-parameter) correlates and anti-correlates with different parameters (X-parameters) in the part of the experiments made with membrane 1.

4.1 Separation properties

- For the hydrophilic membrane high temperatures and high concentrations of salt give a worse separation of oil. For the hydrophobic membrane the separation of oil is more effective at high temperatures.
- An effective separation of surfactants correlates with high flux of pure water after the experiments.
- The separation of oil anti-correlates with the separation of surfactant.
- On the hydrophobic membrane a high temperature lets through more surfactant through the membrane.

4.2 Flux properties

- The experiments made with the hydrophilic membrane have generally higher fluxes than the hydrophobic.
- Generally the flux is higher at higher temperatures.
- The flux consistently increased during the experiments and on the hydrophilic membrane the increase is higher at low temperatures.

- Silica seems to counteract the flux increase on the hydrophilic membrane
- For both membrane types there is a connection between high flux and high amounts of oil and surfactants in the permeate.
- High concentrations of silica and high pHs deteriorate the flux of pure water after the experiments.
- There is a connection between separation of oil and flux of pure water after the experiment – bad separation correlates with bad flux for the hydrophilic membrane. A corresponding connection exists between separation of surfactant and flux for the hydrophobic membrane.

4.3 Influence of the different parameters

Salt: High amounts of salt leads to a deteriorated separation of oil.

Silica: Silica contributes to lower the flux. It also seems to enhance the through letting of both oil and surfactant through the membrane.

Surfactant: High amounts of surfactants counteract high flux increases for the experiments made with the hydrophobic membrane.

Temperature: A high temperature contributes to higher flux for the hydrophilic membrane. For the hydrophobic membrane the situation is the opposite. The separation of surfactants is enhanced by high temperature for the experiments made with the hydrophilic membrane, and the separation of oil is enhanced by high temperatures for the hydrophobic membrane.

4.4 Differences between the two membranes

4.4.1 Membrane 1 (620)

- Hydrophilic.
- Oil in permeate correlates with temperature and salt.
- Flux increase during experiment correlates with surfactants in the concentrate.
- Flux increase during experiment anti-correlates with temp, silica
- Flux reduction in pure water after the experiment correlates with pH at 24 h, flux increase, oil in permeate
- Flux reduction in pure water after the experiment anti-correlates with temp and temp, salt, silica, surfactant conc. squared.
- Flux after 24h correlates with temp, delta conductivity, interaction between silica and surface conc.
- Flux after 2 h correlates with temp, silica, interaction between salt and silica

4.4.2 Membrane 2 (625)

- Hydrophobic
- Surfactants in permeate correlate with temp
- Oil in permeate correlate with flux, surface charge
- Oil in permeate anti-correlate with temp, salt, conductivity at start, delta conductivity
- Flux increase during experiment anti-correlates with surfactants in concentrate, temp, salt and silica squared
- Flux reduction in pure water after the experiment correlates with temp, surface concentration in the permeate
- Flux after 24h correlates with pure water flux, delta COD
- Flux after 24h anti-correlates with temp, surfactants in permeate, delta conductivity, interaction between temp and salt, interaction between silica and surfactants in concentrate.
- Flux after 2 h correlates with salt, interaction between silica and surfactants in concentrate.
- Flux after 2 h anti-correlates with temp.

4.4.3 Similarities – results that are the same for both membranes

- Surfactants in the permeate correlated with COD in the permeates, surfactants in the concentrate.
- Surfactants in the permeate anti-correlated with pure water flux and the content of oil in the permeate.
- The flux reduction of pure water after the experiments correlated with the concentration of silica, pH and with the interaction between temp. and the surfactant concentration and anti-correlated with flux.
- The flux after 24 hours correlated with silica and oil in the permeate and anti-correlated with salt.

4. Discussion

With which membrane the experiments had been performed showed out to have a big significance for the multivariate evaluation, wherefore most of the results and conclusions are built on the evaluations made for each membrane separately. A conclusion that can be drawn from this is that it is crucial to choose the right membrane for the purpose. The membranes used in these tests have the same cut-off, but one of them is more hydrophilic than the other one.

Some of the correlations and anti-correlations are almost obvious, such as the surfactant concentration in the permeate correlating with the surfactant concentration from the beginning, while others are more unexpected.

In accordance with earlier studies, for example in the EU project “Brite Euram”, higher temperatures usually give better fluxes, but also a worse separation. The separation of oil is highly dependent on the membrane properties though; high temperatures have the opposite effect on the separation of oil for the two different membranes.

The results of these experiments confirm the earlier statement that hydrophilic membranes give higher fluxes in general. This conclusion is also drawn from the earlier EU project “Brite Euram”.

In accordance with “Brite Euram” the flux is normally higher at higher temperatures. In these experiments the flux generally increase during the tests and for the hydrophilic membrane the increase is higher at low temperatures. Silica seems to counteract this flux increase for the hydrophilic membrane.

A weakness in the study is the method used to measure the concentration of oil and surfactants; the amount of surfactants are calculated from the amount of total extractable aliphatic hydrocarbons minus the amount of non-polar aliphatic hydrocarbons (=the amount of oil).

The pH in the solutions is higher than one of the membranes can manage. This fact could have influenced the results regarding parameters such as flux and the amount of surfactants etc in the permeate.

Appendix 3. Evaluation of different parameters of cleaning formulations in correlation with membrane filtration

1. Introduction

Within the frames of the European Union project Report, a series of tests has been made in order to state some conditions to enhance membrane filtration of cleaning formulations. Earlier in this project and partly in another earlier European Union projects some knowledge in the area has been found. In this report another final test within this project has been made, where the earlier knowledge has been used for verifying the important parameters. At the end of this report a summary of the conclusions drawn from the project as a whole is found.

To avoid loss of surfactants during membrane filtration, a low degree of separation is desirable. The focus has been on the use of hydrophilic membrane, which in the former studies has shown higher recovery rates for surfactants compared to the more hydrophobic one. The use of the hydrophobic membrane in this work is mainly to confirm the former results.

Two different formulations have been filtrated and compared in terms of flux through the membrane and separation of surfactants (analysis of COD). The formulations were produced specially for this purpose and their different properties are based on the results from earlier experiments and experiences. For the filtration two different membranes are used; one with a hydrophobic surface and one with a hydrophilic one.

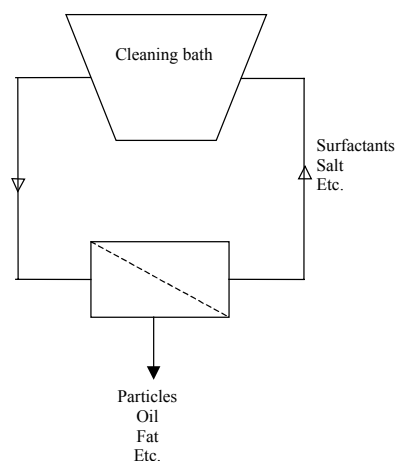


Figure 1 The figure above is a schematic picture of the membrane filtration of the cleaning solution. The chemicals (surfactants, salt, etc.) are recovered to the cleaning bath, while the membrane separates particles, oil and grease.

| Formulation 1 “Good” | Formulation 2 “Bad” |
|--|---|
| - “Good” for membrane applications (hydrophilic membranes) according to earlier studies. | - “Bad” for membrane applications (hydrophilic membranes) according to earlier studies. |
| - High pH (around 12) | - Neutral pH (7) |
| - Low amount of surfactants | - High amount of surfactants |
| - High amount of silicate | - Sequestering agent and corrosion inhibitor |

2. Experimental set up

Castrol prepared the cleaning formulations and their content was put together according to results from earlier studies.

| Formulation 1: | Formulation 2: |
|---------------------------|--|
| 0,25% Sodium silicate | 0,25% Sodium NTA Complexing agents |
| 0,05% Potassium hydroxide | 0,25% Organic corrosion inhibitor (mixture of amine – short chain acids) |
| 0,1% Non-ionic surfactant | 0,4% Non-ionic surfactant (same as formulation 1) |
| Water | Water |

Two different tubular membranes from PCI were used:

| | FP 100 | AN 620 |
|----------------|------------|-----------|
| Pore size | MW 100 000 | MW 25 000 |
| Hydrophilicity | + | +++++ |

The permeate was lead back to the bulk solution all through the experiment and no concentration of the solution was made. Temperature during filtration was 35°C and pressure 8 Bar.

After 24 hours of filtration, 25 ml of antifoam was added to the formulation and the filtration was continued for some hours.

3. Results

3.1 Flux properties

The difference between the formulations affects the flux through the membranes. There are also differences between the two membranes in how their fluxes are influenced by the formulations.

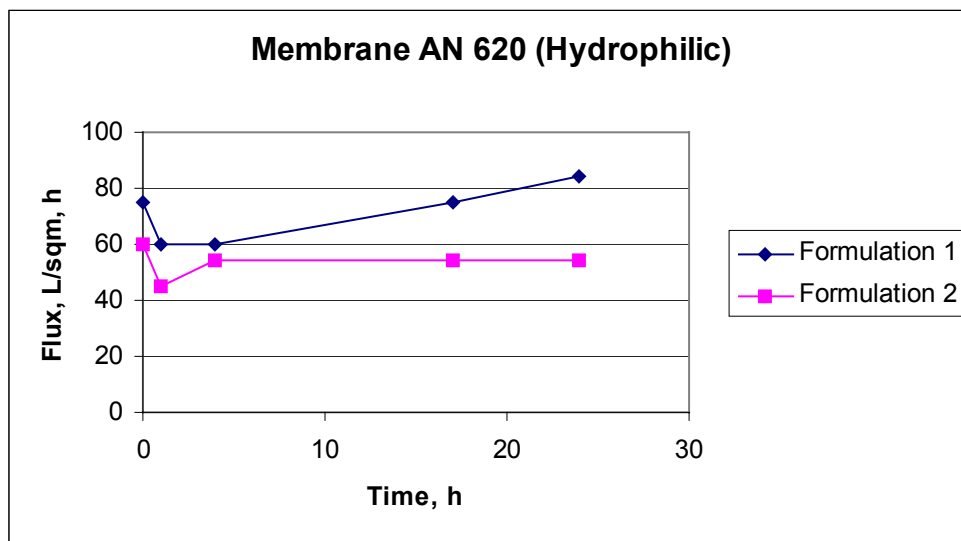


Figure 2. The hydrophilic membrane shows that the formulation 1 (“good”) gives a higher flux through the membrane than the other formulation.

For the hydrophobic membrane the situation is the opposite – the “bad” formulation 2 gives a higher flux.

Flux after 24 hours:

| Membrane | Formulation 1 | Formulation 2 |
|----------|---------------|---------------|
| FP 100 | 120 L/sqm, h | 168 L/sqm, h |
| AN 620 | 84 L/sqm, h | 54 L/sqm, h |

The formulations have the opposite impact on the two membranes; for the hydrophobic FP 100 membrane formulation 2 gives a higher flux through the membrane, while formulation 1 is better suited for the hydrophilic AN 620 membrane. The higher flux through FP 100 is mainly an effect of its larger pore size.

3.1.1 Addition of antifoam

After 24 hours of filtration, 25 ml of antifoam was added to the solutions. The antifoam did not affect the flux of the hydrophilic membrane at all. For the hydrophobic membrane, the flux declined in both experiments – with both formulations.

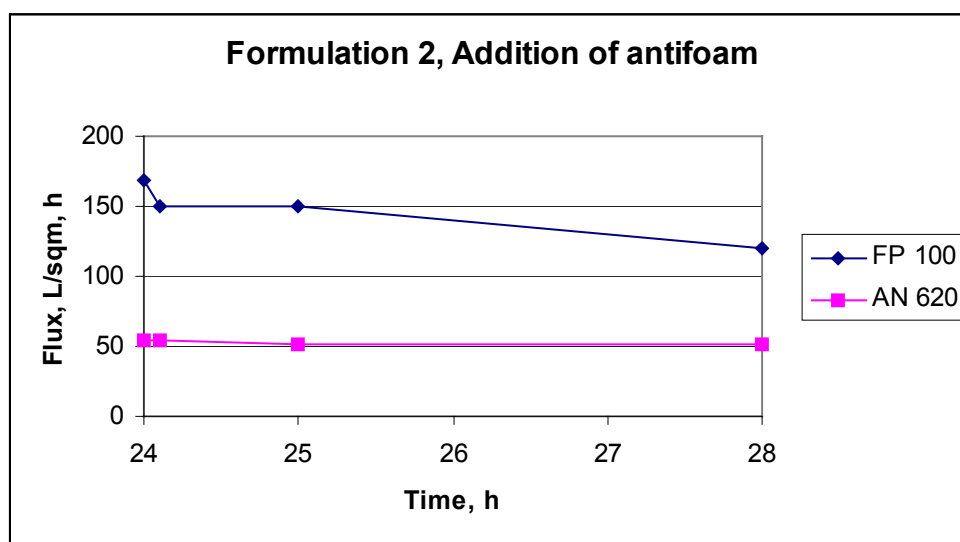


Figure 3 25 ml of antifoam was added after 24 hours of filtration in order to see how it affected the flux through the membranes. The flux of the hydrophobic FP 100 membrane has declined from 168L/m², h to 120L/m², h. The hydrophilic AN 620 membrane shows very little flux decline.

The addition of antifoam affected the flux through the FP 100 membrane in a negative way. The flux through the hydrophilic AN 620 membrane was not significantly affected by the antifoam.

3.2 Separation properties

The separation properties of the membranes was measured through analyse of COD. The COD represents the surfactants and the task is to recover the surfactants to a high degree. The FP 100 membrane shows a recovery of COD of 83 and 78% respectively. The AN 620 membrane lets through all chemicals to the permeate in the formulation 1 experiment and has a slightly less separation of COD than the hydrophobic membrane for formulation 2.

| Membrane | Formulation 1 | Formulation 2 |
|----------|---------------|---------------|
| FP 100 | 83% | 78% |
| AN 620 | 100% | 82% |

The hydrophobic FP 100 membrane has retained the chemicals to a higher degree than the hydrophilic AN 620 membrane, although the FP 100 membrane has a larger pore size.

4. Discussion and conclusions

Looking at the hydrophilic membrane (AN 620) formulation 1 gives a better flux through the membrane than formulation 2 (84 and 54 L/m², h respectively). This supports the thesis from the earlier work done within the project. An interesting result is that for the hydrophobic membrane (FP 100) the situation is the opposite i.e. formulation 2 gives a better flux through the membrane (120 and 168L/m², h respectively).

An interesting result is also that silicates do not cause any problems in membrane filtration. In many cases silicates have been pointed out to cause fouling problems and one reason for that could be that silicates contribute to a high initial flux, and thereafter a quick flux decline. If only looking at the flux change, silica then seem to have a bad effect on the flux, but we have seen, both in this and earlier studies, that the overall flux often is higher with silicates in the formulation (see figure 4 below).

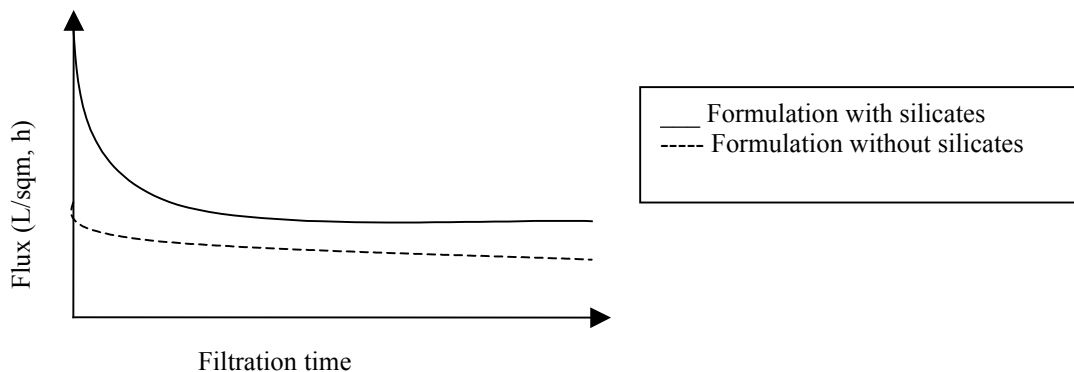


Figure 4 Illustration of the flux curves of formulations with / without silicate. When silicates are added to the formulation, the initial flux is very high. The flux then drops drastically, but when the flux has stabilised, the formulation with silicates still gives a higher flux compared to the formulation without silicates.

The addition of antifoam after 24 hours of filtration has a negative effect on the flux for the hydrophobic FP 100 membrane, while the addition of antifoam shows almost no effect at all on the hydrophilic AN 620 membrane.

For practical reasons a hydrophilic membrane with low cut off is used in these tests (MW 25 000). To achieve a higher flux (capacity) membranes with higher cut off is to prefer. Our experience is that the use of membranes with higher cut off does not have negative effect on the separation properties for oil and grease.

The results show that the choice of cleaning formulation highly affect the ability to extend the life length of the bath through membrane filtration. It is important to chose the right combination of cleaning formulation and membrane, since this study shows that different membrane qualities (hydrophilicity) is suitable for different types of chemical formulations.

Summary of conclusions drawn from this study and earlier work done:

| | Flux properties | Recovery rate |
|--------------------|---|--|
| Membrane | Hydrophilic membrane superior | Hydrophilic membrane superior |
| Surfactants | Low concentrations gives better flux | Low concentrations gives better recovery rate |
| Silicates | Silicates in formulation gives higher flux | Silicates contribute to better recovery rates. |
| Antifoam | Usually no problem when using hydrophilic membranes | No effects seen |
| High pH | A high pH often correlates with higher flux | A high pH correlates with a good recovery rate |

Biocides and wetting agents have shown to counteract flux decline.

These conclusions are valuable information and useful knowledge at the installation of new recycling techniques. In most cases we still recommend to use pilot scale tests to avoid a lot of problems after installation in full scale.

Appendix 4. Rinsing requirement - a small test in lab scale

1. Introduction

Within the frames of the European Union project Report, a minor lab scale test has been performed in order to get a clue of how the cleanliness of the rinse water influences the quality of degreased metal goods.

Usually large efforts are made on cleaning processes, trying to optimise the cleaning formulations with respect to the demands on cleanliness of the goods. Very few references has been found concerning the impact of the rinse water; the stage which almost always follows after a cleaning process, and of course also has a large impact on the quality of the goods. How clean must the rinse water be to reach a satisfactory quality of the product? Could the rinse water be too clean? Some earlier studies indicate that too clean rinse water could cause problems on the goods surface, just like a too dirty solution. To mention one example, the use of de-ionised water in one case caused a larger degree of corrosion compared to rinsing with ordinary tap water. What parameters are important in this context? Should the rinse solution contain a certain amount of some chemicals? Are there any other components that should be strictly avoided? This work is a little effort in order to get a clue about these things.

The experiment was performed with a factorial design, and the results were evaluated with multivariate methods. The factors that represent the quality parameters in the test are the amount of organic carbon at the surface, the amount of particulate CaCO_3 on the surface (analysed with IMC) and the relative corrosion on the surface of the goods (visual comparison of the different test pieces).

All experiments were made on clean iron sheets and the parameters varied in the rinse waters are:

- Amount of particles
- pH
- Concentration of surfactants
- Concentration of salt
- Concentration of oil in the solution

2. Materials and methods

All parameters are varied at two levels and the clean iron sheets are pre-washed before the test through dipping in a strong alkaline cleaning solution containing mild steel

corrosion inhibitor. For each experimental set-up, 3 iron sheets were attached to a holder with a rubber band and vertically put down into a beaker with the test solution. The sheets were exposed for the tempered (40°C) test solution for 2 minutes before they were taken up vertically and put in a drying cabinet before the analyses.

Mild steel was used for test material. Specifically a special reference material was used denoted "Q-panel type R-36" from "Q-panel lab products". This is cold rolled and annealed mild steel that is suitable for deep drawing. The surface, with dull, matt surface texture, is protected by light corrosion protection oil.

Table 1 Varied parameters in the test.

| Parameter | Level 1 | Level 2 |
|------------------------------|----------|-----------|
| Particles, CaCO ₃ | 30 mg/l | 1000 mg/l |
| pH | 7 | 11 |
| Conc. Surfactant | 10mg/l | 300 mg/l |
| Conc. salt (NaCl) | 0,5 mg/l | 200 mg/l |
| Conc. Oil | 2 mg/l | 30 mg/l |

The test has a factorial design and is performed with a total of $2^5=32$ experiments (for the disposition and data of the experiments, see appendix 1).

Three different parameters are analysed after the exposure:

- Organic carbon at the surface of the test goods
- Relative amount of CaCO₃ at the surface of the goods
- Corrosion of the goods surface

The organic carbon and relative CaCO₃ are analysed with IMC and the relative corrosion is assessed by visual inspection. (The total table with all the data is presented in appendix 1).

All results are thereafter evaluated with multivariate methods (Modde), in order to examine which parameters affect one another and which has the largest impact on the quality of the surface. The entire evaluation is enclosed to the report (see appendix 3).

3. Results

For the response parameters, the significant correlations were the following. (The +- signs indicates how strong the correlation is - +++++ indicates the strongest correlation and + the weakest.)

Amount of organic carbon left on the surface:

| Constitution of rinse water: | Impact on steel surface: |
|--|--|
| <ul style="list-style-type: none"> ◆ A high amount of surfactants (+++) ◆ A combination of a low amount of CaCO₃ together with a low pH (+) | Contribute to a larger amount of organic carbon at the surface of the goods. |

Amount of Calcium carbonate left on the surface:

| Rinse water: | Impact on steel surface: |
|--|---|
| <ul style="list-style-type: none"> ◆ A high amount of CaCO₃ (+++++) ◆ A low amount of surfactants (++) | Contribute to a high amount of CaCO ₃ at the surface of the goods. |

Corrosion properties of the rinsed and dried steel:

| Rinse water: | Impact on steel surface: |
|---|--|
| <ul style="list-style-type: none"> ◆ A high amount of CaCO₃ (+++++) ◆ A low pH (++++) ◆ A low amount of oil (++) ◆ A combination of high amounts of CaCO₃ and oil (++) ◆ A combination of high pH and a high amount of oil (+++) | Contribute to a larger extent of corrosion on the goods. |

The “variable importance plots” (see appendix 2) show which parameters have the largest impact on corrosion, CaCO₃-particles and corrosion, respectively. In terms of corrosion, the pH in the rinse solution has a larger impact on the result than the amount of oil (see appendix 2).

The multivariate evaluations indicate that some of the correlations are very weak, and that the varied parameters in the test do not explain all the variation on the goods quality.

One of the correlations is a bit contradictory; a high pH and a high amount of oil, each individually counteracts corrosion on the goods, but the two parameters together seem

to have the opposite effect. The pH, though, has a larger impact on the rinse result than has the amount of oil.

The multivariate evaluation shows that the varied and analysed parameters in the experiment do not explain all variation. There could for instance be a variation of the quality of the test pieces from the beginning.

4. Conclusions

Since this is only a small-scale test, one can only get some indications of how the constitution of rinse water could affect the quality of the steel after degreasing. As what is true for all processes, it is hard to generalise a rinsing process. All degreasing processes have its unique composition of steel quality, surfactants, corrosion inhibitors etc. There are also different demands for different applications and a “general perfect rinse water” does not exist.

For the system studied in this work, some conclusions can be drawn. Surfactants in the rinse water contribute to a higher amount of organic carbon at the surface of the goods. It is interesting to notice that the amount of oil varied in the test has no significant impact on the organic carbon of the goods surface. Neither has the concentration of salt affected the goods quality according to these analyses.

In terms of corrosion, the higher pH, and the larger amount of oil in the rinse solution, individually but not together, has had a good impact on the goods with less corrosion.

The main focus of the project is particles on surfaces, and the best results attaining a particle free surface of the goods (CaCO₃-free) is to keep the content of CaCO₃-particles in the rinse solution as low as possible and have a certain amount of surfactants in the rinse water.

This supports the thesis that a "too clean" rinse solution could have negative effect on the quality of degreased steel. Surfactants in the solution could for instance enhance run off of water with particles from the goods after rinsing. This results in lower amounts of particles left on the surface.

Appendix 4:1

| Nr | Experimental parameter | | | | | Results | | |
|----|---------------------------|----|--------------------|--------------|-------------|----------------------------|---|-------------------------------------|
| | CaCO ₃ mg/l | pH | Surfactant mg/l | NaCl mg/l | Oil mg/l | C org mg/m ² | Relative CaCO ₃ 0=non, 5=most | Relative Corrosion 1=good, 3=bad |
| 1 | 30 | 7 | 10 | 0,5 | 2 | 6,22 | 2 | 2 |
| 2 | 1000 | 7 | 10 | 0,5 | 2 | 7,8 | 3 | 3 |
| 3 | 30 | 11 | 10 | 0,5 | 2 | 12,9 | 1 | 1 |
| 4 | 1000 | 11 | 10 | 0,5 | 2 | 8,8 | 4 | 2 |
| 5 | 30 | 11 | 300 | 0,5 | 2 | 10,7 | 2 | 1 |
| 6 | 1000 | 11 | 300 | 0,5 | 2 | 8,39 | 4 | 1 |
| 7 | 30 | 7 | 10 | 200 | 2 | 7 | 1 | 3 |
| 8 | 1000 | 7 | 10 | 200 | 2 | 7,57 | 4 | 3 |
| 9 | 30 | 11 | 10 | 200 | 2 | 6,35 | 1 | 2 |
| 10 | 1000 | 11 | 10 | 200 | 2 | 7,28 | 3 | 2 |
| 11 | 30 | 7 | 300 | 200 | 2 | 9,68 | 1 | 3 |
| 12 | 1000 | 7 | 300 | 200 | 2 | 11,3 | 2 | 3 |
| 13 | 30 | 7 | 10 | 0,5 | 30 | 8,34 | 2 | 1 |
| 14 | 1000 | 7 | 10 | 0,5 | 30 | 5,82 | 5 | 1 |
| 15 | 30 | 7 | 300 | 0,5 | 30 | 8,14 | 1 | 1 |
| 16 | 1000 | 7 | 300 | 0,5 | 30 | 8,63 | 2 | 3 |
| 17 | 30 | 11 | 300 | 0,5 | 30 | 7,27 | 1 | 1 |
| 18 | 1000 | 11 | 300 | 0,5 | 30 | No data | Analysis failure | 1 |
| 19 | 30 | 7 | 10 | 200 | 30 | 6 | 2 | 1 |
| 20 | 1000 | 7 | 10 | 200 | 30 | 8,41 | 3 | 3 |
| 21 | 30 | 11 | 10 | 200 | 30 | 6,75 | 1 | 1 |
| 22 | 1000 | 11 | 10 | 200 | 30 | 4,5 | 4 | 2 |
| 23 | 30 | 7 | 300 | 200 | 30 | 9,09 | 1 | 1 |
| 24 | 1000 | 7 | 300 | 200 | 30 | 8,23 | 3 | 3 |
| 25 | 30 | 11 | 300 | 200 | 30 | 15,1 | 0 | 2 |
| 26 | 1000 | 11 | 300 | 200 | 30 | 6,6 | 3 | 2 |
| 27 | 500 | 9 | 100 | 50 | 15 | 7,79 | 1 | 3 |
| 28 | 500 | 9 | 100 | 50 | 15 | 5,7 | 2 | 3 |
| 29 | 500 | 9 | 100 | 50 | 15 | 8,68 | 2 | 2 |
| 30 | 500 | 9 | 100 | 50 | 15 | 5,37 | 2 | 2 |
| 31 | 500 | 9 | 100 | 50 | 15 | 7,69 | 3 | 2 |
| 32 | 500 | 9 | 100 | 50 | 15 | 6,12 | 2 | 3 |

Appendix 4:2

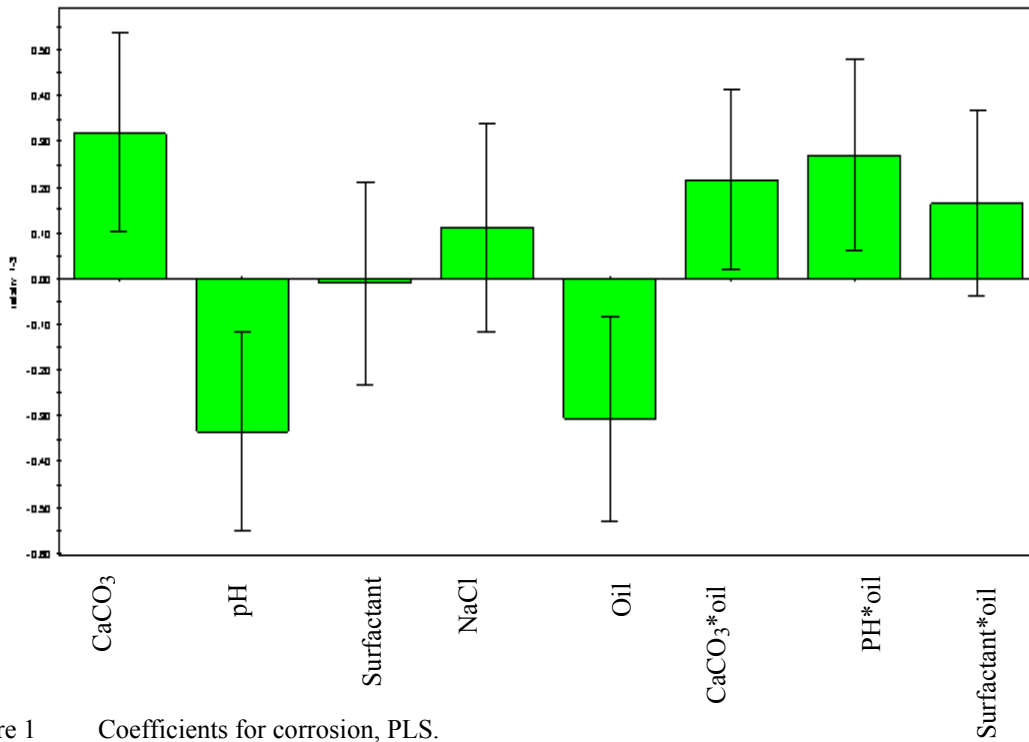


Figure 1 Coefficients for corrosion, PLS.

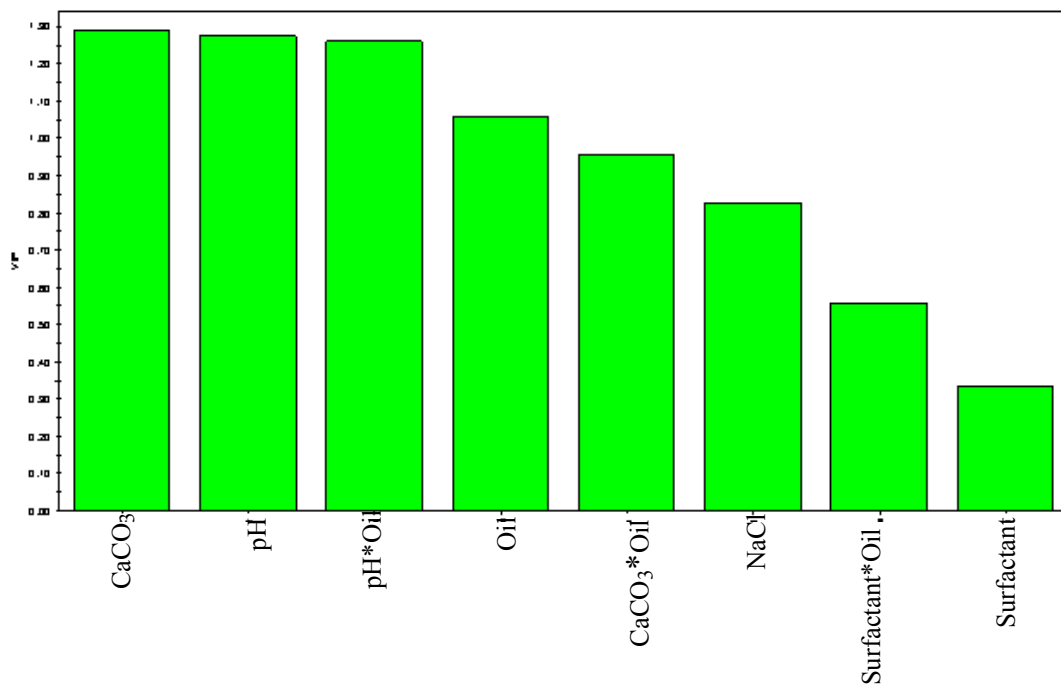


Figure 2 Variable importance plot, corrosion.

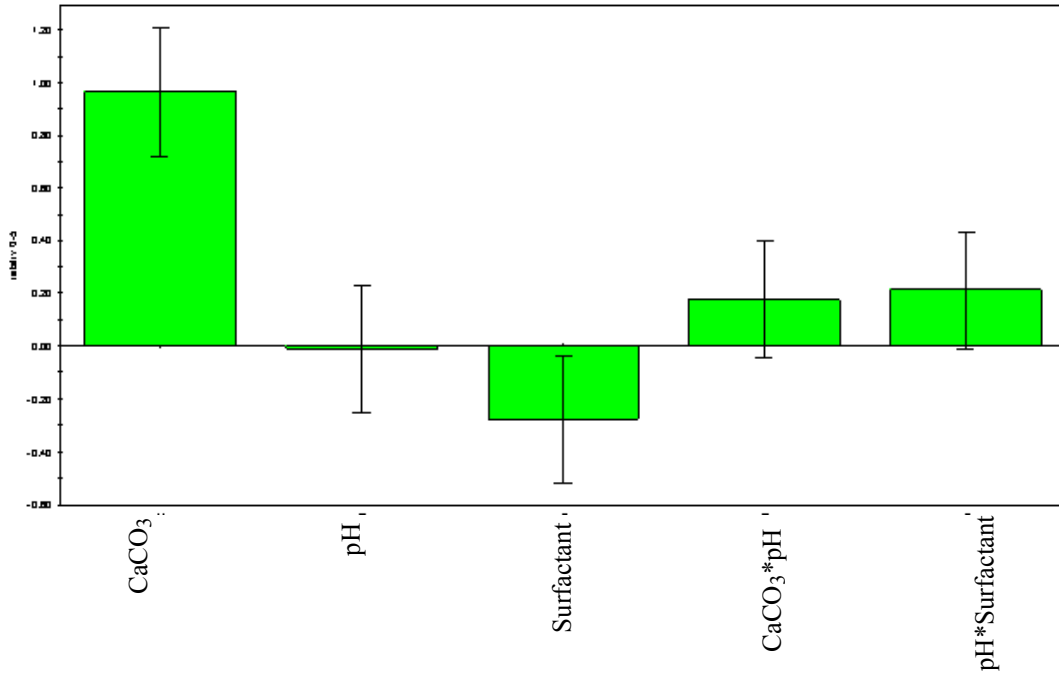


Figure 3 Coefficients for CaCO₃.

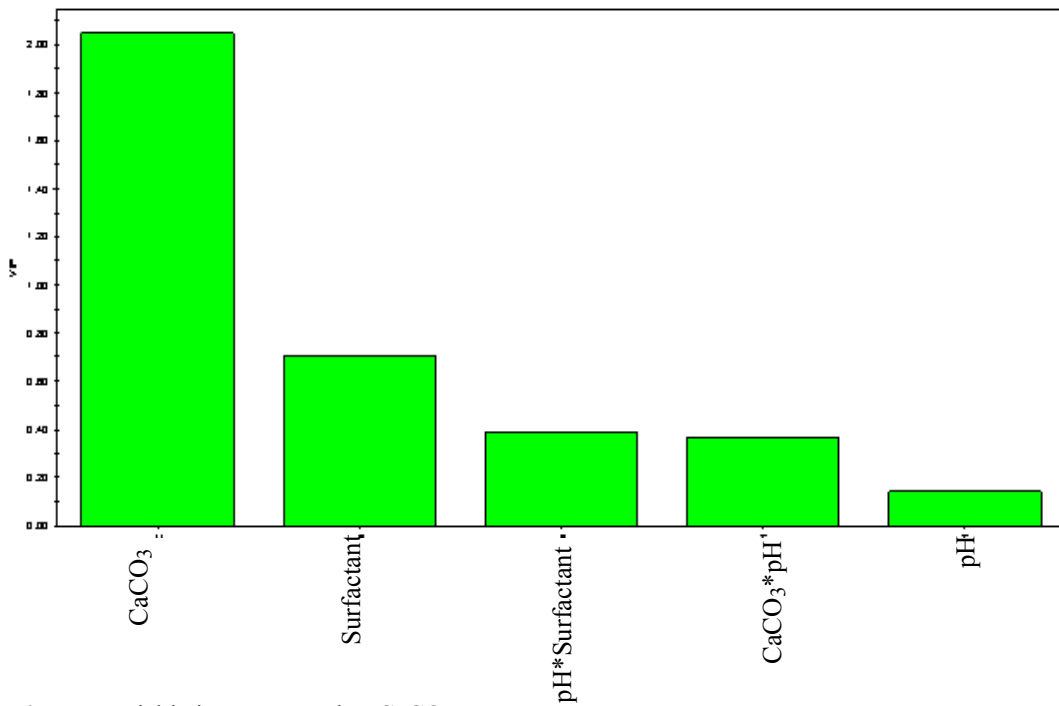


Figure 4 Variable importance plot, CaCO₃.

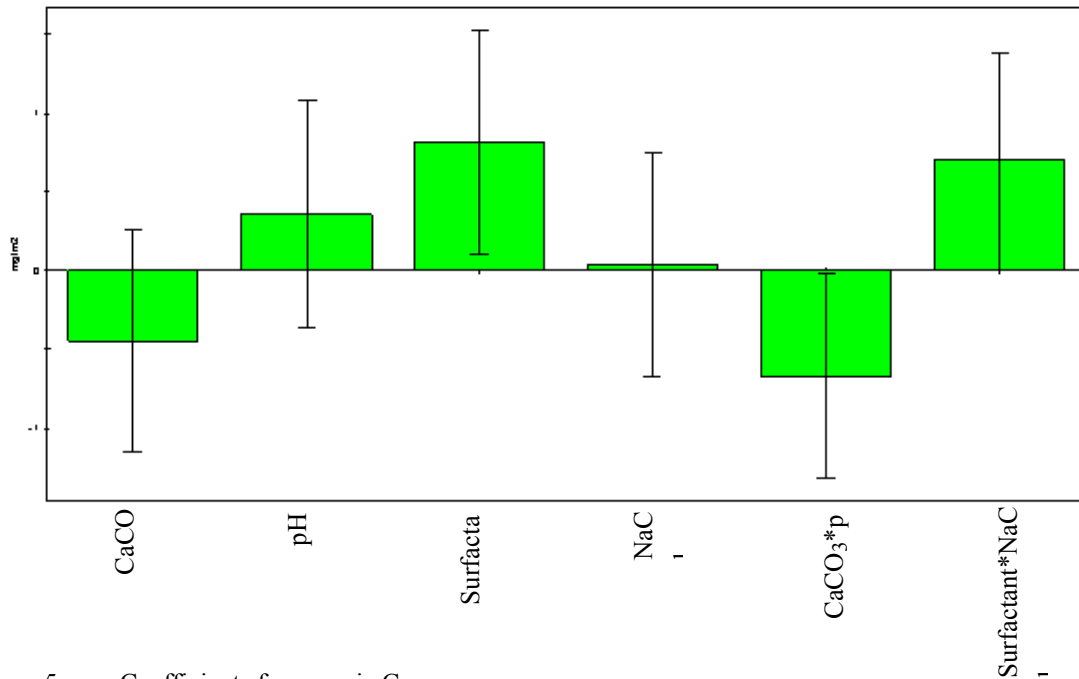


Figure 5 Coefficients for organic C.

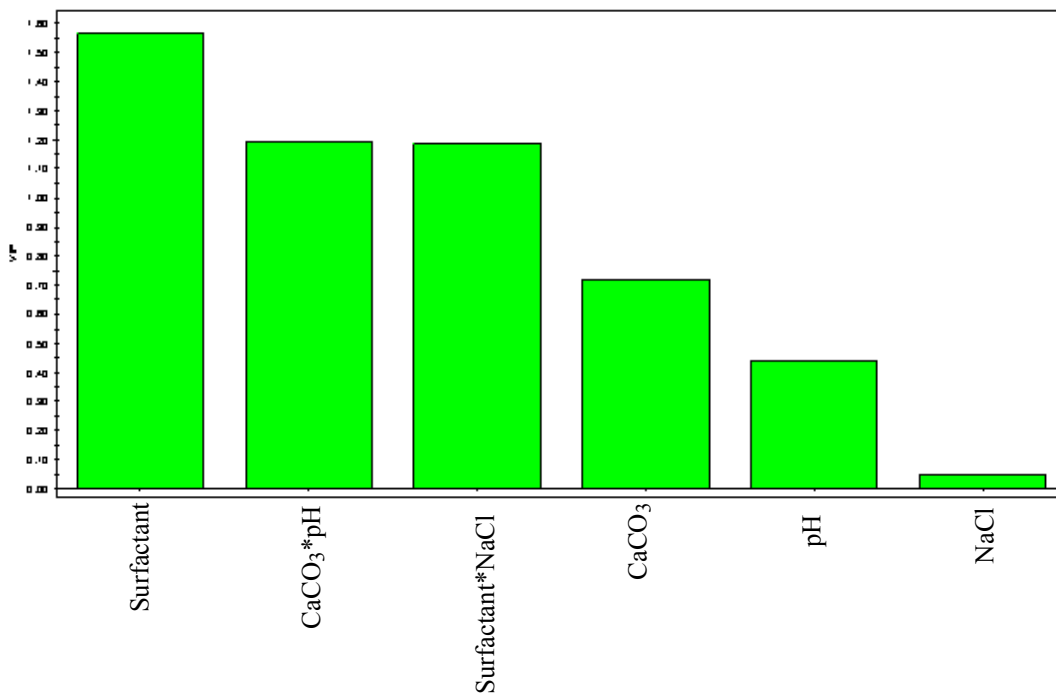


Figure 6 Variable importance plot, organic C.

Appendix 5. Membrane filtration of rinse water after degreasing - How to attain a successful process

1. Introduction

Many industries struggle to minimize their water consumption due to environmental as well as economical or regulatory aspects. One way to reduce the water consumption is to reuse rinse water, for example by introducing closed loop systems. Through installation of separation technologies, it is possible to reuse water as well as chemicals used in the process.

In order to separate water from process chemicals, oil or other impurities, membrane filtration is a coming technique in process and manufacturing industries. It has many advantages, but also some weaknesses. The membranes are sensitive for fouling; some substances can precipitate on the membrane surface and contribute to a lowered flux through the membrane. Due to chemical reactions between different substances in the solution, fouling of the membranes is often a complicated matter, hard to fully understand.

The experience says that it is often easier to attain a well functioning membrane filtration of the cleaning bath, compared to treating the more diluted rinse water. Although problems often occur, little work has been made in the area of rinse water recycling.

In many cases there have been large problems with fouling of membranes in the rinse water system after the degreasing stage. Sometimes the process works out fine, but sometimes and suddenly the flux decrease appreciably. A series of membrane tests has therefor been made in order to identify what causes the fouling problems.

2. Performance

A series of experiments have been performed, with authentic rinse water from the industry as well as synthetically produced rinse water, and a lot of different parameters have been taken under consideration in the work trying to find what causes the fouling problems.

Synthetic rinse water from a degreasing process has been prepared from clean degreasing chemicals mixed with water. In the different tests some parameters have been varied to investigate their impact on the flux through the membrane.

The membrane used in the tests is a spiral wound nanomembrane (Desal DK 2540) and the chemicals used are fatty alcohol polyetoxylate, sodium xylolsulphonat and potassium tetraborate.

Parameters that has been varied and studied through the test are:

- Age of the bath
- Air exposure of the bath
- Content of calcium
- Tap water contra de-ionized water
- Content of oil
- pH
- Addition of complexing agent

The choice of studied parameters is based on realistic conditions – parameters that can vary in the process. For example in some cases the filtration problems appear first after a certain time, why parameters such as ageing are considered. In some processes rinse water is sprayed on to the goods, with high degree of air-exposure as a consequence. Calcium may have its origin as pollution on the goods surface, as filler particles or from tap water. The use of tap water can affect the water quality, with its content of calcium, magnesium or carbonate for example.

Each of the experiments is first filtrated without concentration during 24 hours. The permeate produced is constantly lead back to the bulk solution. Thereafter the solution is concentrated in stages; VRF 2, VRF 5 and in some cases VRF 10. VRF = volume reduction factor, is the degree of concentration of the solution – VRF 2 means that half of the original volume remains, it is concentrated two times, at VRF 10 only one tenth of the original volume remains.

All experiments were performed at 40°C and 15 Bar pressure.

3. Results

Tap water contra de-ionised water

The experiments where clean new chemicals are used in de-ionized water show good results concerning flux. When using de-ionised water the flux was pretty stable even at VRF 10, after 10 times of concentration. When instead tap water was used with the clean new chemicals, the flux falls significantly (see figures 1 and 2 below).

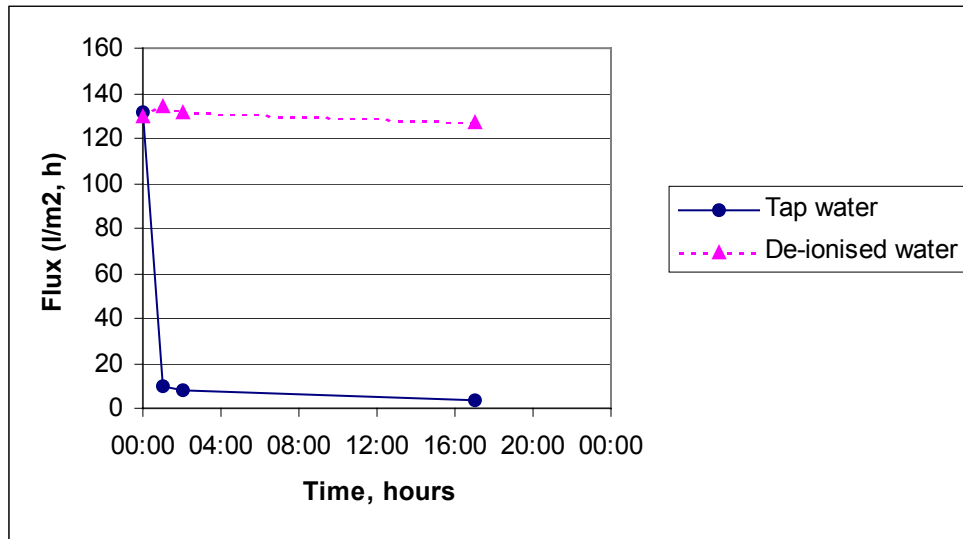


Figure 1 Differences in flux between experiment made with tap water and de-ionised water. When using de-ionised water the flux is stable throughout the separation cycle, but with tap water the flux drops drastically already after short time.

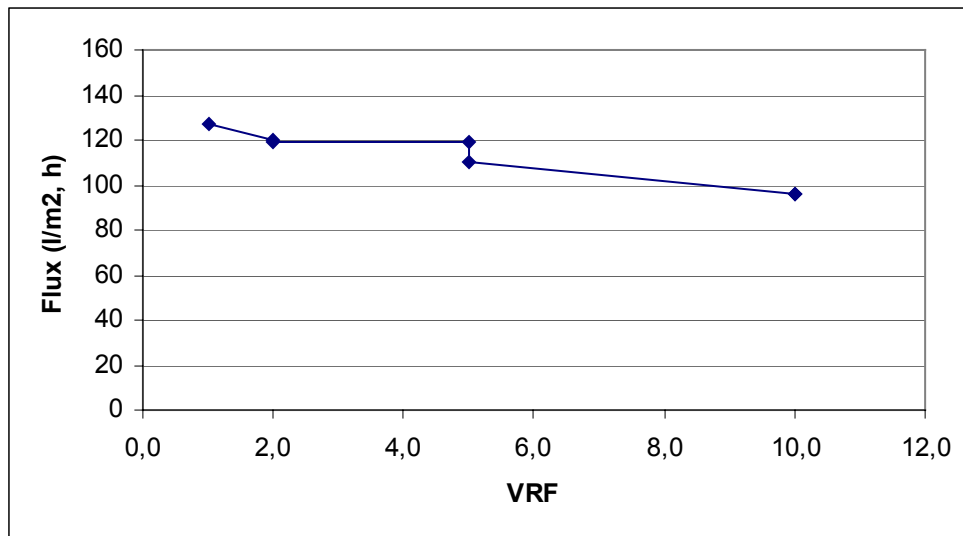


Figure 2 Same experiment as figure 1 above, but concentration of the solution containing de-ionised water. The flux stays almost the same during all the concentration.

Air exposure and addition of calcium

In the next experiment, the synthetically produced rinse bath had been air exposed during two weeks before the filtration. Air was bubbled through the solution constantly during that period. The flux was very stable already from the beginning of the filtration and the air exposure does not seem to have a significant effect on the flux. Since the

solution during the air exposure has been made in room temperature, the conclusion is drawn that aging of the solution does not seem to be a significant problem (see figure 3 below).

In order to resemble a process where tap water is used as rinse water, 30 mg/l of calcium (as CaCl_2) was added to a solution containing clean new chemicals mixed with de-ionised water. The addition of calcium was made after 6 hours of filtration. The stable flux shows a drastic decrease as an immediate response to the addition (see figure 3 below).

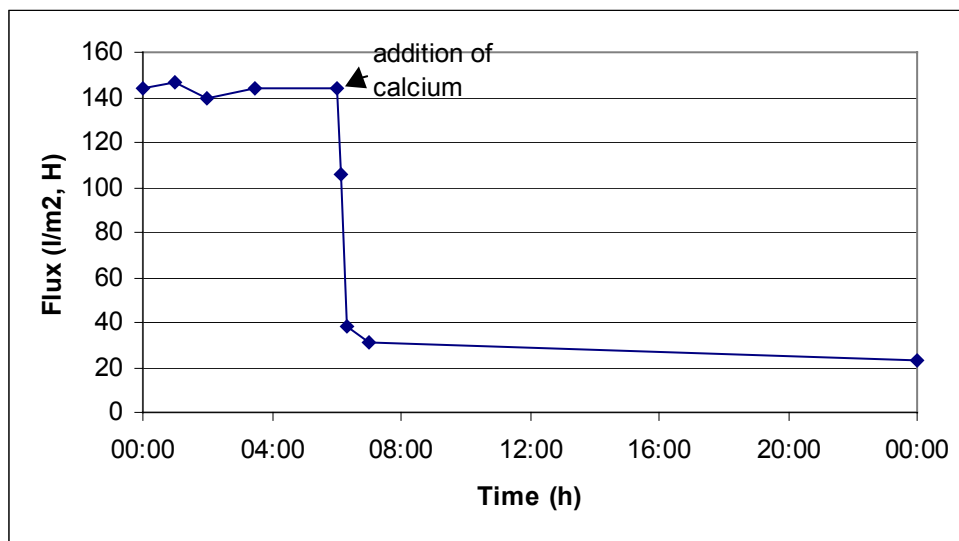


Figure 3 Addition of calcium 30mg/l after 6 hours of filtration. The flux drops drastically within a few minutes after the addition.

Complexing agent

In order to find out whether addition of a complexing agent could prevent fouling of the membrane, 1mM NTA (nitrilotriacetic acid) was added to the simulated rinse water. Initially the NTA was dispersed in 12 litres de-ionized water and filtrated during some hours, to study the impact of the complexing agent itself on the flux over the membrane. The rest of the rinse water containing 30 mg/l Ca was added to the NTA solution during the filtration. The membrane filtration continued during some further hours before concentration of the solution started.

Through this approach one also get an answer to the question how quick the reaction between the complexing agent and the calcium is. If the reaction is slow, an initial flux decline would be seen, before the NTA would have bound the calcium that causes the fouling of the membrane.

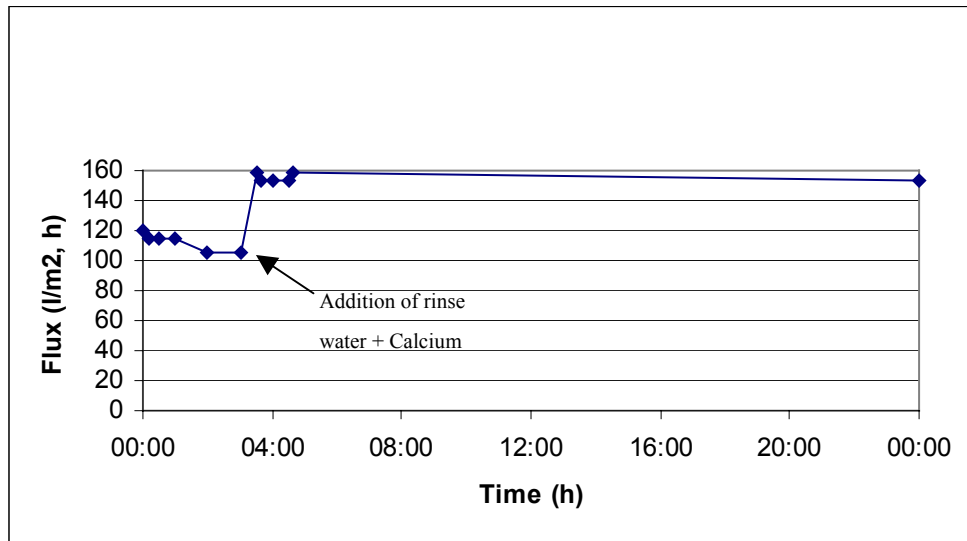


Figure 4 Addition of the complexing agent NTA to the solution contributes to keep the flux up, in spite of the calcium added to the solution. NTA itself, in concentrated form contributes to lower the flux a little bit (see the first 3,5 hours of filtration). When the rest of the solution with calcium is added, and the NTA is diluted the flux is recovered.

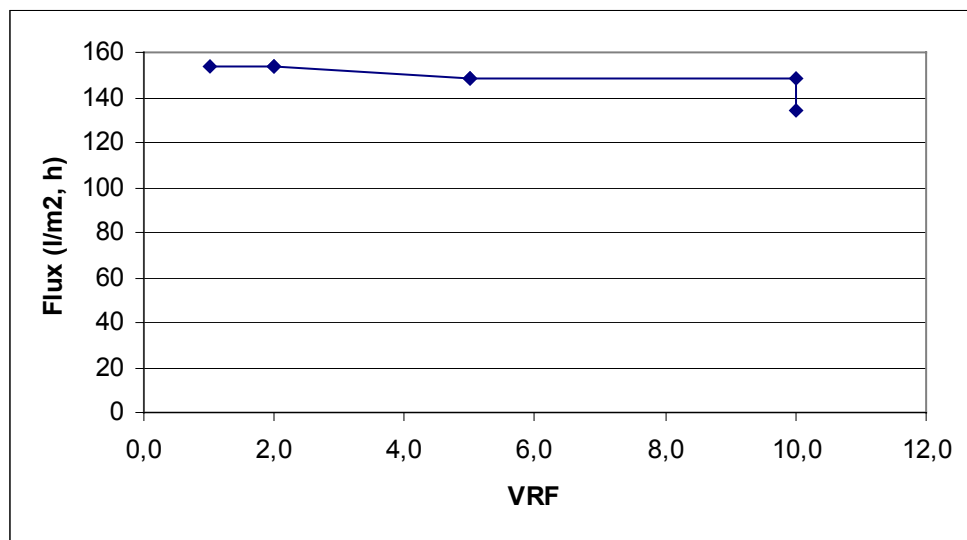


Figure 5 Concentration of the solution containing complexing agent and Ca shows a good flux all throughout the concentration, which is driven until one tenth of the originally solution remains (VRF 10).

The complexing agent itself contributed to lower the flux a little bit, but addition of the rest of the solution shows that this is a possible solution to the fouling problem and that the reaction between the complexing agent and the precipitated chemicals in the solution is a fast reaction.

A similar set-up with another complexing agent – EDTA – shows corresponding results.

Oil

Experiments made with different amounts of oil shows that this is not of any major importance for the membrane flux.

pH

When using tap water in the rinsing bath, the pH has a little impact on the flux. High pH, above 11 gives a slightly better flux than the solutions with lower pH. The flux is however still much lower than with de-ionised pH.

Using de-ionised water, the pH has little importance for the flux during membrane filtration.

4. Conclusions

The most important single parameter is doubtless calcium. Even at such low concentrations as 30 mg/l (=the concentration of calcium in the tap water of Stockholm) calcium decreases the flux drastically.

It is not calcium alone, though, that causes the problem. Without the cleaning chemicals tap water (containing 30mg/l calcium) could be membrane filtrated without significant problems.

A solution to the problem could be avoiding calcium in the solution by using de-ionized water. Another possibility showed in the tests is addition of complexing agent. A concentration of 10 mM of NTA is sufficient to counteract the flux decline caused by the calcium. The chemical reaction between the complexing agent and calcium showed out to be a very quick reaction.

When installing close looped systems and recycling of the rinse water, the water consumption is decreased to a minimum. Since the amount of “new” water added to the system is kept on a low level, the amount of calcium added also becomes low. If the choice for the process is to continue using tap water, only a very small amount of complexing agent is needed when the amount of calcium is minimised. On the other hand, the equipment for producing de-ionised water could be small and will not have to mean investment.

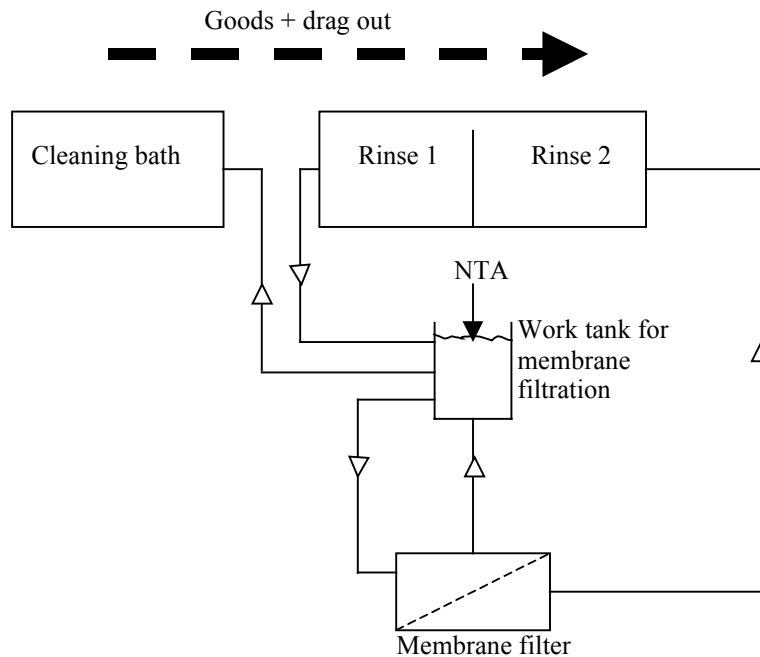


Figure 6 Model for recycling of the rinse water. Complexing agent is added to the work tank and the system is run in batches.

To further minimise the concentration of complexing agent in the baths, a system with a work tank could be used (see figure 6 above). The complexing agent is added to the work tank and will not pass through the membrane with the cleaned rinse water.

New tests at Sandvik, where the rinse water is de-ionised by steam condensation shows promising results.



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