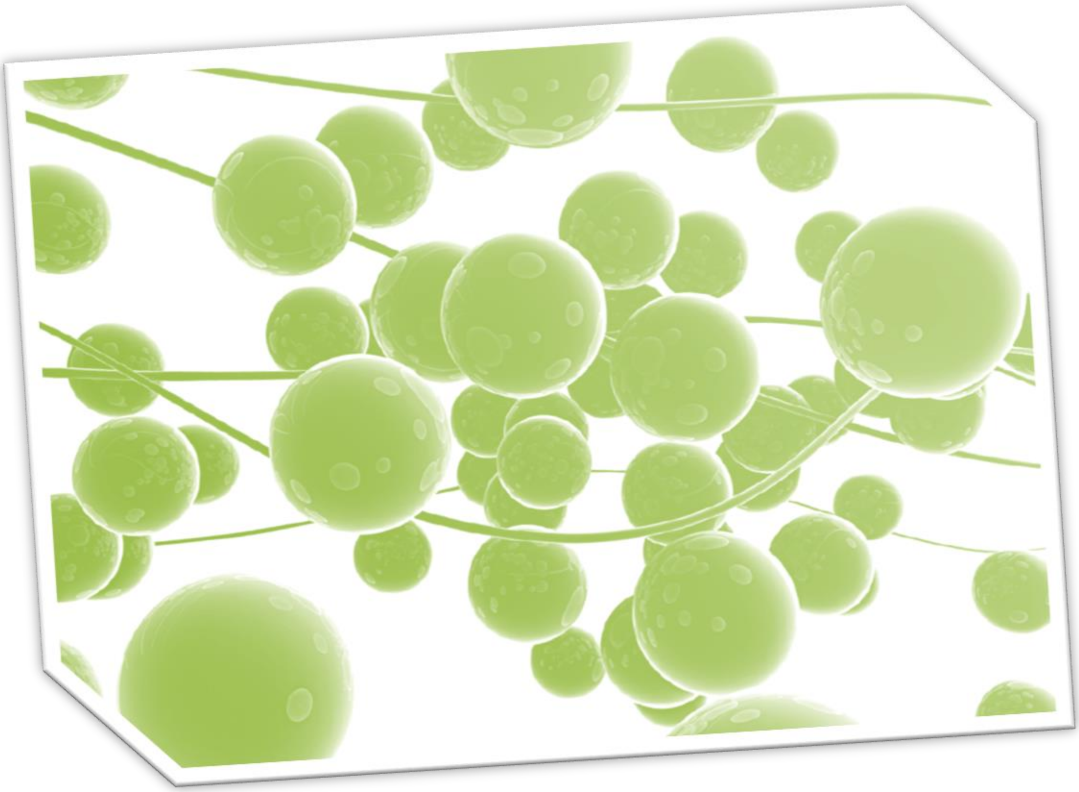

The effect of water quality on the sustainable production of colloidal silica particles

Master of Science Thesis in the Master Degree Programme, Materials Chemistry and Nanotechnology

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Abstract

Over the last few years, sustainability has become firmly anchored and a fully integrated aspect in AkzoNobel's business processes and strategy. As one of the leading producers of synthetic silica sols, major business opportunities can be unlocked by applying sustainability thinking to their industry. As of now, the innovative works of AkzoNobel is often driven by sustainability, who are committed to reduce their environmental impact and deliver more value to their customers, with the use of fewer resources. This sustainability development has lead AkzoNobel "Pulp and Performance Chemicals" in Bohus to try and take back and recycle water streams in their silica sol process.

The recirculation of water has given rise to an infrequent problem in the silica sol process that results in an uncontrolled agglomeration of the colloidal silica particles and ultimately reduces the overall quality of their products. The agglomeration is believed to be the consequence of contamination or certain quality parameters in the recycled water and can be detected as a reduction of the filter capacity of the raw material waterglass over a filter. This problem is the main focus of this thesis, which has been dedicated to investigate recycled waters and understand the cause behind the problem. In order to find a solution and eventually enable more water to be recycled.

The results of the investigation of recycled waters showed that small concentrations of seed-particles greatly influence the filter capacity of waterglass. Further results indicate that the evocation of product into the recycled water streams is a probable cause to the infrequent problem and the influence can be considerable reduced by ultra-filtration.

Acknowledgements

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1 Introduction

The development of industrial colloidal silica or silica sol is growing increasingly in both traditional and novel industries. A silica sol is a stable disperse solution of silica nanoparticles. The surface of the particles can be functionalized with range of different properties to suit numerous different applications, such as glass, ceramics, paper and pulp technology, catalysts, and many more and more to come [5]. The great diversity of colloidal silica makes it a fascinating material and is the biggest reason to its increasing attention.

AkzoNobel is the leading producer of industrial synthetic colloidal silica sols with a large network of industrial plants around the globe. In order to remain on top of the market, it is of outmost importance for AzkoNobel to meet the expectations of their customers and be able to guarantee them consistent high quality products. This includes having an efficient and dependable manufacturing process. However, currently AkzoNobel is facing an infrequent issue relating to the filter capacity of the silica sol process, resulting in spread of the homogeneity which severely reduces the quality of their end products. Previous research carried out on the issue by AkzoNobel has been unsatisfactory and failed to establish the root of the problem. The hypothesis is that the filter capacity issue originates by some means from the low water quality of re-circulated water streams in the silica sol process. Due to both cost and sustainability reasons it is also desired to recycle as much water as possible and consequently it is necessary to study the re-cycled waters more closely.

In this master thesis work an in-depth investigation of the quality parameters of recirculated water is launched, to gain knowledge and try to understand how the recycled water affects the filter capacity in the silica sol process. The purpose, ultimately, is to be able to prevent the reduction in the filter capacity. As it would increase the reliability and efficiency of the silica sol process and allow for more water to be recycled, which in hand increases the sustainability and reduces the impact on the environment.

1.1 Aim of the thesis

This master thesis work is constructed around two main objectives: First, investigating how water quality parameters and relevant trace elements affect the filter capacity. We have decided to focus our attention on re-cycled condensate from the evaporator and permeate waters from the ultra-filters. The second objective is to evaluate the feasibility of different possible solutions to the reduction of the filter capacity. The procedure of the thesis will be done in two major steps:

1 Extensive mapping of the different water quality parameters effect on the filter capacity.
2 Examination and evaluation of possible solutions to the filter capacity issue.

1.2 Questions

In order to accomplish the aim of the thesis the following questions have to be answered:

- What previous research has been done on water quality in the silica sol process, can it be made useful in this thesis?
- What are the different quality parameters of the water streams that are relevant to investigate in the silica sol process?
- How are the quality parameters affecting the filter capacity?
- Can it be a synergic effect between the quality parameters causing the issue?
- What possible solutions or workup procedures could be applied to resolve the problem?

1.3 Limitations

To prioritize the most significant elements of the aim and achieve relevant results within the scheduled time frame, clear limitations were set. The main purpose is to investigate the quality parameters in respect to filter capacity. A selection of the most relevant quality parameters and recirculated water streams were determined by evaluating similar investigations made at AkzoNobel. The parameters were; density, conductivity, pH, turbidity, ratio of SiO_2: Na_2O and the recirculated streams were; condensate and permeate from small and large ultrafilters. Furthermore, the thesis will only cover the effect of the quality parameters in respect to the filter capacity and will not include other operations in the same production process.

Supplementary analyses of samples are limited to samples demonstrating particularly relevant results, due to the expensive cost of each analysis, and will be done by the FOU department at AkzoNobel in Bohus.

It should be realised that the solutions and workup procedures evaluated in this thesis are only but a few of the potential alternatives that could have been studied. As the thesis was planned over a limited time of twenty weeks, the numbers of samples were restricted by the time available.

1.4 Method

The influence of the water quality on the filter capacity of the waterglass filter is simulated by the means of a laboratorial procedure designed by the Chemical Analysis department at AkzoNobel in Bohus. The procedure has been planned to ensure consistent filter values and a close approximation of the filter used in the plant. The purpose of the procedure is to determine the impact of specific water quality parameters have on the filtrated volume of solutions, made from colloidal silica and process waters. Changes in filtration volume are believed to indicate changes in the raw material and/or changes in the amount of nanogel in the sample. The results from this procedure are also believed to represent a similar response in the full scale industrial process.

In addition to analysing water collected from the plant, doped samples are investigated. These samples are prepared by deliberately adding specific ions or particles to more selectively observe their effect on the filter capacity. In Figure 1, below, a general scheme of the working strategy to reach the goals of the thesis is presented.

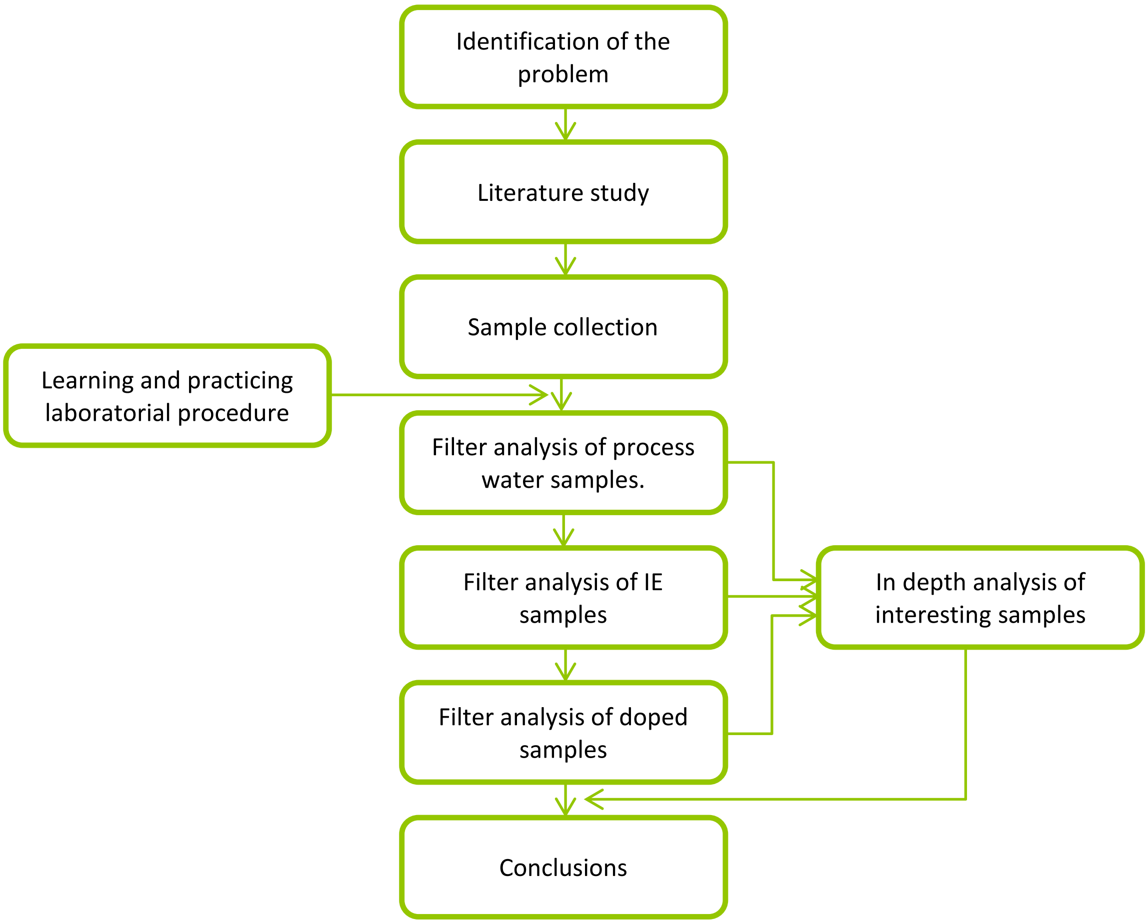


Figure 1: Scheme of working procedure

A more detailed explanation of the laboratorial methodology is included in chapter 4.

2 Theoretical background

In this chapter the necessary chemical knowledge associated with silica and colloids are presented in order to more easily comprehend the chemistry behind the production of sustainable colloidal silica and the reactions that occur in the different stages of the process. First of all some background knowledge about silica is presented in section 2.1. Subsequently the properties and dissolution of the raw material waterglass is presented in section 2.2. Finally the properties and stabilization as well as polymerization and agglomeration reactions of colloidal silica are presented in section 2.3.

2.1 Silica

Silicon dioxide (SiO_2), silica, is the most abundant mineral on earth and the main component of the earth's crust. It is present as silicate minerals of different combinations with other mineral oxides in our rocks and soils, but also found in isolated forms such as sand and quartz [1]. Silica can be found in nature in both crystalline and amorphous arrangements. The most common structure is when bonded with oxygen into tetrahedrons, SiO_4, where the silicon serves as the central atom. The tetrahedrons of silica can bind together by sharing oxygen atoms and form into larger three dimensional structures, where the average formula is SiO_2. The Si-O bonds are very strong and partially ionic in character, which makes these crystal structures exhibit a very important property – making them soluble in water [1][2]. The water solubility has made silica come to play an important role for many forms of life on our planet [1].

The earliest form of life called diatoms, a group of algae phytoplankton, used silica to form their skeletal structures. Various plants benefit from silica, by strengthening their stems and form protective external needles. Even animals make use of silica, as essential trace minerals in bones, blood vessels, skin, hair and nails [1][3][4]. Colloidal silica, where silica particles have been evenly dispersed throughout a continuous liquid phase, also present an importance to life as it participates in many of the diverse processes of our metabolism [5].

2.2 Waterglass

Sodium silicate ($Na_2(SiO)_nO$) is formed in a reaction between sand and sodium under very high temperatures [7]. The compound is a water-soluble glass, also known as "waterglass", and the water solubility of waterglass makes it a convenient source for sodium and silica for industrial processes [8]. Sodium silicate can be produced in varying SiO_2:Na_2O ratio in order to get different physical properties and be used in a diversity of applications according to the equation below [7].

$$\boldsymbol{Na_2CO_3 + nSiO_2 \rightarrow Na_2O \cdot nSiO_2 + CO_2} \tag{1}$$

For the production of industrial silicas, sols, and gels, which is relevant for this thesis, sodium silicate ratio about 3.3 is usually used. The advantage above using lower ratio, in this case, is because it needs less acid to neutralization [7].

The ratio of silica to sodium oxide determines the viscosity and solubility of the water glass. With a higher silica content solubility decreases and the viscosity of the solution increases. Viscosity is increased as a result of the formation of silicate polymers, which form between Si and O atoms that link together into larger ring or chain structures. The silicate polymers are negatively charged and incorporate positively charged sodium ions and also water molecules [8]. Waterglass solutions are usually supersaturated which allows concentrations of silica solute higher than the normal solubility. The ratio of silica to sodium is normally not produced higher than 4 SiO_2:Na_2O since the viscosity of the silica solution of solved waterglass would be too viscous for process equipment to handle [9].

As the quartz used for the production of waterglass contains a multitude of impurity ions, which will contaminate the product, the quartz is washed to minimize the amount of impurities present in the reaction. Although being washed, there will still be traces of metallic ions in the water glass product [9]. These ions will compete with the sodium ions in the ion exchange process step, mentioned in section 2.5 and traces are often still present in the silica sol product in a range up to 0-300 ppm [7].

2.3 Colloidal silica

Colloidal silica is a homogenous dispersion of silica particles throughout a continuous phase of a different composition or state than the silica. [6].The particles are of colloidal size and range in size from about 1 nm up to about 1000 nm [1]. The shape of the silica particles may be spherical or slightly asymmetrical and can be present as separate particles or somewhat structured aggregates. The size rage of the particles can be narrow or wide, it varies depending on the process by which they were manufactured [18].

Figure 2: Left: Anionic silica particle stabilized by sodium ions.
Right: Non-charged silica particle deionized modified [19].

As a consequence of the particles being in the nano-range, it makes them sufficiently small to stay unaffected by gravity and not settle out of solution, but also sufficiently large to display diverging properties from true solutions. Interaction between particles of this small size is dominated by van der Waals forces and surface forces and the particles are often stabilized electrostatically, to allow them to stay suspended in solution [1].

The sizes of the silica particles also greatly affect the appearance of the colloidal silica dispersions. A dispersion of very small particles (<10 nm) is almost completely clear but as the size of the particles increase more light is scattered by the particles and the dispersion becomes gradually more cloudy and white. At large particle size (>50 nm) the dispersion is normally completely white and milky [18].

The maximum ratio of silica in the dispersion is restricted by the average particle size. A dispersion of small average particle diameter has a larger overall specific surface area and is limited to lower concentrations of silica. Equally, a dispersion of larger particle diameter has a lower specific surface area and is available to higher concentrations of silica [18].

Colloids have a number of characteristic properties e.g. they have strong absorption qualities (originating from the large exposed surface area of the colloidal particles); they can also carry an electrical charge (a consequence from electrostatic interaction, attraction or repulsion, within itself) [1].

A stable system of amorphous silica particles in a liquid is called a silica *sol*. It is considered stable when the particles do not settle out of solution or agglomerate at a significant rate [7]. A system made out of a continuous solid network made out of amorphous silica particles surrounding a continuous liquid phase is called a silica *gel* [1].

2.3.1 Stability of colloids

The stability of colloidal systems is generally described by three different mechanisms of stability [1]:

- *Phase stability* - The equivalent to the stability of ordinary solutions.
- *Disperse composition stability* – The stability of dispersity in the system.
- *Aggregate stability* - The particles stability and resistance to aggregate.

A colloidal system is stable when it can remain in the colloidal state – made possible when there is no cohesion between the particles and they resist flocculation or aggregation and maintain a long shelf-life [7]. The stability of colloidal dispersions depends on phenomena involving the complex interaction mechanics between the particles. When the particles approach each other they will experience repulsive electrostatic forces and attractive van der Waals forces [1]. If all particles have a mutual repulsion the dispersion will remain stable. However, if the repulsive forces are few or weaker than the attractive forces some instability mechanism may occur, like aggregation or flocculation, which results in an unevenly distributed dispersion. The long-term stability of colloidal dispersion is important to most applications since the colloids properties change with instability [7].

Commonly colloidal silica dispersions are stable towards aggregation or settling of particles within the pH range of 8- 10.5. These dispersions have often been charge stabilized by the addition of an alkali, usually alkalis of sodium, potassium or lithium. During these pH conditions the particles are negatively charged [18]. However, there are also colloidal silica dispersions stable at low pH below 4. These dispersions have been stabilized by the addition and adsorption of anionic species onto the cationic surface of the particles. The stabilization at low pH can also be obtained if the dispersion is completely deionized, then the particles no longer require the presence of a stabilizing anions to be stable. Relevant to note is that there is a window between pH 4- 8 when the colloidal silica is not stable [18].

2.3.2 Polymerization of silica colloids

Silicic acid, a compound containing silicon bonded with oxide and hydroxyl groups, is soluble and stable at very low concentrations (<100 ppm) in room temperature. As a solution reaches higher concentration than the solubility of the amorphous silica (>100-200 ppm) the $Si(OH)_4$ monomers start to polymerize by condensation into higher molecular structure. The condensation polymerization favours the formation of cyclic silica polymers that with the addition of more monomers link together and into larger spherical structures with hydroxyl groups on the surface. The resulting particles will be of distributed size but will in time grow into an average size due to Ostwald ripening (small particles re-dissolve and the silica is deposited on the larger particles) [7].

The polymerization and depolymerization of colloidal silica is influenced by temperature and pH, mainly the latter since the condensation reaction is of ionic nature. The polymerization behaviour at different pH is illustrated in Figure 3, below.

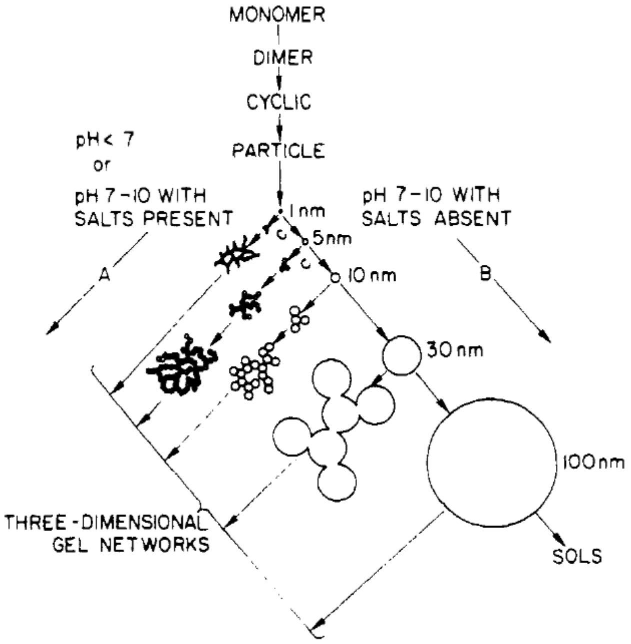


Figure 3: The polymerization behaviour of silica at varying pH [7]

The rate of dissolution and deposition of silica increases with increasing pH and increasing temperature and makes it possible to achieve larger particles at higher pH. The aggregation of the particles is also affected by the pH – above pH 7 the silica particles do not collide because they are negatively charged and stabilized through electrostatic repulsion and which lets the particles continue to grow without aggregation. At lower pH the particles have little charge and the particles can collide and aggregate enabling formation of gel networks [7]. If salts are present at pH 7 or above, aggregation may still occur since the ions will lower the surface charge. In order to be able to control the production of uniform and reproducible silica sols, a better understanding of silica growth and polymerization is required [1].

2.3.3 Gelation of silica colloids

A gel structure is formed when colloidal silica particles in a sol are able to collide and link together (pH 2-7) into branched chains and form a three-dimensional structure, that eventually fills the entire volume of the dispersion without increasing the concentration of colloidal particles [7]. It is essential to comprehend that while a sol is being converted to gel the growing gel phase will maintain the same concentration of silica and water as the surrondning sol [7]. The aggregation process of a silica gel is hard to detect because the density and refractive index remain the same as those of the sol. However, a slow increase in viscosity can be distinguished before the sol starts to solidify. Upon reaching the *gel point* the solution becomes increasingly viscous at a higher rate until it eventually solidifies by a network of particles. The rate of gellation and treshhold for the gel initiation is dependent on the properties of the sol; pH, particle size, particle concentration, and temperature all affect the interaction between the silica particles [1].

2.4 Silica sols

In order to produce stable silica sols, without gelling, it is important that agglomeration is prevented during the growth of the particles. A sol is obtained by letting the particles grow in alkali conditions and low salt concentrations, where the particles are electrostatically stabilized by their negative charge and small particles are readily re-dissolved (as mentioned in section 2.3.1) [6]. The growth of the initial particles is made through condensation between hydroxyl groups at the silica particle surface and on silicic acid, where silicic acid ends up chemisorbed to the surface of the particle, according to the equations below [7].

$$\equiv SiOH_{(s)} + Si(OH)_{4(aq)} \rightarrow \equiv Si - O - Si(OH)_{3(s)} + H_2O_{(aq)} \qquad (2)$$

With ionized surface:

$$\equiv SiO^-_{(s)} + Si(OH)_{4(aq)} \rightarrow \equiv Si - O - Si(OH)_{3(s)} + HO^-{}_{(aq)} \qquad (3)$$

The regeneration of the surface charge:

$$\equiv SiOH_{(s)} + HO^-{}_{(aq)} \rightarrow SiO^-_{(s)} + H_2O_{(aq)} \qquad (4)$$

The reaction rate is proportional to the concentration of silicic acid and charged particles near the surface of the silica particles. The kinetics behind the reaction is still debated, but several sources agree that there are three steps major for the production of silica sol [7][11][12]. First nucleation of silica particles from silicic acid, secondly the growth of the particles via polymerization, and thirdly the surface rearrangement process where chemisorbed silicic acid is fully condensed into the silica particle [7][11]. It is also generally believed that the growth rate is limited by the increased solubility of recently chemisorbed silicic acid and pH which influences the surface charge density [7].

2.5 Ion exchange of silica sol

The ion exchange phase of the silica sol production is where the sodium ions from the waterglass is exchanged with hydrogen ions by interacting with an ion exchange resin. The exchange is done preparing a diluted waterglass solution of 4-6 wt% silica from a concentraded highly alkali waterglass solution and passing it through a column loaded with cation-exchange resin [1][7]. As the diluted solution passes through the resin the sodium ions, as well as other cationic impurities present, reacts with the resin according to the reversible reaction 2, below, where A represents the ions in the solution, B the ions in the resin at the start, and R the resin that is bounded to the exchangeable ion. [3][16]

$$\boldsymbol{A_{(l)}^{n\pm} + nBR_{(s)} \leftrightarrow AR_{n(s)} + nB_{(l)}^{\pm}} \qquad (5)$$

While passing through the ion exchange column, and as ions in the waterglass are exchanged, the pH of the waterglass solution is gradually decreasing. At the end of the exchange the solution leaves the column as an active silicic acid, called acidic sol, which is partly unstable and contains much higher degrees of free silica monomers, making it more receptive to polymerization and agglomeration. The silicic acid is stabilized by increasing the pH to 8-10,5 and is ready for controlled growth [1][7].

2.6 The Production of silica at AkzoNobel

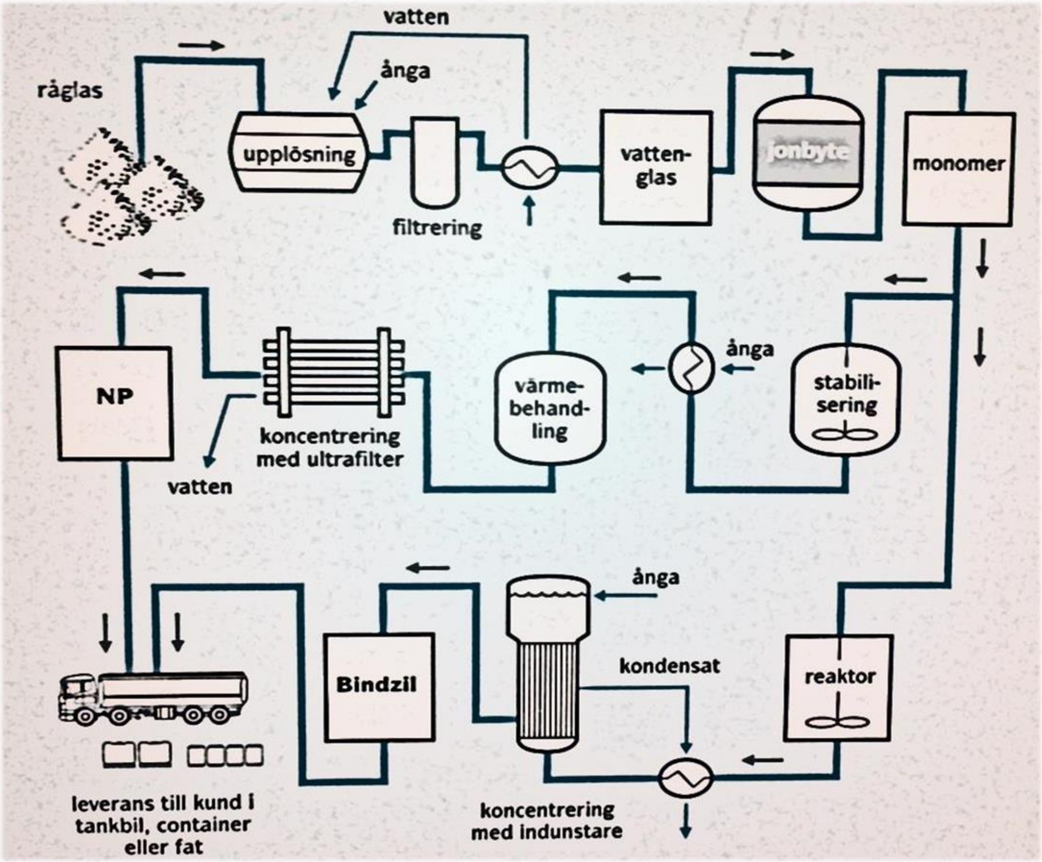


Figure 4: A general description over the silica sol production process at AkzoNobel in Bohus [19].

The production process for manufacturing colloidal silica sol at AkzoNobel in Bohus generally follows the spread sheet presented in Figure 4, above.

The manufacture of colloidal silica sols is a multi-step process, which begins with the dissolution of raw glass. The raw glass is dissolved in pressurized autoclaves together with water and concentrated waterglass in order to get highly alkaline concentrated waterglass. The concentrated waterglass is readily diluted down to concentration ~ 5 wt% silica before it is filtered – *it is also during this filter operation where the filter capacity issue has been noticed*. After filtering the waterglass, sodium is removed with the help of ion-exchange operations. The ion-exchangers gradually remove sodium ions by exchanging them with hydrogen ions, which also gradually lowers the pH of the waterglass to ~ 3 pH, until silicic acid is acquired. The silicic acid is then brought into reactors where controlled growth of the colloidal particles is initiated. The growth is controlled by regulating the pH and temperature parameters that control the reaction rate, which is done by diluting with waterglass or heating. After growth, the sol is stabilized and concentrated. The concentration is done by separating water from the sol and is done with either ultra-filtration or evaporation. The separated water streams are the main sources for recycled water in the silica sol process, and are recycled into the first operation where raw glass is dissolved and waterglass is diluted.

2.7 Characterization methods

2.7.1 Inductively Coupled Plasma - mass spectrometry

Inductively coupled plasma - mass spectrometry (ICP-MS) is a detection technique and analysis method for revealing trace and ultra-trace elements in liquid samples. The technique is capable of analysing high volume samples and has an extremely low limit of detection and can detect quantities down to the part per billion concentrations. The ICP-MS creates plasma of argon gas that contains ions, electrons and neutral particles which are used to atomize and ionize the liquid sample. The resulting atoms and ions are then passed into a high vacuum mass spectrometer where the isotopes are detected and identified by their mass-to-charge ratio. The amount of the isotopes in the sample is proportional to the intensity of the peaks in the mass spectrum [14].

2.7.2 Large Particle Count

Large particle count (LPC), also known as single particle optical sizing (SPOS), is a method that measures and counts the particles that pass through an optical sensor chamber. In the chamber a uniform light produced by a laser is scattered as particles pass through. The diffraction pattern and variation in intensity of diffracted light is detected by a sensor, which signal is then used to calculate the amount and sizes of the passing particles, down to a detection limit of 1 nm. To prevent multiple particles passing the sensor at the same time and being mistaken for a single larger particle, a feedback control system is put between the detector and the feed system. As the frequency of passing particles exceeds a predetermined threshold, the feed system is slowed to reduce the particle flow rate [20]

2.8 Work-up procedure

2.8.1 Ultra-filtration

Ultra-filtration (UF) is a separation method that uses membranes to achieve a size-exclusion based separation in a cross-flow process. Primarily, perforated membranes with known pore size are used to allow exclusive passage for smaller particles and not for larger particles. The membranes can be used in different configurations that are suited for different applications, for the filtration of more concentrated solutions like waterglass a tubular configuration is used. The force of separation is the result of an applied pressure difference over the membrane that drives a convective flow of the smaller particles through the membrane towards the low pressure side. Liquid that comes through the membrane is called permeate. Particles and species larger than the pore size are removed by the membrane and progressively concentrate on the high pressure side. In order for the separation to work the applied pressure difference must exceed the counteractive osmosis pressure, a reverse flow that arises as a result of the increased concentration of smaller particles on the low pressure side [14]. The capacity of the ultrafiltration process is affected by a couple of factors. Likely the most important factor is the flow velocity which affects the permeate rate and fouling. A higher flow velocity results in an increased permeate rate and decrease in fouling. However, a high flow rate requires greater energy consumption. The permeate rate is also affected by the pressure over the membrane and temperature. The applied pressure is directly proportional to the permeate rate but cannot be too high since it increases fouling and compaction of the membrane. The permeate rate can be controlled by increasing or decreasing the temperature, however this is generally unusual as the heat energy is better distributed to other process steps [21].

3 Materials & Equipment

In this chapter the equipment and materials used during the study of the water quality parameters are presented. Note that all the numerical data in this chapter are averages calculated from the collected data throughout the thesis.

3.1 General Equipment & Materials

Equipment: The properties of the waterglass solutions and water samples were measured with an Anton Paar DMA 4500 Density meter (density), WTW Cond 3110 (conductivity), Metrohm Ion Analysis 744 pH meter (pH), HACH 2100N Turbidimeter (turbidity), and Metrohm Ion Analysis 728 Stirrer (SiO_2 ratio). Filter values were measured by using a plastic filter funnel and nylon filter membranes of a specific pore size. Ultra-filtration was done using a pilot scale unit with membranes having a higher molecular weight cut-off than in the silica sol process.

Materials: The ferric chloride (PLUSJARN S314) was kindly provided by Feralco Nordic AB. The calcium chloride (CA0194) was obtained from Scharlau Chemie S.A. Seed particles 8/20 DI was provided from AkzoNobel Asia, Taiwan branch. Hydrochloric acid, sodium aluminate, and sodium chloride were supplied by AkzoNobel AB, Bohus.

3.2 Waterglass

The concentrated waterglass used during the thesis to produce waterglass solutions for the filter analysis was produced by AkzoNobel, Bohus, by dissolving raw solid waterglass in autoclaves with water. The relevant data of the concentrated water glass is presented in Table 1, below.

Table 1: Properties of the concentrated waterglass samples

$M_{waterglass}$ (g/mol)	122,06
Density (g/cm^3)	1,3165
Conc. of silica (wt %)	24,5
Ratio (weight SiO_2:Na_2O)	3,4
Conductivity (mS/cm)	37,2
pH	11,56
Turbidity (NTU)	1,04

3.3 Water samples

The water samples used to dilute the waterglass were collected throughout the thesis from different streams in the plant as different products were being manufactured which influences the quality of the different water samples. The relevant data of the different water samples are presented in the tables, below.

Table 2: Properties of the three main water samples collected.

Water samples	Condensate	Permeate (SUF)	Permeate (LUF)
Density (g/cm^3)	0,998	0,999	1,000
Conductivity (µS/cm)	3	558	838
pH	7,84	9,64	9,99
Turbidity (NTU)	0,292	0,326	0,194

*SUF = small ultra-filter

*LUF = large ultra-filter

3.4 Ion Exchange column

The ion exchanger used during the thesis was a lab-scale column equipped with two pumps with different capacity suited for the regeneration cycle and ion-exchange cycle which requires different flow rates. The dimensions of the ion-exchange column are illustrated in figure 5, below.

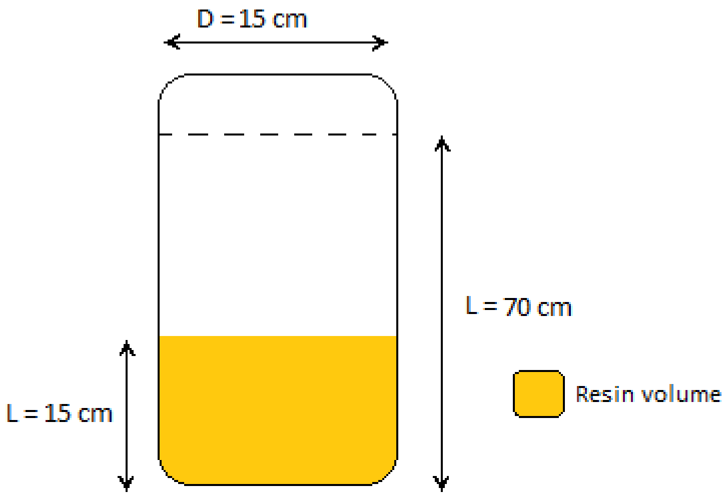


Figure 5: Dimensions of the ion exchange column

The total volume of the column was 12.37 litres and the resin bed volume was 2,651 litres. The flow rate of the ion exchange cycle was kept at 1,970 litres/min and for the regeneration cycle it was kept at 0,244 litres/min. The acid was added over 18 min in order to regenerate the resin with 100 g HCl / litre resin.

3.4.1 Ion Exchange resin

The resin used for the ion exchange was a gel-type strong acid cation exchange resin (SAC), which has a bead shaped matrix made from copolymerization and crosslinking of styrene and divinylbenzene. The relevant data of the resin is presented in Table 3, below [17].

Table 3: Specifications of the ion exchange resin [17]

Matrix	Cross-linked polystyrene
Functional group	Sulfonic acid
Density	1,26
Stable pH-range	0 - 14
Stable temperature range	-20 – 120 °C
Total capacity	1.8 molar eq/l

The resins functional groups are mono-functional, which means it only allows for one variety of ions to be exchanged (in this case, Na^+ and H^+) and are attached to divinylbenzene regions of the matrix [17].

4 Method

In this chapter the different laboratorial procedures used during the thesis are presented in detail.

4.1 Filter test analysis

The filter test analyses were carried out according to a modification of an analytical procedure standard (AP-019) developed by the Chemical Analysis department at AkzoNobel in Bohus. The procedure, with some additional adjustments to ensure the execution would be as dependable as possible, was followed strictly in order to obtain consistent and true filter values.

4.1.1 Preparation of waterglass samples

Samples of water samples were foremost collected from the evaporator, small ultra-filter, and large ultra-filter streams from within the plant as different products were being manufactured. Then the samples were left to temperate to room temperature. After reaching room temperature sample properties were analysed, which included density, pH, temperature, conductivity, and turbidity. The water was then used to dilute concentrated sodium silicate down to 5.5 wt% silica with an allowed error margin of ± 0.1 wt%. The now diluted waterglass was then aged over approximately 24 h, in order to let the colloidal silica particles to be affected by the water quality conditions. As the waterglass solutions had completed the aging process, the properties were analzed once again, this time with the addition of SiO_2 ratio analysis. Filtervalue measurements were carried out, according section 4.1.2 below, after the analyses had been completed.

4.1.2 Filter value measurements

A vacuum pump operating at a fixed constant pressure was connected to a 1000 ml Erlenmeyer filter flask and a nylon filter of a specific pore size, kept the same throughout all the measurements. Sample solutions of approximately 5.5 wt% sodium silicate had been prepared according to the explanation above and measurement of the filter value was achieved by filtering the samples through the filter for exactly 5 min, controlled by a timer. The filtered volume was then measured in a 1000 ml cylinder to obtain the filter value (in ml/5 min).

With the aim of achieving a higher rate of consistency and less variation within the procedure some of the basic steps were carefully planned and carried out in the same way for all filtration tests throughout the thesis.

- The sample bottle was always gently stirred at 120 rpm before each filter test.
- The filter papers were always put on the membrane support of the filter funnel with the same side facing up.
- Each new batch of filter papers was always calibrated towards Millipore water (0.22 µm filtered) to control that the permeability of the filter papers were not inconsistent.
- Each newly diluted sample solution was stirred at 240 rpm for 5 min to reach homogeneity before aging.

- In-between each filter test the membrane support was thoroughly washed and rinsed with deionized water.

4.2 Filter test analysis with ion exchange

The analyses of ion exchange samples were performed with the intention of enhancing the effect of the water quality parameters and how it affects the filter. The procedure was carried out according to another study made at AkzoNobel in Bohus that had been performed with the same apparatus used in the thesis and with similar samples. The preparation of the samples was carried out in the same manner as for the filter test analysis, to achieve sodium silicate of 5.5 wt% silica (± 0.1 wt%).

4.2.1 Ion exchange procedure

Sodium silicate samples were pumped through a TRIX lab column loaded with approximately 3 l of SAC resin. The flow was kept at 0,800 ml/min during every exchange. To get a good sample the first 3 l were not collected to ensure steady-state through the column was reached. The conductivity of the outflow was continuously monitored and the samples were collected in 1 l plastic containers to prevent breakthrough to ruin the entire sample. In between every ion exchange the SAC resin was regenerated with HCl. Rinsing and backwashing was done by using DI water. Rinsing continued until the conductivity came down below 20 µS/cm, before another sample could be run. The SAC resin was thoroughly washed with 5% NaOH in between every 10th sample to dissolve the silica content that may have accumulated during the ion exchanges. In order to see the effect of the ion exchange the samples were aged for 24 hours before the properties of the solutions were analysed as well as tested for filter values.

4.3 Filter value: Time dependency

As soon as a sample of waterglass solution has been prepared there is a possibility that the dispersed colloidal silica particles may start to polymerize into larger particles or forming a gel structure which would significantly lower the filter values of said samples. The time dependency of the waterglass solution samples needed to be examined in order to being able to properly interpret the results from the filter test analysis.

The time dependency of the waterglass solutions was measured by preparing four different alkali samples, see 4.1.1 above, from condensate, permeate (SUF), permeate (LUF) and MilliQ water and determining their filter values over the course of five days. Filter values were examined every second hour the first days and two times a day the four remaining days to observe the potential changes in the filter value.

4.4 Filter value: Sample variation in method

Even though many precautions were made to reduce the inconsistency of the filter test analysis, minor deviations within the method will still remain. In order to minimize the influence of these data-fluctuations all samples during the thesis were measured a minimum of five times and an average was calculated. Moreover, an experiment was also performed to examine how large the deviation of the filter value for a single sample could be. It was carried out by preparing a 10 l waterglass solution, see 4.1.1 above, for which the filter value was measured 15 times over a short period of time. The results are included in Appendix B.

4.5 Filter value: Mass content sensitivity

During the preparation of the waterglass solutions an error margin of ± 0.1 wt% is allowed from the targeted 5.5 wt%. The mass content relates to amount of silica content within the samples and has an obvious effect on the filter value. Even small variations within the error margin could influence the filter value to some degree. Three waterglass solutions were prepared with the mass contents of ranging from 5.46 – 5.66 wt% and five filter values were measured for each sample in order to examine the mass content sensitivity. The results are included in Appendix B.

4.6 Filter value: Variation over time

To ensure that time had not affected the concentrated waterglass used in all samples throughout the thesis, and consequently affected the measured filter values, a simple safeguard test was made. Waterglass solutions of 5.5 wt% silica (±0.1%) were prepared according to the same method mentioned previously in section 4.1.1. One sample was made and measured at the beginning of the thesis and the other was made in the end to see if they had about the same filter values. The results are included in Appendix B.

4.7 Ultra-filtration: Work-up procedure of water samples

The ultra-filtration was carried out in pilot scale with a procedure and equipment that had been used in a previous study at AkzoNobel, and is considered a close approximation to the ultra-filtration operation in the silica sol plant.

4.7.1 Water sample preparation

Water sample was collected in a 260 l barrel, from either the silica sol plant or the alkali pellet plant. The barrel was then weighed in order to estimate the sample volume, for which both were about 240 l. Water from the silica sol plant was already contaminated with particles and needed no further preparation. Water from the alkali pellet plant was milliQ water and 8/20 DI seed-particles were added at a concentration of 100 ppm.

4.7.2 Ultra-filtration procedure

The water samples were pumped through a parallel flow ultra-filter column, at a pressure of about 10 bars and room temperature. 200 l of the water samples was pumped through before collecting a 10 l samples for further analysis by filter value measurements and LPC.

5 Results and Procedure

In this chapter the results from filter value measurements and sample analysis are presented. Firstly, the results from the 5.5 wt% waterglass samples are presented. Secondly, the results from ion-exchange experiments are presented. Thirdly, the results from doped samples are presented. These are followed by the results of the analysis of outliers and evacuation of product in recirculated condensate water. Lastly, the results from the work-up by ultra-filtration are presented.

5.1 Results of water and waterglass investigation

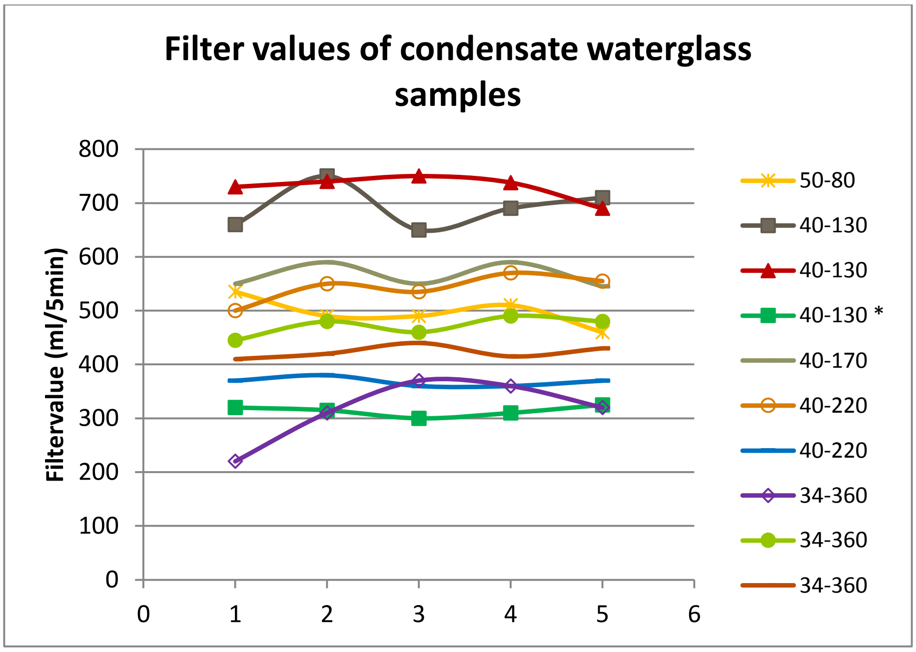
A multitude of different 5.5 wt% waterglass solutions were studied. They were made from a variety of different recirculated water samples, in order to get a good diversity of the water qualities and get a better understanding of the effect it had on the filter capacity.

5.1.1 Analysis of water quality parameters

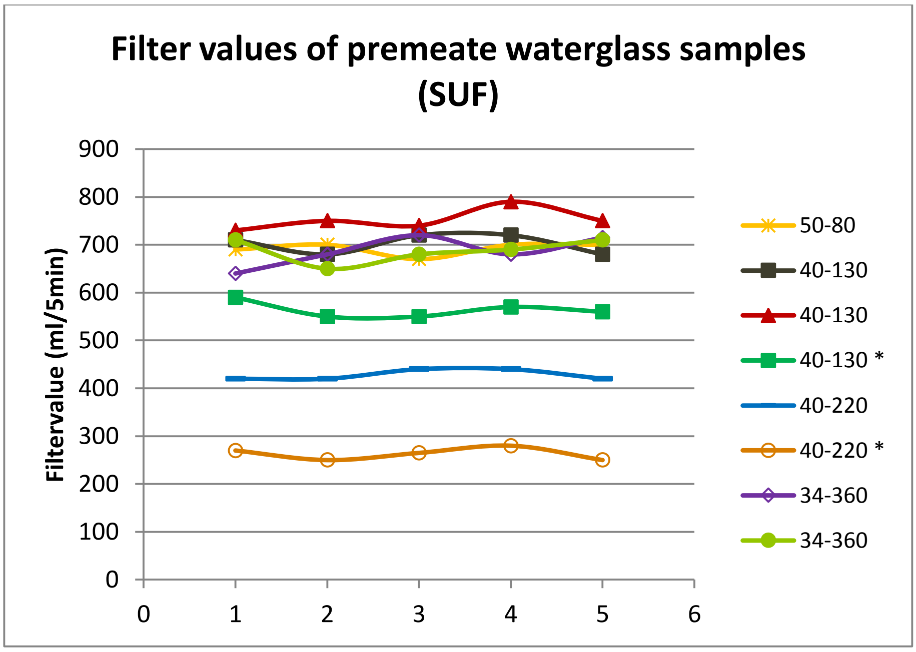
The effect of the water quality parameters were analysed by overseeing the large amount of collected water quality data, and attempting to find a connection between water quality and filter value. However, the data were erratic and completely inconsistent, which made it difficult to understand or make any practical predictions. The degree of uncertainty within the data was too high and the analysis failed to reveal any reliable connections between water qualities and filter value. As a consequence, the investigation of water quality parameters was judged to be of little use to the goal of this thesis and the results are not included in this chapter, (results are included in Appendix).

5.1.2 Filter value measurements

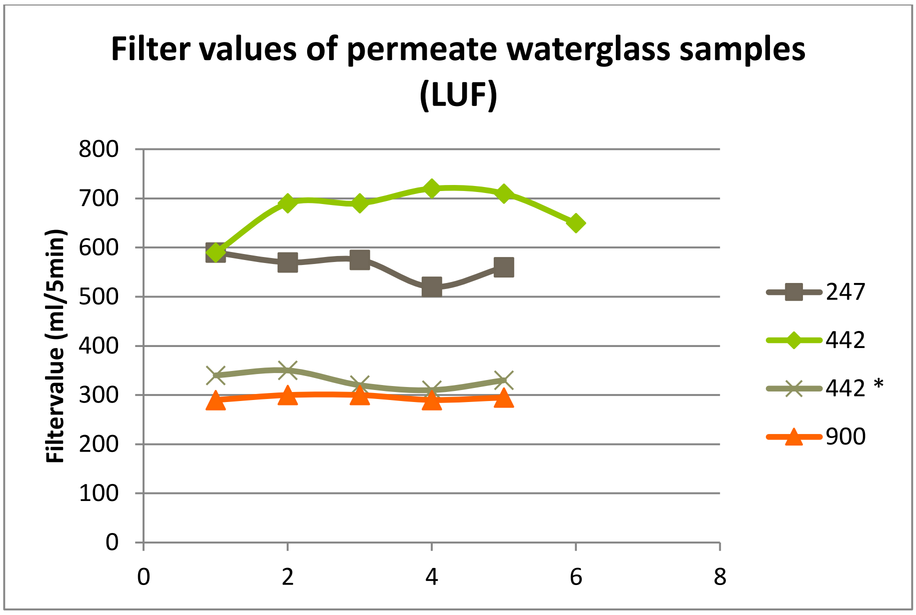
The filter values obtained for the 5.5 wt% waterglass samples were plotted in three graphs, one for each different type of recirculated water stream. The samples have been given names according to the silica sol product being manufactured in the plant, as the water samples were collected. During the course of the thesis several different silica sols were manufactured, and the filter values observed in the graphs demonstrate that the product has an apparent effect on the filter capacity. A large spread in filter value is displayed between samples originating from different products waters, while samples of the same product waters show more similar values. See graph 1, 2 and 3, below.



Graph 1: The filter values obtained for the different 5.5 wt% waterglass solutions diluted by water from the condenser.



Graph 2: The filter values obtained for 5.5 wt% waterglass solutions diluted by permeate water from the small ultra-filter.



Graph 3: The filter values obtained for the 5.5 wt% waterglass solutions diluted by permeate water from the large ultra-filter.

Particularly interesting outliers in the graphs are marked by an *, these samples displayed a much lower filter value than other samples of the same product waters. These samples were further investigated in order to find out what caused them to have a lower filter value and to be able to compare them with the samples of the same product. First, the outliers were investigated through production management software called EPI, which provided detailed information about the internal and external process operations as the water samples for the outliers were collected. It was of interest to know if there had been irregular occurrences in any of the process operations, which might have caused the lower filter value.

The EPI analysis did not reveal anything out of the ordinary for any of the outlying samples, in terms of water quality. However, the analysis exposed that the outlier samples had been collected a longer time after the production start than the reference samples. As there were no notable differences of the water quality, it led us to believe that evacuation of product into the recirculated water streams could have caused the lower filter values. The evacuation is not seen by the EPI analysis and is known to have occurred. The fact that the outliers were also at a later time in the production than the reference samples was also intriguing. The evacuation of product present in the outlying samples and the effect of time were analysed by LPC analysis, for which results are presented later on in this chapter.

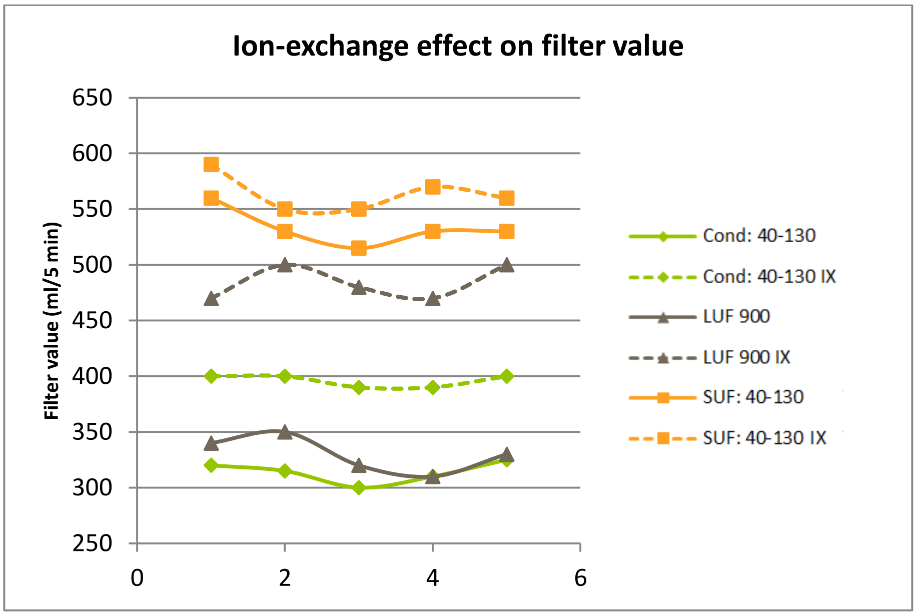
Concerning the results above, it ought to be noted that neither should be regarded for any quantitative purposes. Still, the vast quantity of data collected for water and waterglass samples have frequently been returned to, in order to offer insight and comparison during the other experiments.

5.2 Results of ion-exchanged waterglass samples

As it was discovered that the water quality parameter analysis results were unsatisfactory, ion-exchanging samples were the next step in the investigation. Ion-exchange of waterglass is large part of the silica sol production process and is of particular interest because it gradually changes the pH of the waterglass solutions from a stable alkali pH (above 10) to only partly stable acidic pH (below 4), as mentioned in section 2.3.2 and 2.5.

5.2.1 Filter value measurements of ion-exchanged samples

The ion-exchange measurements were carried out to examine how the treatment affects the filter capacity of the 5.5 wt% waterglass samples. Also, it was carried out to see if it might generate a stronger and more consistent response from any of the water quality parameters previously analysed in alkali conditions. The assumption was made that a lower filter value would be measured for ion-exchanged 5.5 wt% waterglass samples, as the acidic conditions would allow the colloidal silica particles to more easily interact and lead to gelling or aggregation to occur. The results are presented in graph 4, below.



Graph 4: Filter values obtained from representative ion-exchanged samples from each type of recirculated water stream.

The results turned out to be the exact opposite to what we had expected. For all ion-exchanged 5.5 wt% waterglass samples the filter value was marginally increased.

5.3 Results of doped waterglass samples

Doped samples were studied in order to observe and understand the influence of specific compounds on the filter capacity of 5.5 wt% waterglass samples. The measurements were done on precise waterglass samples without the interference of impurities from undefined water samples. Four compounds were studied during the doped sample measurements. They were selected as they were known to have an effect on the colloidal silica particles and to sometimes be present as trace elements in the process waters. The latter had been established by standard ICP-MS quality control of process waters, performed by AkzoNobel.

$NaAlO_2$

Sodium aluminate is a compound used by AkzoNobel to modify the surface of the colloidal silica particles. It was tested in the doped experiments to see how traces of this compound would affect the filter capacity of waterglass samples.

$CaCl_2$ and $NaCl$

Calcium chloride and sodium chloride are general ions which are always present in the recirculated water streams. They were used to simulate and study the effect of these ions as they were present in high concentrations.

$FeCl_3$

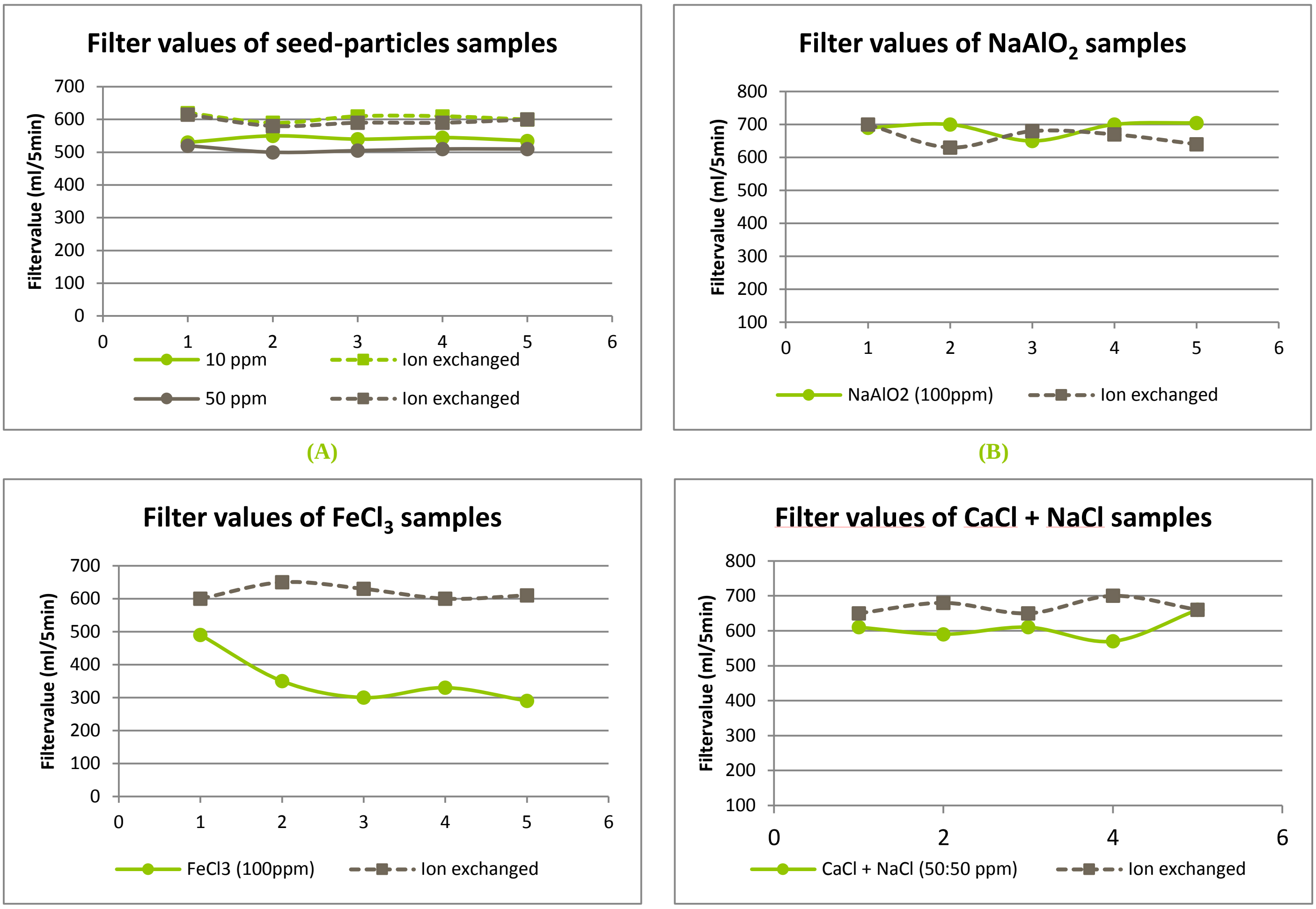
A large amount of the process water in the silica sol process is supplied by flocculated water from Göta Älv, which has been purified though filtration, chlorination and eventually flocculation. Iron chloride is a flocculating agent and was included in the doped experiments as it was of interest to see how a flocculating agent affected the filter capacity of waterglass.

Seed-particles

Addition of seed particles, 8/20 DI, was used to simulate the evacuation of product into the recirculated water streams. It was selected as it has the smallest particle size and largest specific surface area which makes it the most reactive. As it was deionized we could also consider it clean from impurities.

5.3.1 Filter value measurements of doped samples

Filter value measurements of the doped 5.5 wt% waterglass samples were performed on both alkali and ion-exchanged acidic samples. See graph 5, below.



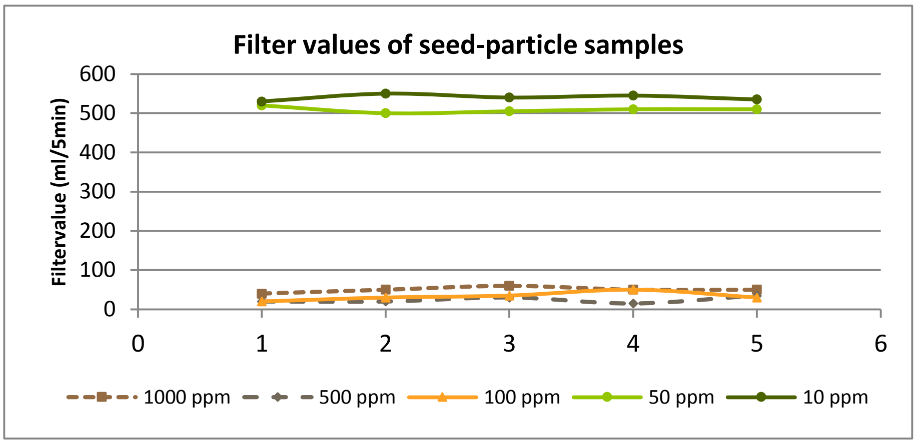
(A) (B)

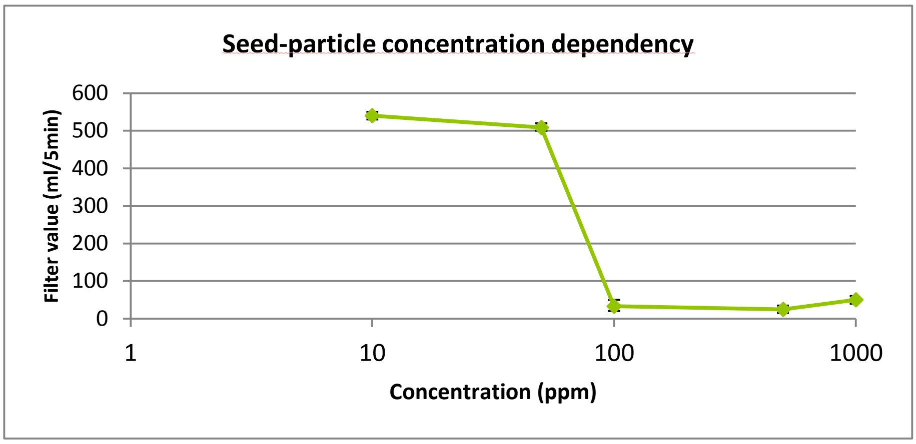
(C) (D)

Graph 5: Filter values obtained from 5.5 wt% waterglass samples diluted with milliQ water doped with different compounds. **(A)** Seed-particles, 10 and 50 ppm. **(B)** NaAlO$_2$, 100 ppm. **(C)** FeCl$_3$, 100 ppm. **(D)** CaCl$_2$, 50 ppm + NaCl, 50 ppm.

5.3.2 Seed-particle concentration variaton

Samples doped with 8/20 DI seed-particles were analyzed further by looking at 5.5 wt% waterglass samples doped with gradually increasing concentration, from 10 – 1000 ppm. The concentration dependency was studied in order to better understand the effect of seed-particles on waterglass samples and how it influences filter capacity. Three 5.5 wt% waterglass samples for each concentration was prepared and the average filter values and concentration dependence is illustrated in graph 6, below.





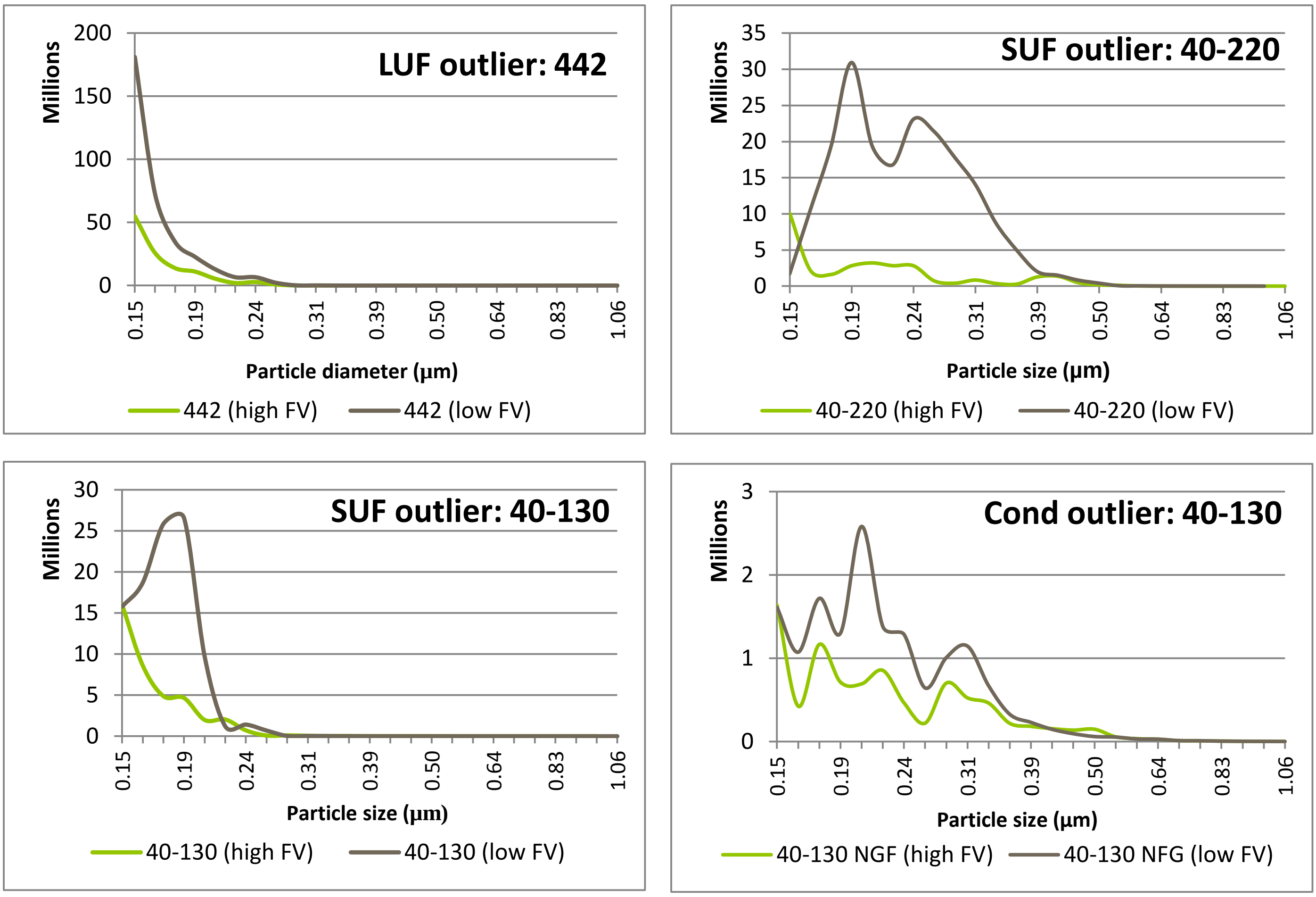
Graph 6: Above: Average filter values of 5.5 wt% waterglass samples doped with different concentration of 8/20 DI seed-particles. Below: Seed-particle concentration plotted against the average filter value.

As can be observed, there is a clear impact on filter value for the 5.5 wt% waterglass samples even at the lowest concentration of 10 ppm. The filter value obtained for 5.5 wt% waterglass diluted with milliQ water without any seed-particles is normally measured to 700-800 ml/5min. Morever, the results show that there is a drastic increase in the filter value as the concenteration of seed-particles increases above 50 ppm, which decreases the filter capacity to the extent that almost nothing gets filtered through during the measurment.

The results confirm the suspicion that evacuation of product into the recirculated water might be what caused the much lower filter value for the outlier 5.5 wt% waterglass samples, mentioned in the beginning of this chapter.

5.4 Analysis of outliers

From the first waterglass measurements it was suspected that evacuation of product into the water might be a possible explanation to the lower filter value of the outlier samples. With the later obtained results from the seed-particle analysis, it was obvious that small concentration of product had an apparent effect on the filter capacity of 5.5 wt% waterglass. Therefore, it was of interest to analyze the water samples used to dilute the outlier 5.5 wt% waterglass samples for elevated concentrations of particles. LPC analysis was used to give an indication of the amount of particles in the outlier water samples and reference samples. See graph 7, below.

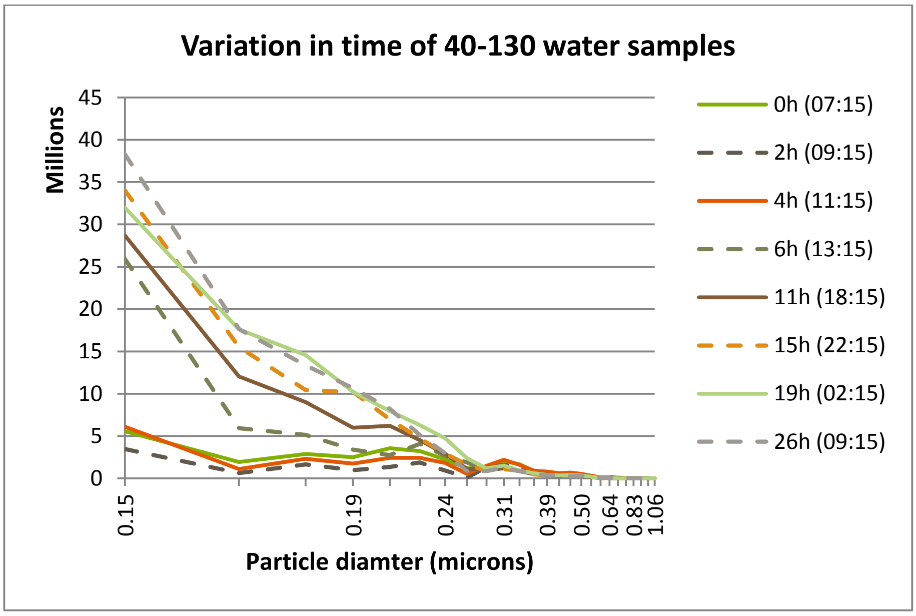


Graph 7: LPC analysis of water samples which were used to dilute outlying 5.5 wt% waterglass samples

The results of the analysis showed with consistency, that all the water samples that had produced outliers contained larger amounts of particles. The results are regarded as a verification of the hypotheis that small concentrations of particles in the water decrease the filter capacity of waterglass.

5.4.1 Analysis of condensate water over time

As it had been established that there was evacuation of product into the recirculated water streams, a final analysis was performed. The degree of evacuation of product over time into the condensate water was analyzed, as it was of interest to see if there was an increasing or constant evacuation as well as to examine the performance of the particle separator in the condenser. Water samples were collected over the course of 26 hours, beginning at the frequency of once every two hours. The water samples were later analyzed by LPC in order to observe the difference in evacuation of product between the samples. See graph 8, below.



Graph 8: The LPC results of the condensate water samples collected over 26 hours

From the results of the analysis it was detected that the evacuation of product was increasing with time. For the first 4 hours, shortly after the start-up of 40-130 had begun manufacture, the evacuation was held low and reasonably constant. However, after 4 hours it is percived that the evacuation began to increase steadily throughout the whole 26 h period water samples were collected.

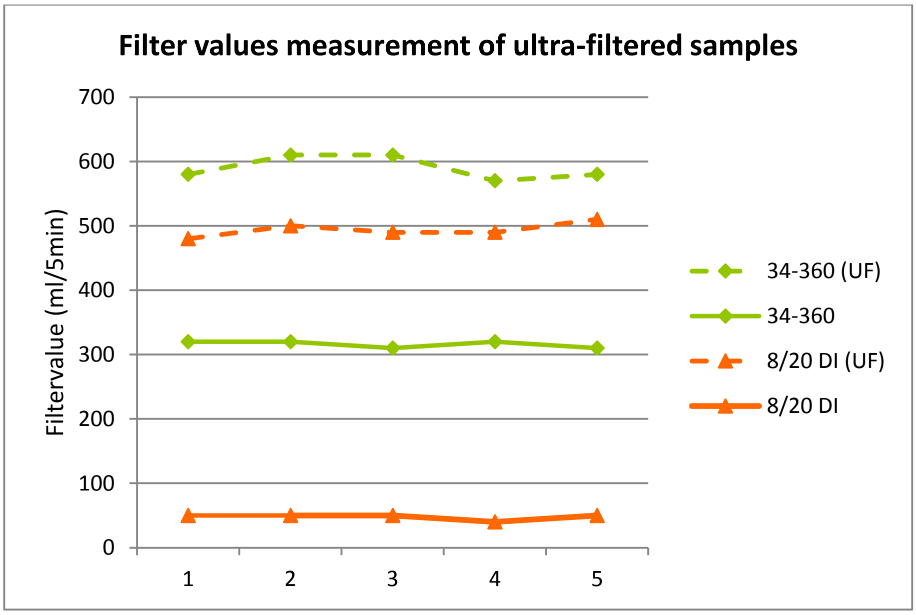
5.5 Results of ultra-filtration

Particles evacuated into the recirculated water were the most likely cause of the filter capacity issue in the plant, according to the obtained results of this thesis. Thus, a work-up procedure that could easily separate and get rid of small concentrations of particles from water streams needed to be evaluated. Ultra-filtration was chosen as it was already a known separation technique used by AkzoNobel in the silica sol process. However, the ultra-filtration membranes used in the work-up procedure had a much smaller cut-off than the membranes used in the plant.

The work-up procedure was performed on two different water samples. The first water sample was of milliQ water doped with 100 ppm of 8/20 DI seed-particles, in order to see if the filtration would work on nano-particles. The second water sample was collected from the plant and had been analysed beforehand, in order to make sure it produced low filter values and contained evacuated particles.

5.5.1 Filter value measurement of ultra-filtered samples

The outcome of the work-up procedure was analysed by measuring the difference between 5.5 wt% waterglass samples that had been diluted with water samples before and after work-up. The results are presented in graph 9, below.

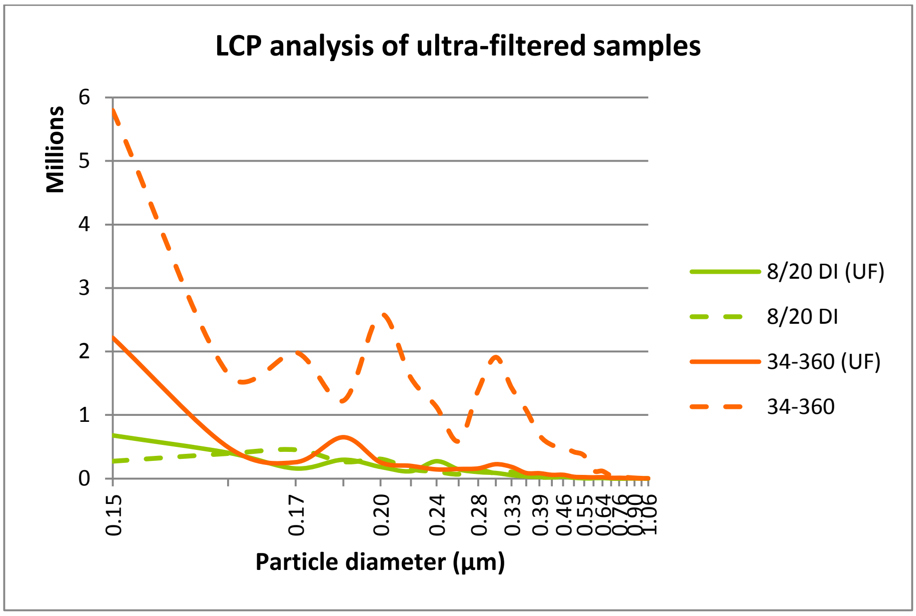


Graph 9: The measured filter values for 5.5 wt% waterglass samples diluted with water samples before and after work-up by ultra-filtration.

The results of the filter value measurement were promising. The filter values for the samples that had passed through the work-up procedure by ultra-filtration were much higher.

5.5.2 LPC analysis of ultra-filtered samples

To strengthen the results of the filter value measurements, and make sure separation of particles had actually been achieved, they were analysed by LPC. See graph 10, below.



Graph 10: The LPC results of the water samples before and after work-up by ultra-filtration

The results for the 34-360 samples show a clear difference in the amount of particles. As for the 8/20 DI samples, no clear difference can be observed. The particles of the 8/20 DI seed are smaller than the detection limit of the LPC instrument.

6 Discussion

6.1 Waterglass investigation

The larger part of this thesis was spent on the waterglass investigation. The sampling and evaluation of analytical data and filter value measurements for the recirculated waters and waterglass solutions was a time consuming task. The acquired results from the investigation could unfortunately not be used to make a qualitative estimation concerning the relation between quality parameters of the samples and the filter capacity of waterglass, due to the lack of consistency and high uncertainty in the data. Nevertheless, the vast amount of data entails a high quantitative value and worked as a substantial source of information for the comprehension of the other experiments performed during the thesis.

One important discovery which the waterglass investigation did lead to, although not part of the aim of the thesis, was the information gathered for the condensate water stream. The analysis of the condensate water samples exposed a much higher contamination and inconsistent quality then what had previously been acknowledged.

6.2 Ion-exchange experiments

The result obtained for the ion-exchanged measurements unmistakeably demonstrates that the procedure has an effect on the filter capacity of waterglass. The filter values indicate that the ion-exchange process slightly increases the filter capacity of waterglass, which was the opposite result to what we had initially expected. One explanation for the outcome of the ion-exchange is that the filter value is increased due to a slight dilution of the waterglass sample, which is hard to completely avoid during the experiments, and also that the cationic exchange resin works as a sand filter and reduces the silica content slightly.

The dilution of the waterglass samples occurs because the ion-exchange column is initially filled with water. Precautions were taken in order to avoid dilution in the collected samples. Before collection of sample 3 l of waterglass were let to pass through the column to purge it of the initial water. The data from the density data of the samples before and after ion-exchange still suggest that the samples have been slightly diluted. However, the dilution of the samples is not enough to explain the entire increase of the filter value measurements, which is why the resin is also thought to work as sand filter. The resin is a porous granulates material and has a particle size which is larger by several magnitudes to that of the colloidal silica particles in the water glass, and the ionic exchange of the silica particles takes place within the resin granulates. During the ion-exchange the silica particles diffuse in and out of the porous cavities of the resin granulates at a rate which is determined by the concentration gradient of the Na^+. It is exceedingly plausible that the resin granulates also acts as porous sand filter, trapping small amounts of the silica particles without the cavities. The assumption is also strengthened by the analysis of the samples before and after, which demonstrates a decrease in silica content of the samples after the ion-exchange.

For all intents and purposes of the ion-exchange process, it is not believed that the technique should be considered as a method for increasing the filter capacity of waterglass. As the increase is most likely due to the loss of silica content and dilution which are undesired accidents that lower the overall efficiency of the silica sol production.

6.3 Doped experiments

The doped sample experiments consisted of four different systems that were tested in regular and ion-exchanged filter value measurements as to see the effect they had on the filter capacity. The systems were primarily prepared to distinguish which compounds showed a definite influence the filter capacity, and which compounds showed diminutive influence and could be excluded from further inquiry.

6.3.1 General Ions and Sodium Aluminate

The systems doped with general ions (Na^+, Ca^{2+}, Cl^-) and sodium aluminate (Na^+, Al^{3+}) showed little to no effect on the filter capacity of both the alkali and ion-exchanged acidic waterglass samples. The concentration of the ions in these compounds had been increased by a factor ten to what is normally measured for the recirculated waters. The effects on the filter capacity of these systems were judged to be within tolerable limits and they were excluded from further examination.

6.3.2 Iron Chloride

The system doped with iron chloride (Fe^{3+}, Cl^-), a flocculation agent, demonstrated a distinct influence on the filter capacity for the alkali waterglass samples and very little effect on the ion-exchanged acidic waterglass samples. When the samples were prepared and the waterglass was introduced to the iron chloride a visible discolouring could be observed, as they went from clear transparent to opaque brownish, over a short period of time. This indicates that the iron chloride had induced flocculation of the colloids and the change of colour of the samples is explained by the growth of aggregates large enough to scatter light. As the filter value measurements were performed a thin layer of particles could also be seen at the surface of the filter papers. The results are intriguing but yet of little relevance as it come to explain the issue of the filter capacity. AkzoNobel no longer uses the flocculating agent used in this experiment but another which contains Al^{3+} instead. Still, it should be recognized that the effect from Fe^{3+} even in very small concentrations has a strong effect on the filter capacity of alkali waterglass and should be used with great caution and consideration.

6.3.3 Seed Particles

The systems doped with seed-particles were analysed over a concentration distribution, ranging from 10 – 1000 ppm of 8/20 DI. The results from the filter value measurements displayed a clear reduction of the filter capacity and that the effect was concentration dependant, as it became more apparent with a higher concentration. At concentrations between 10 – 50 ppm, the effect on the filter capacity was relatively small. Then, at the juncture between 50 – 100 ppm, the effect of the seed-particle spiked and increased immensely. For the concentrations above 100 ppm, up to a 1000 ppm, the effect was practically constant and did not increase beyond what was measured for 100 ppm. It is also important to understand that the 8/20 DI seed-particles themselves have a perfectly good filter capacity and the particles are about sixty times smaller than the pore size used during the filter value measurements. With this in consideration when looking at the behaviour of the seed-particle experiment, it suggests that the introduction of seed-particles have initiated nucleation [22].

The behaviour at the juncture between 50 – 100 ppm of seed-particles can be seen as the concentration threshold for a nucleation event to occur. The already existent and larger colloidal silica particles act as nucleation sites for the seed-particles. The surface of the colloids allows for partial wetting of the seed-particles, which reduces the Gibbs energy barrier for nucleation and allows the seed-particles to initiate heterogeneous precipitation and forming particle clusters, gelling, at the sites of the colloids. In a controlled environment the high supersaturation of the waterglass would favour uniform spherical growth of the colloids. In this case, however, since the growth of the cluster takes place at the spinodal of the waterglass solution and because the effect on the filter capacity is so immense, it is believed that the clusters grow in fractal branches. That way, the branches could link with other clusters and colloids forming a mesoporous labyrinth-like structure, which would have the capacity to get large enough to clog the filter during the measurements. If there had been uniform spherical growth, the colloids would have had to grow by several magnitudes in order to be able to clog the filter, which is not plausible at such low concentrations of seed-particles [22].

At a concentration below the threshold for the nucleation event, the seeds have most likely also formed clusters and gel around colloidal silica. However, since the concentration is so low only a few colloids have been nucleated which is not enough to form a large gel structure and clog the filter.

6.4 Analysis of Outliers

During the investigation of waterglass samples and water quality parameters, the suspicion that evacuated particles from the product had been the cause of the lower filter values for the outliers had already been set into motion. The results from the seed-particle experiments backed-up those suspicions further, by giving clear indications that small concentrations of particles have a great reducing effect on the filter capacity of waterglass. Thus, we began to analyse the outlier water samples with LPC to see if they contained elevated levels of particles. The resulting graphs showed with consistency that all the outlier samples that were analysed contained higher concentrations of particles. I would like to argue that this is the main reason for the poorer filter values of the outliers and the most likely cause for the filter capacity issue at AzkoNobel, with the failed results from the water quality investigation and the indicative results from the seed-particle experiments to support my case.

The next step was of course to try and understand how the evacuation of particles into the water streams might transpire. Due to the little time that was left on the thesis, we chose to only look briefly at condensate water from the evaporator. Samples were taken over a period of 26 h, from the upstart of a new product, which then were analysed by LPC. The results that were obtained suggest that the demister, which enhances the removal of droplets in the evaporator and increases the vapour quality, becomes less effective over time. The results show that the particle content in the samples is readily increasing over time. A possible explanation could be that the capacity for separation of droplets and particles is reduced as the demister gets dirty.

6.5 Ultra-filtration

Ultra-filtration was a filtration technique already used and known by AkzoNobel, and was chosen to be tested as a work-up procedure of water samples that contained elevated amounts of particles. The permeate water samples in this thesis have already been through ultra-filtration in the silica sol process, before being collected. However, as we had determined through the analysis of several samples from both SUF and LUF permeate waters, the membranes have failed to filter many particles. Therefore, new membranes were bought with a 100 times better retention character, or cut-off, in order to get an even better separation than in the plant. In the plant, the separation over the membranes is also dependant on the build-up of filter cake, which helps increase the effect of separation. In our case, we used very small concentrations of particles and would not get a filter cake and speculated that this might cause a problem.

The results that were obtained from the LPC analysis, before and after ultra-filtration, demonstrated much lower particle count for filtered samples even though not all particles had been removed. The filter value measurements of the samples gave much better values for the filtered samples and showed that the filter capacity had increased with a better removal of particles. It is important to consider that before we had only tested different concentrations of seed-particles and showed that a lower concentration of 8/20 DI resulted in a better filter capacity of the waterglass. Now, however, we had also verified that a better separation of actual evocated particles from the plant also resulted in better filter capacity of the waterglass.

7 Conclusion

7.1 Waterglass filter value measurements

- The water quality parameters of the recirculated water streams do not have as strong influence on the filter capacity of waterglass as it was previously assumed.

- Empirically, permeate water from the small ultra-filter has more consistent and higher filter capacity compared to the other investigated waters. This makes it the best choice for recycling in the future.

7.2 Doped samples analysis

- Seed particles have a reductive influence on the filter capacity of waterglass. The effect is prominent at small concentrations and rapidly increased with increased concentration of seed.

- The concentration behavior points toward a nucleation event which is initiated upon exceeding a certain concentration threshold.

- The nucleation of the seed particles is initiated on already present colloidal silica sites in the waterglass and likely grows in fractal cluster formation. By exceeding the concentration threshold enough clusters have formed to link together into a gel-like structure that utterly reduces the filter capacity.

7.3 Analysis of outliers

- Low filter capacity of waterglass solutions was recognized to be related to higher concentration of evacuated particles in the recycled water samples.

- Evacuation of particles into the recycled water streams is likely the cause behind the filter capacity issue in the silica sol process.

7.4 Ultra-filtration

- Ultra-filtration with filter membranes of a higher retention character can be used to effectively reduce the amount of particles of water samples.

- Reducing the amount of particles in water samples successfully increases the filter capacity of waterglass.

8 Future work

This thesis has approached the filter capacity issue briefly from several angles in order to outline the most probable cause of the reduction and erratic behaviour of the filter capacity. Ultimately, the study managed to exclude and determine which factors are the most relevant. Due to limited time the research have only grazed at the surface of the possible explanations and there is still much work left to be done in order to fully understand the influences on the filter capacity.

Future work that could be performed on the subject might be to further investigate the effect of seed-particles in waterglass solutions; Testing different combinations of particle sizes, size distributions, concentrations and conditions in the waterglass. It would also be interesting to analyse the particle clusters morphology, in order to further understand the mechanism behind the precipitation.

Moreover, future work should also be concentration on trying to develop possible work-up procedures for both water and waterglass. More in-depth studies could be done on the ultra-filtration techniques, looking at different setups and filter and also trying to determine the capacity of the method. Other techniques that might be useful would also be interesting to investigate, such as reverse osmosis. One might also what to look at the difficulties of dissolving seed-particles in water and waterglass samples.

Lastly, it is of importance to continue to investigate the evacuation of product in the silica sol process. Which process operations can evacuate product into recycled streams and how can it be prevented?

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10 Appendix

10.1 Appendix A

Collection of raw data for water samples, waterglass samples, ion-exchanged samples, and doped samples.

Table 4: The data collected for the different water samples collected during the thesis.

Water samples							
Nr	*Product*	*Water*	*Density*	*pH*	*Cond.*	*Turbidity*	*Date*
#	-	-	*g/cm3*	-	*µS/cm*	*NTU*	-
1	40-170	Condensate	0.998	8.72	3	0.103	10/11/2013
2	40-130	Condensate	0.999	8.63	3	0.138	10/18/2013
3	40-130	Permeate (S)	0.999	9.57	231	0.103	10/18/2013
4	442	Permeate (L)	0.999	9.76	548	0.196	10/22/2013
5	40-130	Condensate	0.996	8.66	4	0.158	10/22/2013
6	40-130	Permeate (S)	0.999	9.70	523	0.128	10/22/2013
7	40-220	Condensate	0.996	8.66	4	0.158	10/30/2013
8	40-220	Permeate (S)	0.999	9.70	523	0.128	10/30/2013
9	34-360	Condensate	0.999	6.86	4	0.230	10/31/2013
10	34-360	Permeate (S)	0.999	9.74	825	1.250	10/31/2013
11	50-80	Condensate	0.999	6.06	3	0.523	11/4/2013
12	50-80	Permeate (S)	0.999	9.87	877	0.140	11/4/2013
13	34-360	Condensate	0.998	6.93	3	0.355	11/11/2013
14	34-360	Permeate (S)	0.999	9.58	485	0.261	11/11/2013
15	247	Permeate (L)	0.999	9.98	793	0.202	11/13/2013
16	34-360	Condensate	0.998	7.61	2	0.260	11/15/2013
17	900(442)	Permeate (L)	0.999	10.02	747	0.140	11/16/2013
18	900	Permeate (L)	1.001	10.22	1264	0.238	11/20/2013
19	40-130	Condensate	0.999	8.46	4	0.699	11/21/2013
20	40-130	Permeate (S)	0.999	9.34	441	0.243	11/21/2013
21	40-220	Condensate	0.998	9.14	3	0.444	2/4/2014
22	40-220	Permeate (S)	1.000	9.69	776	0.137	2/4/2014

*The #nr value is used to connected related water samples, waterglass samples and ion-exchanged samples

Table 5: The data collected for the different waterglass solutions prepared during the thesis.

Waterglass samples									
Nr	*Prod*	*Water*	*Density*	*Mass cont.*	*pH*	*Cond.*	*Turbidity*	*Ratio*	*Filter value*
#	*-*	*-*	*g/cm^3*	*SiO_2 wt%*	*-*	*µS/cm*	*NTU*	*SiO_2:Na_2O*	*Avg*
1	40-170	Condensate	1.0592	5.56	11.62	22.4	0.35	3.24	565
2	40-130	Condensate	1.0589	5.53	11.64	22.5	0.37	3.23	692
3	40-130	Permeate(S)	1.0593	5.57	11.65	22.5	0.307	2.72	702
4	442	Permeate(L)	1.0593	5.57	11.58	22.5	0.205	3.29	675
5	40-130	Condensate	1.0578	5.44	11.57	22.1	0.225	3.32	729
6	40-130	Permeate(S)	1.0591	5.55	11.6	22.6	0.25	3.26	752
7	40-220	Condensate	1.0588	5.52	11.43	22.5	0.393	3.26	542
8	40-220	Permeate(S)	1.0585	5.5	11.53	22.5	1.06	3.23	263
9	34-360	Condensate	1.0588	5.52	11.55	22.4	0.7	3.27	316
10	34-360	Permeate(S)	1.0598	5.54	11.52	22.6	0.394	3.25	687
11	50-80	Condensate	1.0585	5.49	11.48	22.4	0.57	2.81	497
12	50-80	Permeate(S)	1.0589	5.53	11.43	22.6	0.58	3.25	692
13	34-360	Condensate	1.0588	5.52	11.61	22.4	0.45	3.25	471
14	34-360	Permeate(S)	1.059	5.54	11.52	22.6	0.394	3.25	688
15	247	Permeate(L)	1.0589	5.54	11.41	22.6	0.448	3.28	563
16	34-360	Condensate	1.0588	5.52	11.61	22.4	0.45	3.25	423
17	900(442)	Permeate(L)	1.0588	5.52	11.63	22.6	0.421	3.23	295
18	900	Permeate(L)	1.0586	5.5	11.53	22.3	0.571	3.26	330
19	40-130	Condensate	1.0588	5.52	11.53	22.3	0.275	3.27	314
20	40-130	Permeate(S)	1.0581	5.46	11.54	22.3	0.275	3.21	564
21	40-220	Condensate	1.0582	5.47	11.48	22.2	0.491	3.23	368
22	40-220	Permeate(S)	1.0588	5.52	11.51	22.5	0.271	3.18	428

Table 6: The data collected for the different ion-exchanged waterglass solutions prepared during the thesis.

Ion-exchanged samples								
Nr	*Prod*	*Water*	*Density*	*Mass cont.*	*pH*	*Cond.*	*Turbidity*	*Filter value*
#	*-*	*-*	*g/cm3*	*SiO_2 wt%*	*-*	*µS/cm*	*NTU*	*avg*
17	900(442)	Permeate (L)	1.0311	5.46	2.4	990	1.21	580
18	900	Permeate (L)	1.0310	5.44	2.47	993	1.27	484
19	40-130	Condensate	1.0309	5.4	2.39	581	1.57	396
20	40-130	Permeate (S)	1.0314	5.49	2.46	1105	1.27	553

Table 7: The data collected for the different doped waterglass solutions prepared during the thesis.

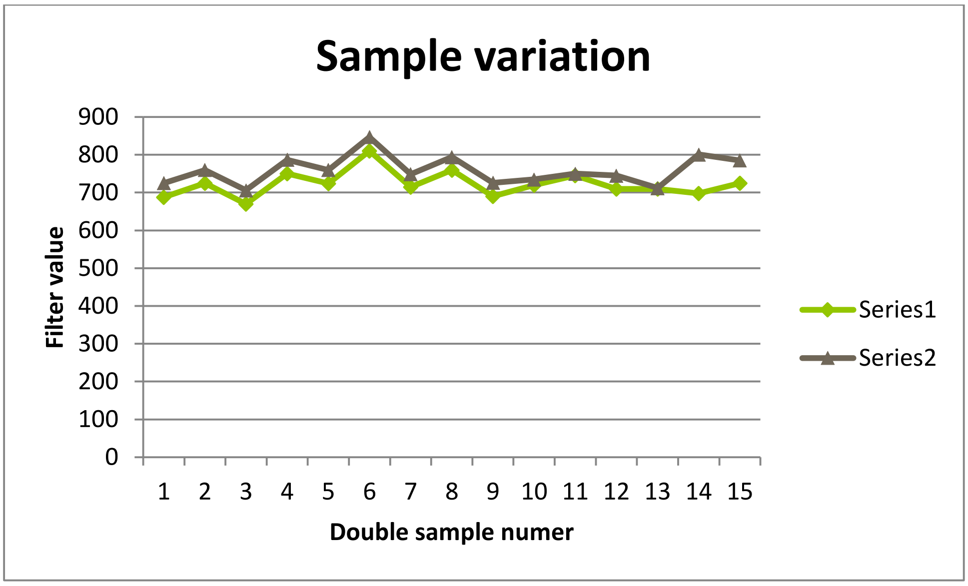
Doped Samples									
Chemical	*Conc.*	*Density*	*Mass cont.*	*pH*	*Cond.*	*Turbidity*	*Ratio*	*Filter value*	*IX*
-	*ppm*	*g/cm^3*	*SiO_2 wt%*	-	*µS/cm*	*NTU*	*SiO2 : Na2O*	*avg*	-
Aluminate	100	1.0593	5.56	11.51	22.5	0.288	3.194	689	B
Aluminate	100	1.0300	5.27	2.5	727	0.755	-	664	A
$FeCl_3$	100	1.0583	5.52	11.5	22.5	0.47	3.243	352	B
$FeCl_3$	100	1.0309	5.41	2.39	1072	1.39	-	618	A
$CaCl_2$/NaCl	50 / 50	1.0594	5.58	11.53	22.5	0.197	3.288	608	B
$CaCl_2$/NaCl	50 / 50	1.0308	5.41	2.56	1008	1.29	-	668	A
8/20 DI	1000	1.0587	5.52	11.58	22.1	114	3.183	50	-
8/20 DI	500	1.0579	5.45	11.59	22.1	19.6	3.260	24	-
8/20 DI	100	1.0581	5.46	11.67	22.4	6.97	3.189	33	-
8/20 DI	50	1.0587	5.52	11.6	22.3	0.54	3.193	509	B
8/20 DI	50	1.0309	5.43	2.52	558	1.44	-	595	A
8/20 DI	10	1.0590	5.54	11.65	22.4	0.36	3.207	540	B
8/20 DI	10	1.0312	5.45	2.49	601	1.37	-	606	A

*A = after ion-exchange
B = before ion-exchange

10.2 Appendix B

10.2.1 Sample variation in method

The results and data obtained from the investigation of sample variation within the filter value measurement method.

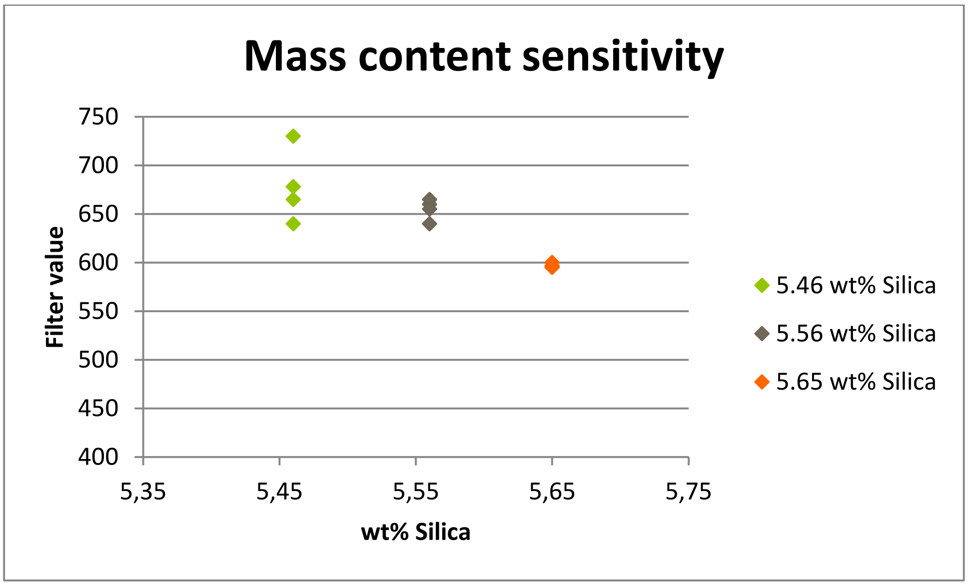


Sample Variation		
#	**Filter value**	
	Trail 1	**Trail 2**
	(ml/ xmin)	*(ml/ xmin)*
1	688	725
2	725	760
3	670	706
4	750	787
5	724	760
6	810	847
7	715	749
8	760	794
9	690	726
10	720	735
11	745	750
12	710	745
13	710	712
14	698	801
15	725	785

Trail 1 = 5.5wt% VGL
Trail 2 = 5.52wt% VGL

10.2.2 Mass content sensitivity

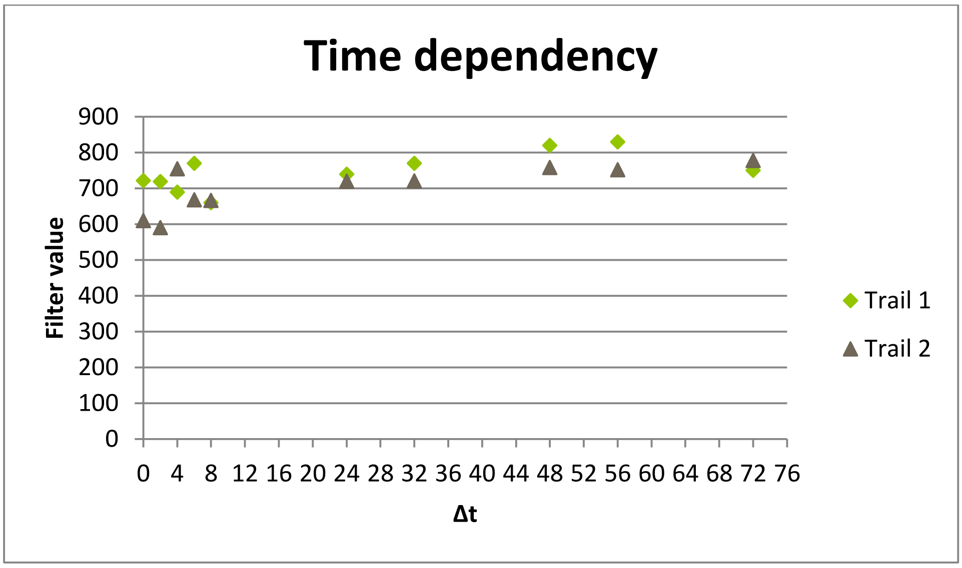
The results and data collected for the investigation of how the measured filter values vary at different levels of silica content.



wt% variation			
#	Filter value		
	5.46 wt%	**5.56 wt%**	**5.65 wt%**
	(ml/5min)	*(ml/5min)*	*(ml/5min)*
1	730	660	595
2	640	640	600
3	665	665	595
4	678	655	596

10.2.3 Variation over time

The results and data collected for the investigation of how the filter values of waterglass sample vary over time with aging.



Time dependency		
Δ**t**	**Filter value**	
	Trail 1	**Trail 2**
(h)	*(ml/x min)*	*(ml/x min)*
0	722	610
2	719	590
4	690	755
6	770	668
8	660	666
24	740	720
32	770	721
48	820	758
56	830	752
72	750	778

Trail 1 = 5.45wt% VGL + permeat (stora UF)
Trail 2 = 5.55wt% VGL + permeat (lilla UF)