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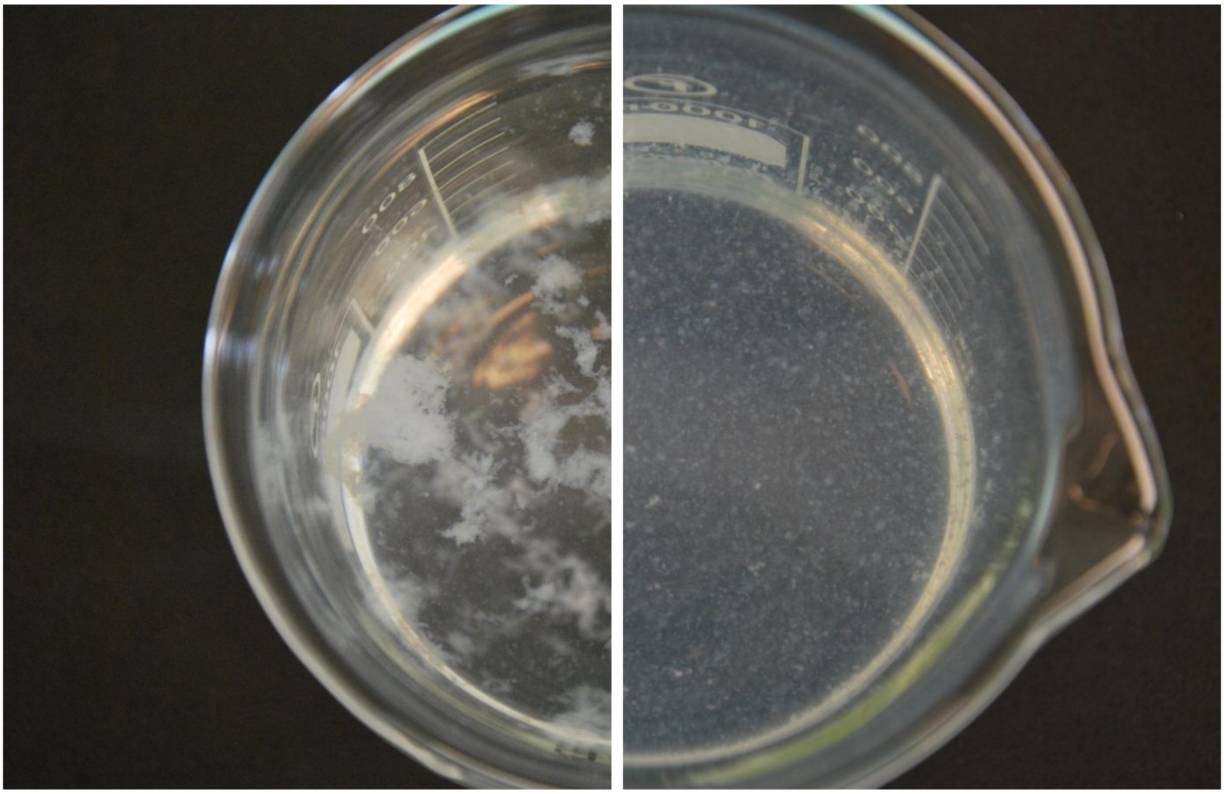

Optimising the surfactant system in semi-neutral deinking

Master of Science Thesis within the Materials and Nanotechnology Programme

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Department of Chemical and Biological Engineering
Division of Applied Surface Chemistry
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, 2011

MASTER´S THESIS

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Cover: The difference in precipitation behaviour between magnesium and calcium ions. To the left is the precipitation of oleic acid potassium soap and magnesium ions, to the right the precipitation of mixed unsaturated fatty acid potassium soap and calcium ions.

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Abstract

In this master thesis the surfactant chemistry of the flotation deinking process was studied. The focus was on the chemicals added in the pulping step and their influence on the deinking efficiency. The differences between traditional flotation deinking using NaOH as an alkali source and semi-neutral deinking, using BIMPRO® were evaluated. BIMPRO® is a concept for semi-neutral deinking developed by BIM Kemi Sweden AB and contains $Mg(OH)_2$ as the major alkali source. By substituting NaOH with BIMPRO® the pH is lowered in the deinking process and several benefits can be achieved, e.g. lower COD values.

Three fatty acid potassium soaps (oleic acid, mixed unsaturated fatty acids and stearic acid) and one non-ionic polymeric surfactant were evaluated in the pulper step and all except the stearic acid soap showed promising results concerning brightness and ERIC.

The influence of parameters such as hardness, alkalinity and pH on the deinking performance was considered. Different amounts of BIMPRO® and sodium silicate were also tested but no clear trends could be found. However, by excluding calcium ions in the pulping step better flotated values of brightness and ERIC were achieved.

The ageing of ink was also evaluated and the result was obvious; fresh old newsprint (ONP) and old magazines (OMG) gave the best performance. No difference could be found between a fatty acid potassium soap and a non-ionic polymeric surfactant when the raw material was ageing.

The agglomeration kinetics of soap formation were evaluated using the Turbiscan Online technique. The differences in precipitation behaviour between fatty acid potassium soap and calcium ions and/or magnesium ions were investigated. When using a system including both calcium and magnesium ions the mixed system behaved more like a pure calcium system. The same trend was found in surface tension measurements.

Thus, in future work concerning semi-neutral deinking including $Mg(OH)_2$ as an alkali source the effects of mixing magnesium and calcium ions will have to be considered.

Key words: Deinking chemistry, semi-neutral deinking, flotation deinking, ageing of ink, agglomeration kinetics, fatty acid potassium soap, calcium ions, magnesium ions

Optimering av tensidsystemet vid semi-neutral avsvärtning av returfiber
Examensarbete inom masterprogrammet Material och nanoteknologi
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Sammanfattning

I detta examensarbete undersöktes ytkemin i processen kring avsvärtning av returfiber. Fokus låg på kemikalierna som doseras i uppslagaren och på deras effekt på avsvärtningsprocessen. Skillnaderna mellan traditionell avsvärtning med natriumhydroxid som alkalikälla och semi-neutral avsvärtning med BIMPRO® som alkalikälla studerades. BIMPRO® är ett koncept för semi-neutral avsvärtning som utvecklats av BIM Kemi Sweden AB, och är baserat på $Mg(OH)_2$ som främsta alkalikälla. Genom att ersätta natriumhydroxid med BIMPRO® sjunker pH i hela avsvärtningsprocessen vilket ger flera fördelar, exempelvis lägre COD-värden.

Tre kalifettsyratvålar (oleinsyra, en blandning av omättade fettsyror samt stearinsyra) och en polymerisk nonjontensid utvärderades i uppslagningssteget. Alla utom stearintvålen visade lovande resultat med avseende på ljushet och ERIC.

Inverkan av vattnets hårdhet, alkalinitet och pH på avsvärtningen studerades. Varierande mängder av BIMPRO® och silikat testades, men inga tydliga trender kunde ses. Om man däremot uteslöt kalciumjoner i uppslagaren kunde ett bättre resultat med avseende på ljushet och ERIC uppnås.

Inverkan av åldring av trycksvärta på avsvärtningsresultaten utvärderades och trenden var tydlig: färsk råvara av tidning (ONP) och magasin (OMG) gav bättre avsvärtning. Däremot kunde inga skillnader ses mellan kalifettsyratvålar eller polymerisk nonjontensid när råvaran har åldrats.

Agglomerering och utfällning mellan kalitvål och kalciumjoner och/eller magnesiumjoner utvärderades i en Turbiscan Online. När ett system innehållande både kalcium- och magnesiumjoner analyserades betedde sig systemet som ett rent kalciumsystem. Samma trend fanns vid ytspänningsmätningar.

I ett framtida arbete om semi-neutral avsvärtning där $Mg(OH)_2$ ingår som alkalikälla måste effekterna av ett mixat system bestående av både kalcium- och magnesiumjoner beaktas och utvärderas.

Nyckelord: Avsvärtning, semi-neutral avsvärtning, flotation, åldring av trycksvärta, agglomerering och utfällning av tvålsystem, kalifettsyratvål, kalciumjoner, magnesiumjoner.

Table of contents

1. Introduction

In chapter 1 the background, setup and aim of this project are described. Also, a short presentation of BIM Kemi AB can be found.

1.1 Background

Paper was invented in China in the year 105 A.D. A man called Ts'ai Lun had got orders from Emperor Hoti to work on a substitute to papyrus. He made paper from the bark of mulberry trees that was treated with bamboo, lime and cloth. The Chinese kept the invention a secret for many centuries until it slowly made its way westward, to the Arabs and, in 1496, to England.

One important milestone in the history of papermaking was the development of the paper machine. The first model was patented in France 1799, by Louis Robert. The development was then led by two brothers; Henry and Sealy Fourdrinier. The two brothers and a third man, Bryan Donkin, developed the first practical paper machine in 1804, in England.

The paper machine was refined many times between 1804 and 1830. At last, still in the beginning of the 19th century, it was the fibre supply that was the limitation since cotton was the largest source to papermaking. The next step in papermaking was therefore the development of the technology to convert wood to pulp suitable for paper production (1).

In the last decades, the fibre supply has once again become a limitation. This fact, together with rising prices on virgin pulps, has made recycled fibres a very important substitute for virgin pulps (2).

Today, in Sweden, 91 percent of all used newspaper, magazines, catalogues and papers advertisement are recycled. Paper fibres can be recycled five to seven times before they are too short to be used (3). Sweden was the first country in the world to introduce legislation to assist paper recovery. This was in 1975 (4).

1.2 Deinking today

One important part in the recycling process is to separate the ink particles from the fibres and a common way is to use flotation deinking (5). This is actually not a new invention. As early as 1774, even before the invention of the paper machine, when paper were made of rags, Claproth in Göttingen, Germany, invented a process where he removed optically disturbing inks or printing inks. In flotation deinking both mechanical force and chemical reactions participate in the detaching of the ink particles from the fibres. Today, the most common process is alkaline deinking which means that the pH is quite high, 8-11. The chemicals used are sodium hydroxide, hydrogen peroxide, sodium silicate, fatty acid soaps and non-ionic surfactants (6).

1.2.1 The industrial process

The industrial flotation deinking process can be seen in figure 1. This is however a simplified schematic picture showing some of the steps in the process. In the pulping drum staples, plastic bags, rubber bands and other big parts are collected and removed. The fibres are mixed with water and chemicals and passed through to several sieves before they reach different reaction towers. The next step is the flotation process which is often containing several flotation cells in series to be more efficient. The pulp is then washed and once again passed through sieves. The last process steps are often concerning bleaching of the pulp and even more flotation steps before the pulp is passed on to the paper, board or tissue machine.

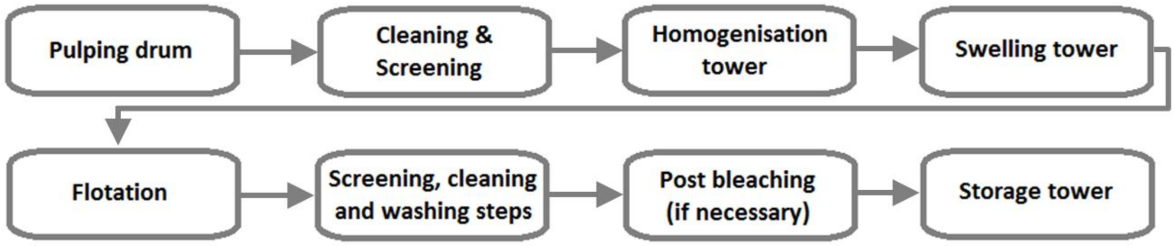

Figure 1: The industrial flotation deinking process, simplified.

1.3 Deinking at lower pH

The traditional alkaline deinking process has some drawbacks. It operates at a much higher pH than the rest of the processes in a paper mill, meaning that an acidification of the deinked pulp is sometimes necessary. This may lead to an increase of the water hardness causing e.g. yield reduction (7).

One way to make the process operate at a lower pH is to reduce or eliminate the use of sodium hydroxide as an alkali source. Replacing the sodium hydroxide with magnesium hydroxide, $Mg(OH)_2$, has been tested with good results (8) (9).

The most important advantages with semi-neutral over traditional alkaline deinking are:
less yellowing of mechanical fibres, lower chemical costs, lower residual ink, less problems with stickies and lower COD (chemical oxygen demand) values (7).

1.3.1 BIMPRO®

BIMPRO® is a concept for semi-neutral deinking developed by BIM Kemi AB. It is based on the chemistry of magnesium hydroxide, $Mg(OH)_2$, and no or very limited amounts of sodium hydroxide is necessary in the process. Magnesium hydroxide is dissolved slowly which is the reason why BIMPRO® gives lower COD values than traditional deinking. It may also be used with traditional emulsions and soaps that originally are developed for alkali deinking (10). The amount of hydrogen peroxide used in the process can also be reduced since yellowing of pulp is very limited with the BIMPRO® concept, apart from the advantages already mentioned.

1.4 The aim and setup of the master thesis

The aim of this master thesis was to study and evaluate the effects of different combinations of fatty acid potassium soaps and non-ionic surfactants in both a traditional alkaline deinking system and a semi-neutral deinking system based on BIMPRO®. The work comprised

- Flotation deinking
- Ageing of ink
- Surface tension measurements
- Agglomeration kinetics
- Particle size measurements

The thesis was limited to technical aspects. Neither economic considerations nor environmental differences between fatty acid potassium soaps and a non-ionic polymeric surfactants were evaluated (although both these aspects tend to be in favour of semi-neutral deinking).

1. 5 The company

This master thesis was performed in cooperation with BIM Kemi Sweden AB in Stenkullen outside Göteborg and the Division of Applied Surface Chemistry at Chalmers University of Technology.

BIM Kemi AB is a family owned company which develops and produces specialty chemicals and solutions to the pulp and paper industry. BIM Kemi AB is a research intensive company that invests substantially in research and development, mainly in advanced surface treatment. The headquarters are located in Stenkullen but the company is found in several countries in Europe (10).

2. Theory

The theory behind the deinking process is found in chapter 2. The added chemicals, several parameters affecting the process and ageing of ink are also described.

2.1 The different wastepaper categories

The wastepaper that is collected is divided into several different categories where the three most important are old newsprint (ONP), old magazines (OMG) and mixed office waste (MOW). In this mater thesis ONP and OMG were be used.

Old newsprint has a very high amount of mechanical fibres. At the same time, the chemical pulp can be up to 30 weight percent of the furnish. Due to a high recovery rate for ONP, there are always recycled fibres in the process. Old newsprint is often printed with offset, but both letterpress and flexographic techniques are also used. The ink content is between 1-2 weight percent of the furnish.

Magazine is defined as coated paper that is bound with staples or glue. The raw material can be both Krafft pulp and groundwood giving high variability in the fibre component. Magazines may contain several different additives such as fillers and dye. The ink content ranges from 1-7 weight percent and the magazines are often printed with rotogravure inks (11).

2.2 Printing ink

Ink is an important additive in the paper industry. It is composed of a pigment, a vehicle and additives. The pigment is the colouring agent which is nearly insoluble in the medium in which it is used. The most used pigment in the printing industry is carbon black, which is produced by the incomplete combustion of hydrocarbons. The pigments for coloured inks are often organic molecules from chemical synthesis.

The vehicle is used to transport the pigment during printing. It is often composed of a hard resin, which is solid at room temperature, a solvent and a diluent.

The reason to add additives in to the ink is to achieve a specific quality requirement or to give the ink a specific performance. The most common additives are filling materials, gel formers, waxes and wetting agents. The additives affect the deinkability of the printing inks (12).

2.2.1 Ageing of ink

Ageing of printed ink is a big problem, both at laboratory scale and at the paper mills. The degree of ageing depends both on which ink and which technique, like offset and rotogravure that is used (12). In offset ink formulation the vehicle is of great importance considering ageing. Studies have shown that it is more difficult to detach mineral oil based ink than vegetable oil based ink in an early stage after offset printing. After ageing, the result is instead similar for the two types of ink. Both mineral and vegetable oils have the tendency to convert from liquid to solid over time if exposed to air and/or heat (13).

The problems with ink detachment in aged paper are due to multi-step oxidopolymerisation. The ink forms cross-links that improve the cohesiveness of the ink particles as well as the bond strength between the ink particles and the substrate (14). Oxidation of mineral oil ink takes up to 4-6 months while oxidation of vegetable oils is much faster (15).

Vegetable oil based inks change significantly when exposed to oxidation, both carbonyl groups and hydroxyl groups are formed (14). In vegetable oils the oxidation results in cleavage of fatty acids. One way to prevent the oxidation could be to use antioxidants, such as phenols, in the ink formulae (15).

The problem is often called the summer effect since the problem is due to thermal drying of newsprint inks and elevated storage temperatures, which is a bigger problem during the summer months. The drying leads to increased ink fragmentation and ink re-attachments on the fibres (16).

According to Johansson et al. non-ionic surfactants can be of great interest to improve ink detachment, especially concerning aged inks (17).

2.3 Deinking chemistry

Deinking is the term used to describe the detaching and removing of ink particles from recycled fibres (18). The process improves the quality of recycled fibres, meaning better optical properties. The process has several steps but the two most important considering ink removal are the re-pulping and the froth flotation / pulp washing steps. Flotation is more common to use in deinking than washing. According to Beneventi and Carre (6), the deinking chemistry needs to be formulated so the most appropriate surface properties are received, namely;

- Highly hydrophobic-unstable surfaces to permit ink agglomeration and strong adhesion to air bubbles for the flotation process.
- Hydrophilic-stable surfaces to avoid ink agglomeration and redeposition on fibres for the washing process (6).

Flotation deinking is the most efficient process for removing ink particles that are large, 20 – 300 µm, while washing is better considering removing smaller particles (19). In this master thesis, the focus was on flotation deinking since it is the most common type of deinking process.

One of the first steps in a deinking process is the re-pulping step. Here, the ink is detached from the fibres by both mechanical force and by added chemicals. The pulp is disintegrated in water at a consistency that varies depending on the mix of paper, often in the range of 5 – 18 percent (7). It is in the re-pulping stage many of the chemicals important for the flotation stage are added, e.g. dispersants, collectors, foaming agents, pH regulators etc. They are added in the re-pulping stage to assure good mixing and dissolution (19). The most common chemicals used for these purposes are sodium hydroxide, hydrogen peroxide, sodium silicate, fatty acid soaps and non-ionic surfactants (6). This is called traditional alkaline deinking (20).

2.3.1 Flotation

Air flotation is an efficient way to separate hydrophobic particles from a hydrophilic phase. The particles will adhere to the air bubbles, by absorption or adsorption, and be flotated off from the liquid phase. Flotation is a widely applied technique used in e.g. metal plating, mineral ore separation and soap manufacturing (21).

In the deinking of recycled fibres, flotation is the most common method used since it gives a high yield of fibres, i.e. a low amount of reject. When the fibre suspension enters the flotation stage, the detached ink particles have a specific size distribution that is depending on the composition of the ink and the hydrodynamic regime of the specific pulper.(7). This is one of the reason why flotation is sometimes a difficult process to simulate in laboratory scale, where the hydrodynamic conditions are very different from the full scale mill deinking process.

2.3.2 Sodium hydroxide

Sodium hydroxide (NaOH or caustic soda) is used in the process to adjust the pH to the alkaline region (pH 8-11). The high pH makes the fibres swell which helps the release of ink from the fibres. The fibres become more elastic than the ink, which will break into smaller particles. Caustic soda also causes ionization of the carboxylic groups on the cellulose fibres which will increase the repulsion between negatively charged fibres, dispersing the pulp suspension (6).

2.3.3 Hydrogen peroxide

The use of sodium hydroxide in deinking has some drawbacks where yellowing (also called darkening) of the fibres is the most unwanted. To prevent yellowing hydrogen peroxide is added to the process. It is the perhydroxyl anion, generated from hydrogen peroxide, and hydroxide ions that are responsible for the bleaching effect: (22)

Bleaching is the most significant role of hydrogen peroxide but it is also discussed that hydrogen peroxide has some more effects in the deinking process. It is suggested that hydrogen peroxide breaks bonds in the ink networks, and also creates smaller ink particles. This would make it easier for the ink particles to detach from the fibres. It is also suggested that peroxide destroys materials, possibly alkali-extracted material from fibres. This may give the ink particles hydrophilic surfaces which will make it harder for them to attach to air bubbles during flotation (23).

2.3.4 Sodium silicate

Sodium silicate is mainly used due to its property to stabilize the hydrogen peroxide. It inactivates metal ions which prevents the peroxide to catalytically decompose. Sodium silicate also works as a buffer regarding pH, giving hydrogen peroxide its best conditions to work. Literature suggests that sodium silicate has multiple roles in deinking, such as buffering and saponification properties, assisting the dispersion of ink particles and also working as an ink collector. However, there are also articles that refute these findings (24).

2.3.5 Fatty acids

Fatty acids consist of a long hydrophobic chain with a carboxylic group (COOH) in one of the ends, giving the fatty acid its weakly acidic properties. The chains are either unsaturated or saturated, where unsaturated means at least one double bond in the chain (11). Fatty acids and fatty acid soaps are both important and widely used chemicals in flotation deinking. In traditional alkaline deinking with sodium hydroxide, fatty acids are neutralized by sodium hydroxide. Saponification gives origin to a soluble salt which is dissociated as an anionic surfactant ($RCOO^-$) and a sodium counter ion. In the presence of calcium ions the anionic fatty acids reacts with the bivalent cation precipitating as a calcium salt. This generates highly hydrophobic soap flakes which act as ink collectors (6).

The fatty acids used in deinking flotation are often blends of C 14-18 carbon chains, see table 1 (19). The amounts of carbon atoms and double bonds in the chain govern the fatty acids properties. Therefore, a mix of several fatty acids will have different compositions of chain lengths and numbers of double bonds. Small changes in the fatty acid composition can influence the amount of foam, amount of reject and ink selectivity in the deinking process.

Table 1: Different fatty acids.

Fatty acid	Carbon atoms	Double bonds	Iodine value
Stearic acid	18	0	0
Oleic acid	18	1	90
Palmitic acid	16	0	0
Linoleic acid	18	2	181
Linolenic acid	18	3	???

2.3.5.1 Fatty acid potassium soaps

In this master thesis three different fatty acids (stearic, oleic and a mix of unsaturated fatty acids) were saponified to fatty acid potassium soaps. These soaps were tested with both BIMPRO® and sodium hydroxide, and in some studies with a non-ionic polymeric surfactant. One reason to use potassium as a counter ion is that it gives a higher soap concentration than sodium soaps, which is an advantage for transportation purposes.

The saponification reaction is as follows:
$RCOOH \text{ (fatty acid)} + KOH \text{ (aq)} \rightarrow RCOO^- K^+ \text{ (aq, soap)} + H_2O$

2.3.6 Surfactants

A surfactant is a surface active agent. Its driving force is to adsorb at an interface and lower the free energy of the phase boundary. It exist five different interfaces; solid – vapour, solid – liquid, solid – solid, liquid – vapour and liquid – liquid, and surfactants can adsorb to all five.

Surfactants always have two different parts where one part is soluble in water and may be called the hydrophilic (or “water loving”) part and the other part is water insoluble (the hydrophobic or “water hating” part).

Surfactants are categorized by means of the charge of the hydrophilic part, often called the polar head group. The classes are anionics, cationics, non-ionics and zwitterionics (25). In deinking non-ionics are the most used surfactants (5). The fatty acid anions described above are a type of anionic surfactants although they are mostly referred to as “fatty acid soaps” in practical terms. In the deinking mill, the word “surfactant” is mostly used for synthetic non-ionic surfactants as described below

2.3.6.1 Non-ionic surfactants

Almost every non-ionic surfactant has a polyether chain consisting of oxyethylene units as its polar group. The typical number of oxyethylene groups is between five and ten, but dispersants often have much longer oxyethylene chains (25). The non-ionic surfactants in deinking are often built up by ethylene oxide (EO) and propylene oxide (PO). According to Theander and Pugh, several patents show that the optimum length of the hydrocarbon chain is 16 – 18 carbons and that the ratio between EO and PO should be ranging from 1:2 to 4:1 (19). Non-ionic surfactants of high molecular weight are often denoted polymeric surfactants and may be defined as polymers.

2.3.6.2 Surfactants in the deinking process

Surfactants are found in the whole papermaking and recycling process. They are added intentionally but they can also be a part of the raw material used in the process (26). Surfactants can have multiple roles in flotation deinking. According to Zhao et al. there are three general roles of surfactants;

- as dispersants to separate the ink particles from the fibre surface and also to prevent redeposition of separated particles on fibres
- as collectors to agglomerate small ink particles to larger ones and to change the surface of the particles from hydrophilic to hydrophobic
- as foaming agents to generate a foam layer at the top of a flotation cell for ink removal.

It is important to notice that surfactants also can have adverse impact in deinking, and most surfactants have multiple roles. One example is that the adsorption of dispersants and foaming agents onto fibre surfaces may reduce the fibre – fibre bonding and create foaming problems (5). Different studies, collected by Johansson and Johansson (17), also show that surfactants affect the processes in deinking both negatively and positively. Reduced ink redeposition onto fibres and decreased size of air bubbles are both positive effects, while increased ink fragmentation and reduced ink agglomeration are considered negative effects (17).

Today, non-ionic surfactants are mostly used as dispersants but can also be used, as mentioned above, as collectors and foaming agents. Surfactants working as dispersants have two major roles in deinking. Firstly, they assist in separating the ink particles from the fibres by lowering the surface tension of the fibre. Secondly, they prevent redeposition of separated ink particles to fibres during the flotation step by creating a stable emulsion. Non-ionic surfactants are widely used since their functions do not depend on water hardness (5).

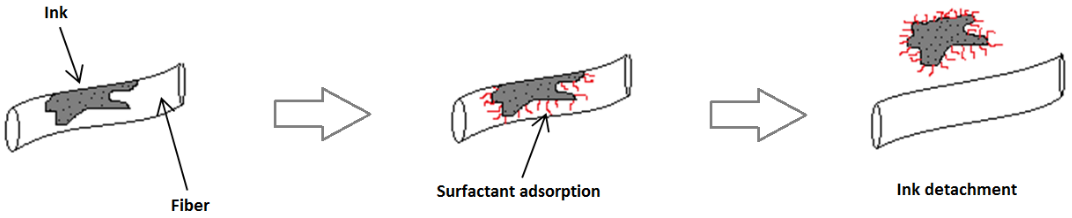

Figure 2: The separation of an ink particle from a fibre assisted by non-ionic surfactants.

2.5 Ink flotation surface chemistry

The flotation process with surfactants present is still not fully understood. There are however many proposed models for the mechanisms and some of them are described here.

The Schweizer mechanism explains that the soap molecules absorb at the ink surface reducing the hydrophobicity of the ink particles. The particles are, after detaching from the fibres, collected by air bubbles. However, the Schweizer mechanism does not consider the soap precipitation with calcium ions, the surfactant adsorption onto air bubbles or the electrical interaction between charged surfaces.

Another theory is the Bechstein mechanism. It describes how hydrophobic soap flakes collect ink particles to a larger complex which is flotated by air bubbles.

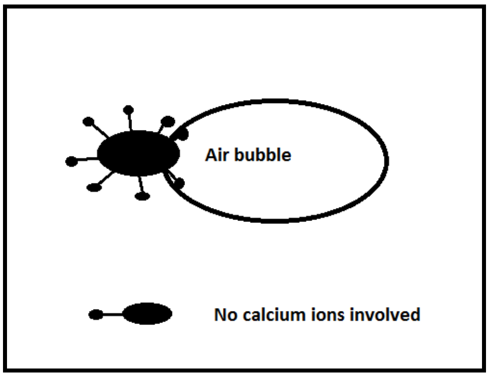

Figure 3: The Schweizer ink flotation mechanism.

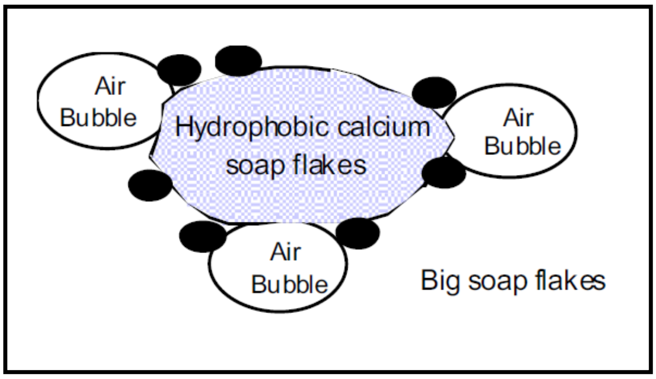

Figure 4: The Bechstein ink flotation mechanism. (Fig. from (6))

The Ortner mechanism is a bit more complex than the Bechstein mechanism. It defines that main cause of ink particle – air bubble adhesion is the precipitation of soap molecules adsorbed at the ink and the air bubbles surfaces. The process is described in three main steps. Firstly, soap is adsorbed on ink particles and they are detached from fibres. The second step describes the formation in the flotation cell of a system consisting of ink particles and air bubbles with hydrophilic-negatively charged surfaces. In the third step of the process calcium ions play a major role and activate the flotation (6).

The most complete theory for ink flotation with soap is the Larsson mechanism. It suggests that the main parameters influencing the ink flotation efficiency are the concentration of calcium ions, the zeta potential, the precipitation of soap and the flocculation of ink particles. The process is described in five steps:

1. The fatty acid ($RCOO^-$) is ionized by the alkaline medium at the ink surface. This gives an electrical stabilization to the suspended ink particles.
2. Adsorption of surfactants onto ink particles decreases their negative zeta potential. The adsorption is due to dispersive interactions between ink particles and surfactants.
3. When calcium ions are added to the process the negative zeta potential of ink particles and soap molecules increases. The surfaces of the ink particles become more hydrophobic.
4. Increasing zeta potential and repulsive forces cause ink particle aggregation.
5. The hydrophobic aggregates are flotated (6) (27).

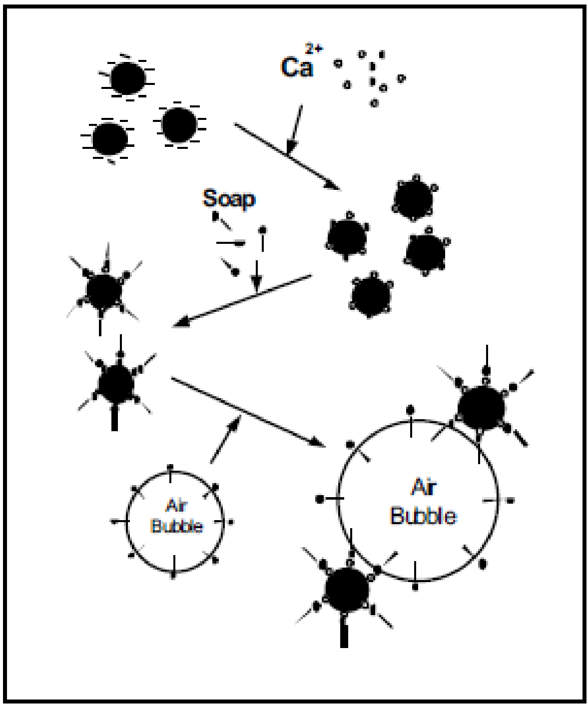

Figure 6: The Ortner ink flotation mechanism. (Fig. from (6))

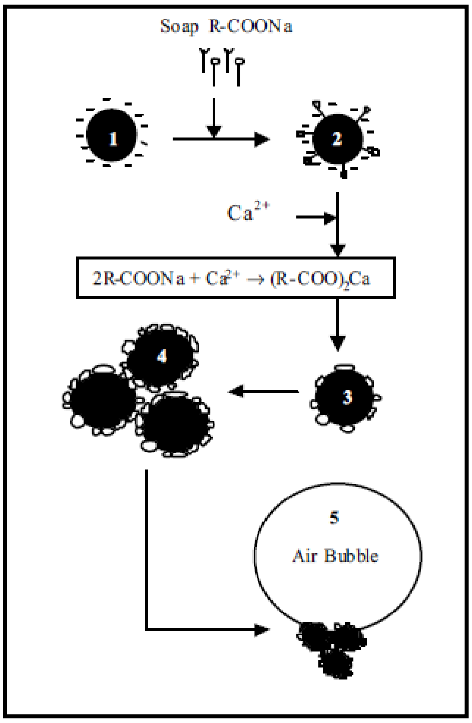

Figure 5: The Larsson ink flotation mechanism. (Fig. from (27))

2.6 Chemical oxygen demand

The chemical oxygen demand (COD) test measures the organic content in e.g. domestic and industrial wastes. The test measures the total quantity of oxygen required for oxidation to carbon dioxide and water. It considers that almost all organic compounds can be oxidized by strong oxidizing agents under acid conditions. Wood-pulping waste is an excellent example when COD test works well since it has high lignin content (28).

COD is an important parameter when considering the pH in deinking. By lowering the pH to a neutral or semi-neutral level the COD release will decrease, which is advantageous. The decrease in COD release depends on the decrease in use of sodium hydroxide since the COD release is basically linearly proportional to caustic charge.

Especially in Europe there has been a strong demand for pulp mills to have a minimum environmental impact. COD tests are used to measure if the mills are reaching the goals. Thus, a reduction in COD is a major benefit for the mills in Europe. United States do not use COD measures in the same extent yet but COD tests have been recommended to be used as guidelines. However, if COD becomes a major measurement or requirement for permitting over the whole world, it will lead to that the benefits of lowering the pH and i.e. work with neutral or semi-neutral deinking will possibly compensate any other problems (29).

2.7 Parameters affecting flotation deinking

There are several parameters affecting the flotation deinking process and many of them are individual for the different mills.

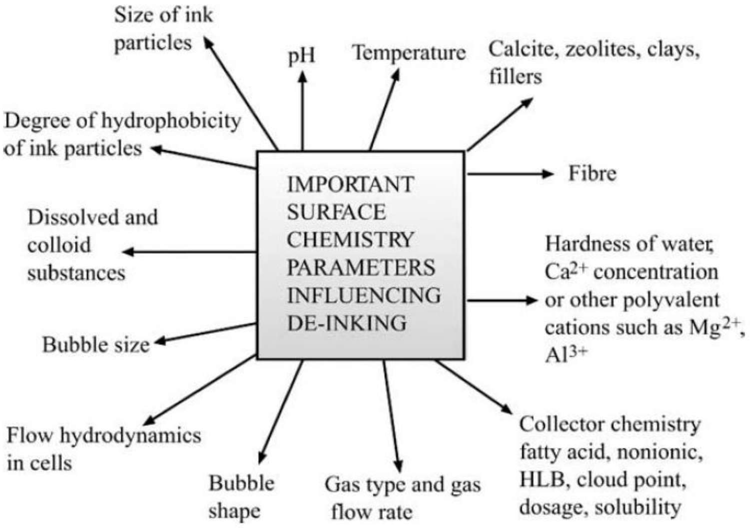

Figure 7: The most important parameters affecting flotation deinking. (Fig. from (19))

2.7.1 Temperature

The deinking process is often performed at a process temperature in the range of 40 – 60 °C. Different laboratory tests have given opposite results concerning whether if a lower or a higher temperature is preferable in the deinking process, but in general, an increase in temperature can help the detachment of ink particles from fibres (19). Processes using non-ionic surfactants are more sensitive to temperature influence due to the effect of cloud point and HLB on the surfactant deinking performance. In practice the flotation deinking process for a specific mill is kept within a certain temperature range, where the chemical dosages and other process parameters have been optimised for that temperature. Changing the temperature will affect the deinking performance, but it is hard to tell in which direction since many other parameters are involved.

2.7.2 pH

It is most common to carry out the flotation at an alkaline pH, often up to 10. At higher pH the flotation efficiency decreases, which may be due to higher surface charge on the ink particles making them more highly dispersed and difficult to attach to the bubble. pH can also affect the chemicals in the process, as the solubility of fatty acids (19). A high pH will dissolve more of the extractive content that may still be present in the fibres, giving a lower fibre yield and a higher COD. Also, the problem with so-called stickies (tacky components from the recycled pulp consisting of e.g. latex and polymer residues) will increase with pH.

As mentioned in the introduction (1.3, page 2) it is interesting to carry out the flotation deinking process at a lower pH, using e.g. magnesium hydroxide based techniques. So called semi-neutral or neutral deinking has several advantages, such as lower chemical costs, lower COD and less problems with stickies (7). However, deinking efficiency may be negatively affected by the lower fibre swelling and lower chare on the ink particles. Optimising the composition of the deinking chemical system and developing new formulations for the new pH will help overcome these problems, as well as optimisation of other parameters in the process.

2.7.3 Hardness of water

Hardness of water is caused by multivalent metallic cations, mainly calcium ions and magnesium ions. These are capable to react with soap to form precipitates (30). The concentration of calcium ions in the process water in the flotation deinking process is a very important parameter, especially regarding fibre losses. Higher hardness due to calcium ions means higher losses and it may also cause deposits on paper machines. However, a certain level of calcium is necessary to ensure soap formation in the flotation step.

Using fatty acids in the deinking process makes the system sensitive to the hardness of water, and very small changes in hardness may change the results. On the other hand, one of the benefits using non-ionic surfactants instead is that the system becomes insensitive to calcium ions.

If using a calcium soap flotation system, the best flotation occurs when there is an excess of free fatty acid. This ensures that all calcium ions are removed, and the excess of fatty acid ensures a low surface tension for bubble formation. However, if the excess of sodium salt of fatty acid is too high the ink removal efficiency will be lowered. It may also lead to fibre losses due to entrapment of fibres in the bubbles. The problem is often too low hardness of the process water. If the process water is not hard enough the fatty acid will not completely convert to calcium salts (19).

There are two types of water hardness; temporary and permanent hardness. Temporary hardness is due to the presence of calcium hydrogen carbonate and magnesium hydrogen carbonate. Total permanent hardness is calcium hardness plus magnesium hardness. It is the concentration of calcium and magnesium ions expressed as equivalent of calcium carbonate, giving the equation below (note that the relative influence of magnesium ions is bigger than for calcium ions) (31).

$$[CaCO_3] = 2{,}5 \cdot [Ca^{2+}] + 4{,}1 \cdot [Mg^{2+}]$$

2.7.4 Alkalinity

Alkalinity is a measure of water's capacity to neutralize acids. The alkalinity of neutral water is primarily depending on the concentration of salts of weak acids, although weak or strong bases also may contribute. Since salts of weak acids and strong bases acts as buffers to resist a drop in pH resulting from acid addition, alkalinity is a measure of the buffer capacity. Many materials contribute to the alkalinity of natural water but the three most important groups are hydroxides, carbonates and bicarbonates, ranked in order of their association with high pH. The alkalinity of a sample can be measured titrating with a strong acid until the buffering capacity of the mentioned ions is consumed, at pH 4,5 (32).

2.8 Optical properties

The most common parameters to discuss when evaluating the quality of deinked paper are the optical properties, i.e. brightness and effective residual ink concentration (ERIC). Both are measured by spectrophotometry, a quantitative measurement of the reflection or transmission properties of a sample. The most important parts of a spectrophotometer is the light source, a monochromator removing all wave lengths except one and a detector which measures the intensity of the light after the sample.

2.8.1 Brightness

Presence of ink influences the brightness and colour of the paper, and traces of ink can make the recycled paper darker compared to paper made from virgin pulp. However, brightness is not a perfect tool to use in the deinking process since it is affected not only by the presence of ink but also by the wavelengths of lignin and dye. The brightness is measured from 0 – 100 % (ISO brightness), where a high value of brightness is favourable.

2.8.2 ERIC

Effective residual ink concentration (ERIC) is often considered as a better evaluating method than brightness, concerning the deinking process. The ERIC method performs reflectance measurements in the infrared spectrum since just ink, not dye, lignin or other colorants, is predominant in this area. The ERIC value expresses the effect of the remaining ink in the sample, not the amount of remaining ink. This is shown in figure 8**.** The part to the left will appear whiter, and give a lower ERIC value, than the part to the right where the ink particles are distributed. (33). The results from ERIC measurements are strongly depending on the kind of ink, the particle size of the ink and the dispersion or agglomeration of the ink. ERIC is expressed in ppm where a low ERIC value means a low presence of remaining ink.

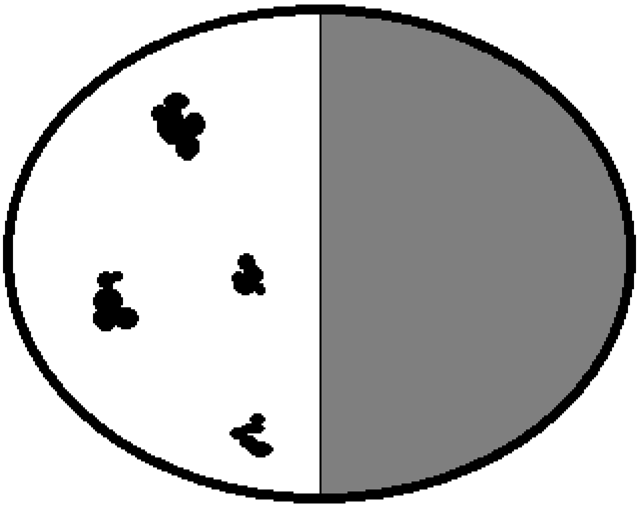

Figure 8: The difference in ERIC values. The sample to the left will give a low value while the right sample will give a high ERIC value.

2.9 Agglomeration kinetics

The differences in agglomeration behaviour between fatty acid potassium soap and calcium ions and magnesium ions (both individually and in a mixed system) are interesting to study since they may affect deinking performance. Also, when using BIMPRO®, a larger amount of magnesium ions are added to the deinking system than would normally be the case. Calcium ions, on the other hand, are always present in a deinking mill. The interaction of these ions on soap formation (and consequently ink detachment) is therefore crucial to study when aiming for a semi-neutral system based on magnesium hydroxide chemistry.

2.9.1 Hach Turbidimeter

A Hach 2100P portable Turbidimeter is a quick and easy instrument to use when studying precipitation and was used to find the right concentration levels of soap and ions before using the other instrument used in the agglomeration studies, the Turbiscan online.

The Hach Turbidimeter operates on the so-called nephelometric principle of turbidity measurement, using that a particle will scatter light. The detector setup can be found in figure 9**.** If there are many small particles in the solution more light will reach the detector. The Hach Turbidimeter uses the unit NTU, Nephelometric Turbidity Units. A high NTU value corresponds to many particles in the solution.

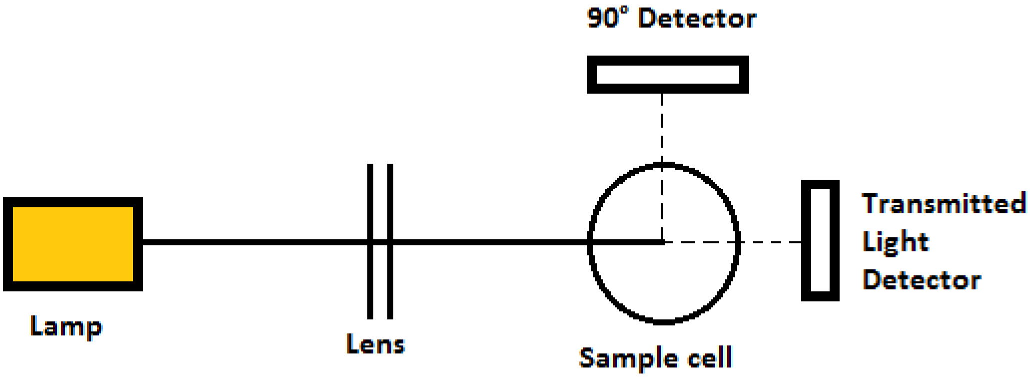

Figure 9: The setup of the Hach Turbidimeter.

2.9.2 Turbiscan Online

The Turbiscan Online from Formulaction is an instrument used to analyse both transmission and backscattering of a solution. The solution is pumped through a measuring cell where it is irradiated by infrared light, and transmission and backscattering of the solution is detected by optical sensors, as a function of time. High transmission means opaque solution, whereas an increase in backscattering indicates particle formation. For example, In this project, precipitation of soap particles from a soap solution induced by the addition of calcium or magnesium ions could be followed by the increase in backscattering over time.

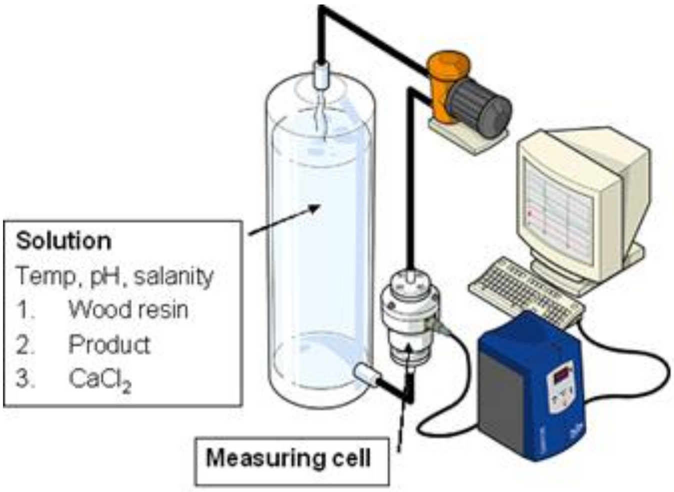

Figure 10: The setup of Turbiscan Online.

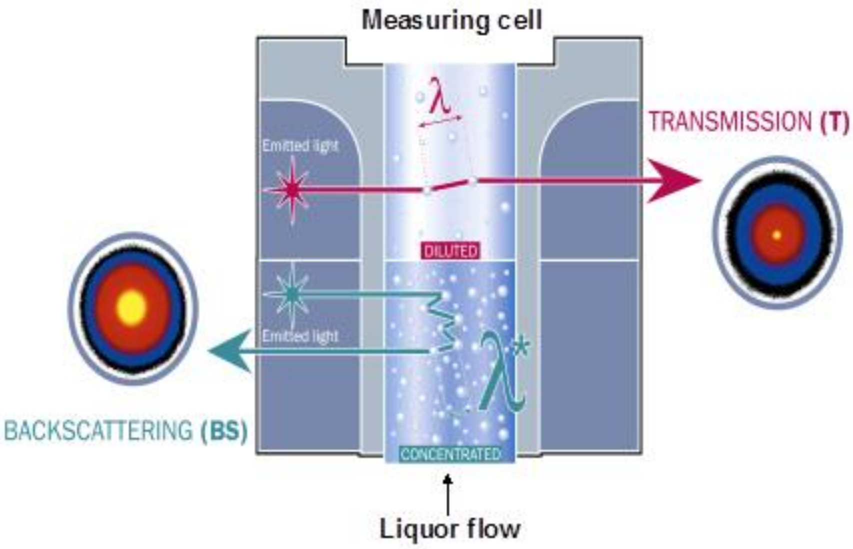

Figure 11: The measuring cell of a Turbiscan Online.

2.9.3 Particle size measurements

To evaluate the particle size distribution a Mastersizer 2000 from Malvern instruments was used. The Mastersizer 2000 uses laser diffraction to decide the size of particles in a solution. Laser diffraction is based on the principle that particles passing through a laser beam will scatter light at an angle directly related to their size. Large particles scatter light at narrow ranges with high intensity while small particles scatter at wider angles with low intensity.

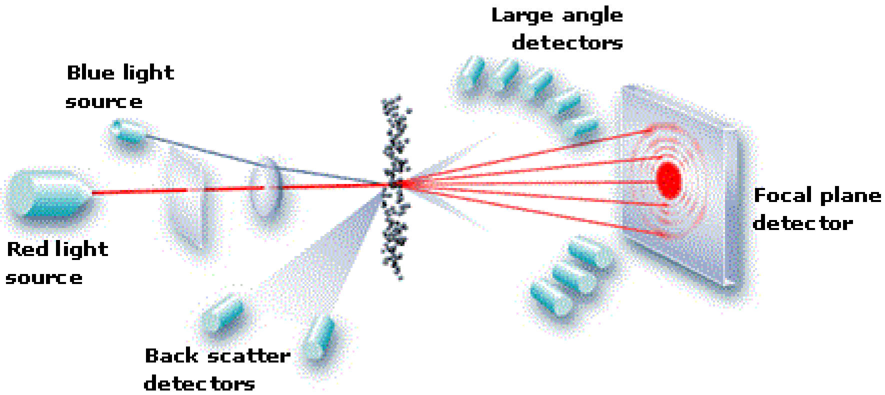

Figure 12: The setup for laser diffraction. A laser hits a sample and a series of detectors measure the light pattern produced over a wide range of angles (34).

2.9.4 Surface tension measurements

In the article “Surface chemistry of flotation deinking: Agglomeration kinetics and agglomerate structure” (35), the authors have studied the precipitation between calcium ions and a sodium oleate soap by evaluating the surface tension as a function of time. The increase in surface tension is found to be due to precipitation of calcium soap flakes. The surface tension was also tested in this master thesis to evaluate the precipitation between calcium and/or magnesium ions in an oleic acid potassium soap solution. A Du Noüy ring method was used in the measurements, using a Sigma 70 tensiometer.

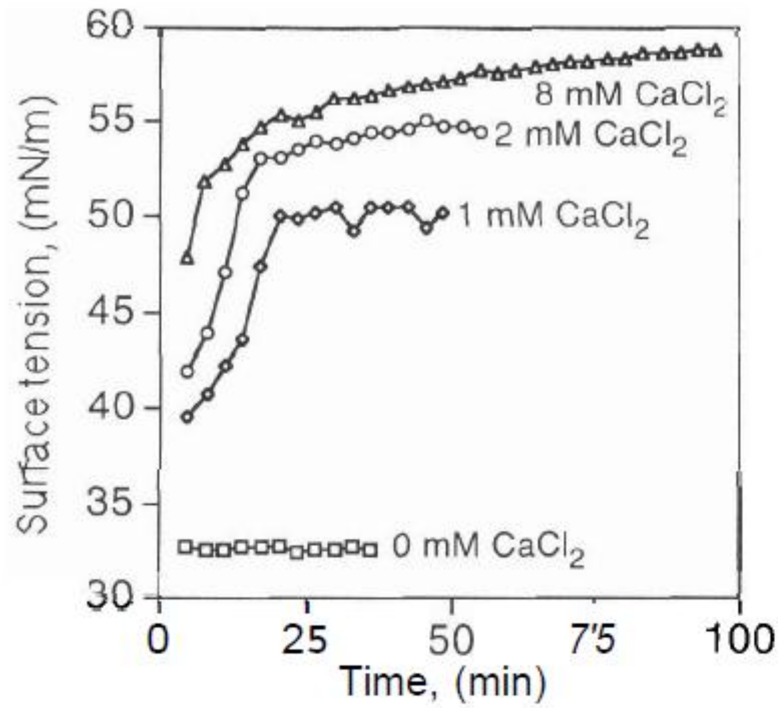

Figure 13: The surface tension as a function of time (fig. from 35).

The Du Noüy ring method measures the surface tension of a liquid by slowly lifting a ring from the surface, and the force required to raise the ring is measured and related to the surface tension of the liquid. The ring is raised until a maximum force is found, when the surface no longer is in contact with the ring. The procedure is performed several times and by plotting the maximum force versus time a curve is established giving the surface tension of a solution and its changes in time.

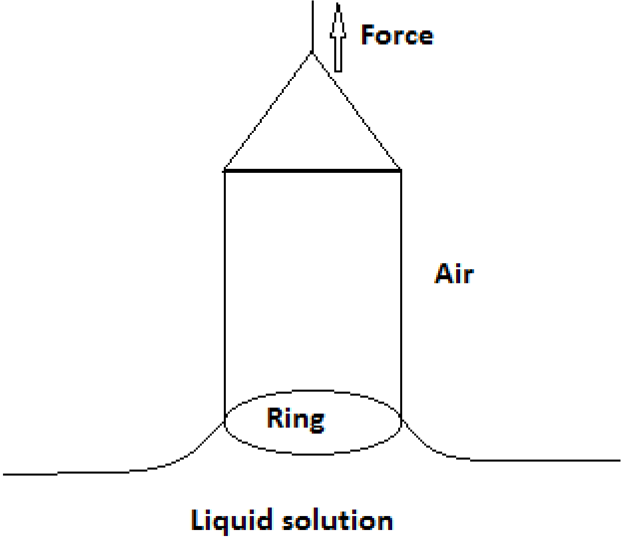

Figure 14: The Du Noüy ring method.

3. Experimental

In this chapter the experimental part of the work is described. The used materials are listed and the procedure of all the different experiments, e.g. the deinking experiment and the ageing of ink, are fully described. A list of the apparatus and instruments used in the project can be found in Appendix 13.

3.1 Materials

In all tests Göteborgs-Posten was used as old newsprint (ONP). As old magazines (OMG) different Swedish and Norwegian magazines were used. Batches were collected three times from Stora Enso Hylte Mill and VTAB Göteborg.

Table 2: The raw material used in this thesis.

Material	**Issue**
Göteborgs-Posten	2010-12-28
Se & Hör and Hänt extra	Week 50, 2010
Göteborgs-Posten	2011-03-03
Se og Hør	Week 7, 2011
Göteborgs-Posten	2011-04-27
Se & Hör	Week 18, 2011

3.1.1 Chemicals

Table 3: The chemicals used in deinking experiments.

Chemical	**Origin**
BIMPRO® BI7101 X (40% conc.)	BIM Kemi Sweden AB
Sodium hydroxide (45 % conc.)	Commercial
Sodium silicate BI3340 (41.19 % dry cont.)	BIM Norway AB
Hydrogen peroxide	30 % conc. Reagent grade, Scharlau
A non-ionic polymeric surfactant	Commercial
Fatty acid potassium soap	Bim Kemi AB
Calcium chloride, dehydrated	Fluka Chemie
Stearic sodium soap	Stora Enso Hylte Mill
Magnesium chloride, anhydrous	Alfa Aesar

3.1.2 The flotation cell

The lab flotations were performed in a Voith Laboratory Flotation Cell Delta 25, figure 15. It mimics the actual flotation step at a deinking mill and is constructed to be operator-friendly and give results with high reproducibility.

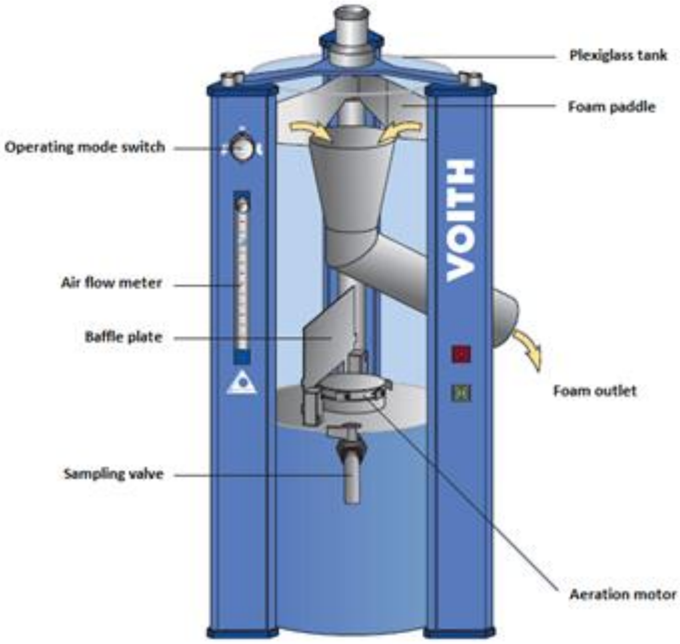

Figure 15: Voith Laboratory Flotation Cell Delta25. (Fig. from (36))

The cell has a 25 dm^3 plexiglass tank where the flotation takes place. In the bottom the aeration rotor is placed. The foam paddles are moving when operated and removes the excess of foam in to the foam outlet where a reject bucket are placed to collect the reject. Some of the process variables are the air content, aeration intensity and frequency and stock consistency (36).

3.2 Synthesis of fatty acid potassium soaps

Three different potassium soaps were synthesized, based on either mixed unsaturated fatty acid, oleic acid or stearic acid. The fatty acids were mixed with potassium hydroxide and water. The solution was heated and stirred for approximately one and a half hour and the temperature was never above 90 °C. The soaps were stored in a refrigerator during this project.

3.3 Deinking experiments

In this master thesis a lab method from BIM Kemi AB was used. That is based on the different steps in the actual mill deinking process. The detailed setup and recipe of the deinking experiments can be found in Appendix 1. A brief overview is given below.

In all experiments a mix of 70 percent old newsprint (ONP) and 30 percent old magazines (OMG) was used. The staples and loose advertisements were removed before the paper was cut in to small pieces, approximately 2 times 2 cm^2.

To ensure a water hardness of 10 dH, $CaCl_2$ was added to the water to be used in the experiment. The water was also put in a water bath to ensure a high and even temperature.

The chemicals were added to the paper mix and the pulp was put in a Kitchen Aid for 20 minutes to distribute the chemicals evenly in the paper slurry simulating the drum pulper. The dry content was now approximately 15 %.

More water was then added, which reduced the dry content to approximately 6,25 %. The pulp was put in a water bath for 45 minutes. In this step, many of the chemical reactions takes place and the fibres will swell, making it easier for the ink to detach.

The pulp was then diluted to approximately 4% consistency and blended in a high-energy Hobart mixer, imitating the disperger step stage in the deinking process.

The pulp was then transferred to the Voith flotation cell, which was filled with hot tap water to the 23,5 dm^3 mark. An unflotated sample was collected and the cell was re-filled with water. Soap and $CaCl_2$ was poured in to the cell before the flotation was started. The flotation constancy was approximately 1%

The flotation was going on for 6 minutes, where after a flotated sample was collected. The reject bucket was weighed before and after the flotation to calculate the amount of reject from the experiment.

Both the unflotated and the flotated samples were divided into two different batches. This gave four different samples to analyse: unflotated hyper washed, unflotated not hyper washed, flotated hyper washed and one flotated not hyper washed.

The samples not collected for hyper wash was filtered by suction to form sheets. The sheets was pressed before dried and then ready for brightness and ERIC analysis.

3.3.1 Hyper washing

Hyper washing is a method to clean the sample from all detached ink particles by using a large amount of tap water, simulating a “perfect” ink removal. Both 1000 ml of the unflotated and the flotated sample was individually hyper washed. By comparing the hyper washed flotated ERIC value with the normal flotated ERIC value the amount of ink that has been detached but not removed by flotation can be evaluated.

The hyper wash setup is shown in Fig 16. Water is poured in to the beaker and the propeller is started. Then the sample is poured in slowly. The water inlet is adjusted to find a speed comparable to the water speed leaving the beaker.

When 10 litres of water have been poured through the beaker the water inlet is closed and the propeller is stopped. The sample above the filter is collected and used for sheet formation. The hyper washing procedure is described in detail in Appendix 2.

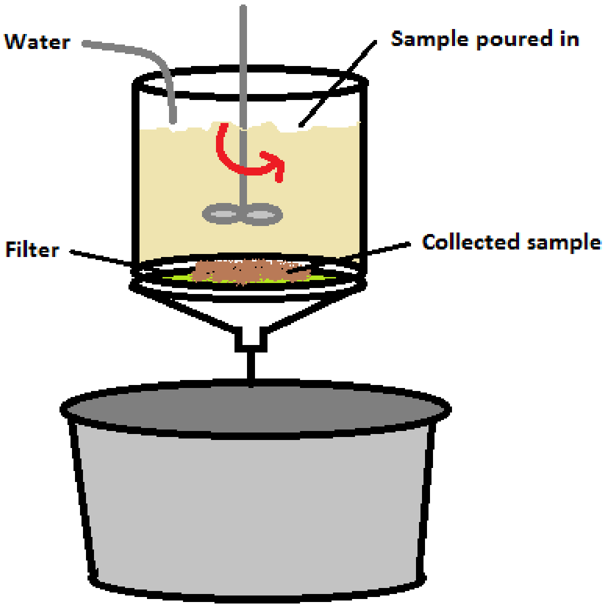

Figure 16: The setup for hyper washing.

3.3.2 The reject

By collecting the reject from the flotation step values for dry and wet reject, yield measurements and the ash content of the reject could be evaluated.

Yield losses are crucial to investigate since fibre is an expensive raw material that has to be used efficiently. Good ERIC and brightness results are often possible to achieve, but if the cost in terms of yield loss is too high the flotation is not optimised.
The total yield loss (fibre + ash) is calculated as

$$Yield\ loss\ (\%) = \frac{Dryied\ reject}{Dry\ weight\ of\ ONP+OMG} \times 100$$

A more detailed description of the reject collection can be found in Appendix 1.

In many applications, the ash content is important since it reflects how much filler is entrapped in the reject together with the fibre. The ash content is calculated by analysing the inorganic content in the dry reject (see Appendix 1).

$$Ash\ content\ (\%) = \frac{c-a}{b} \times 100$$

3.4 Ageing of ink

Two different recipes for the ageing measurements were elaborated, one with a fatty acid potassium soap and one with a non-ionic surfactant. The chemicals were BIMPRO®, oleic acid potassium soap or the non-ionic polymeric surfactant, sodium silicate and hydrogen peroxide. The experiments were following the procedure described in 3.2. The recipes are found in appendix 4.

3.5 Agglomeration kinetics

3.5.1 Hach Turbidimeter

The first tests in this project about agglomeration and precipitation were performed using a Hach Turbidimeter. This is not a perfect method since the amount of light that is reflected also depends on shape, size and colour of the particles. Therefore, at the same time as the solution was tested in the Turbidimeter it was evaluated by the eye to see if there was any visual precipitation.

The standard recipe used in the Hach Turbidimeter can be found in table 4. To be able to implement the same recipe as in the Turbiscan Online three beakers were used. In beaker 1 the pH was adjusted to approximately 9. This was to ensure that the experiment was performed above pH 6,5, which has been found to be the critical pH for precipitation concerning $CaCl_2$ in sodium oleate (35). This was also used in the tests with $MgCl_2$. In beaker 2 the soap was fully dissolved in the distilled water. In beaker 3 $CaCl_2$ or $MgCl_2$ dissolved in the distilled water. When pH had been adjusted in beaker 1, beaker 2 and 3 were poured in to beaker 1, the solution was properly stirred, and the time was noted. By using the Hach Turbidimeter values in NTU were collected over time. Also, pH was measured during the experiments.

Table 4: The recipe used in agglomeration and precipitation experiments.

Number of beaker	Chemical	Amount
1	Distilled water	800 g
1	Diluted NaOH	10-16 drops
2	Distilled water	100 g
2	Fatty acid potassium soap	0,050 g (50 mg/l)
3	Distilled water	100 g
3	$CaCl_2$ OR $MgCl_2$	Varied

3.5.2 Turbiscan Online

The experiments with Turbiscan Online were performed using the same recipe as for the Hach Turbidimeter, (see table 4). Beaker 1 was poured in to a container which was connected to the measuring cell and to a pump, pumping the solution in a closed loop for 250 rpm. When the transmission value was stabilized the experiment was started. After 140 seconds beaker 2 was poured in to the container, and 60 seconds later beaker 3. The transmission curves were recorded and analysed.

3.5.3 Particle size measurements

Four beakers with different systems of fatty acid potassium soaps and magnesium or calcium ions were prepared in the same way as described in table 4. The three beakers were mixed and the solutions were left over the night, where after the particle size was analysed in a Malvern 2000 laser diffraction unit using a refractive index of 1,46 representative for a fatty acid soap. The four experiments are found in table 5.

Table 5: The four solutions prepared for particle size measurements.

Potassium soap	$CaCl_2$ or $MgCl_2$
50 mg/l oleic acid	5 mM $CaCl_2$
50 mg/l mixed unsaturated fatty acid	5 mM $CaCl_2$
50 mg/l oleic acid	5 mM $MgCl_2$
50 mg/l mixed unsaturated fatty acid	5 mM $MgCl_2$

3.5.3 Surface tension measurements

A Du Noüy ring tensiometer was used for surface tension measurements. Distilled water with pH 9 (adjusted with diluted NaOH) was poured in to a small beaker. The soap dissolved in distilled water was added to the beaker that was placed in the tensiometer with a small magnet rotating at the bottom to stir the solution. The next steps were difficult to perform in exactly the same way in every experiment. The test was started with the stirring device on while the ring was moving downwards to the liquid surface. Before it reached the surface, the desired amount of $MgCl_2$ and/or $CaCl_2$, dissolved in distilled water, was added to the beaker using an automatic pipette, and shortly after the stirring device was turned off. It is difficult to estimate the time between the stirring device was turned off and the ring was reaching the surface, but it was not the same time in every experiment. It was also difficult to know exactly when to add the salt solution when the ring was going downwards and to stir the complete solution the same amount of seconds in every test. It was tested if the salt solution could be added directly after the soap, but that required re-starting the experiment. Considering the experimental difficulties, the surface tension results should be interpreted with some care.

4. Results and discussion

In chapter 4 all results in this master thesis are collected. First the results from the different deinking experiments are presented, as reproducibility and ageing of the ink. The results from Turbiscan online measurements, surface tension measurements and the particle size comparison can also be found in this chapter.

4.1 Deinking chemistry

26 flotations were performed during the project. Two different standard recipes for BIMPRO®, one with oleic potassium soap and one with a non-ionic polymeric surfactant were used, the latter especially to investigate the role of ageing. The two standard recipes for BIMPRO® can be found in Appendix 4**.** For the NaOH flotations, a similar standard recipe was used.

Many different variants of the standard recipe have also been used, often to analyse the role of different important parameters in the deinking process, such as hardness. Three different fatty acid potassium soaps and one non-ionic polymeric surfactant have been tested and the doses of some of the chemicals used in the process have been changed. BIMPRO® has most often been used as alkali source but sodium hydroxide has also been investigated.

The first experiments were evaluating the reproducibility of the deinking experiments. Tests with BIMPRO® and oleic acid potassium soap, and BIMPRO® and mixed unsaturated fatty acid potassium soap were used.

The two experiments with identically amounts of both BIMPRO® and oleic acid potassium soap gave very similar results, considering e.g. pH, alkalinity, ERIC and brightness measurements. The conclusion is that there is reproducibility in the deinking experiments.

4.1.1 Comparison of different fatty acid potassium soaps and sodium hydroxide

In an early stage of the master thesis three different fatty acid potassium soaps, oleic, mixed unsaturated fatty acid and stearic, were compared, using both BIMPRO® and sodium hydroxide as alkali source. The paper was approximately 50 days old when the experiments were performed. But all tests were performed in a narrow range of days, so they should be comparable.

The differences between using oleic acid potassium soap or mixed unsaturated fatty acid potassium soap in the system with BIMPRO® were not big. Oleic acid potassium soap showed a little bit better values of ERIC and brightness in all cases except for the unflotated sample. On the other hand, using BIMPRO® and mixed unsaturated fatty acid gave less reject, giving a lower yield loss. Stearic acid potassium soap gave poorer results in all experiments with BIMPRO®.

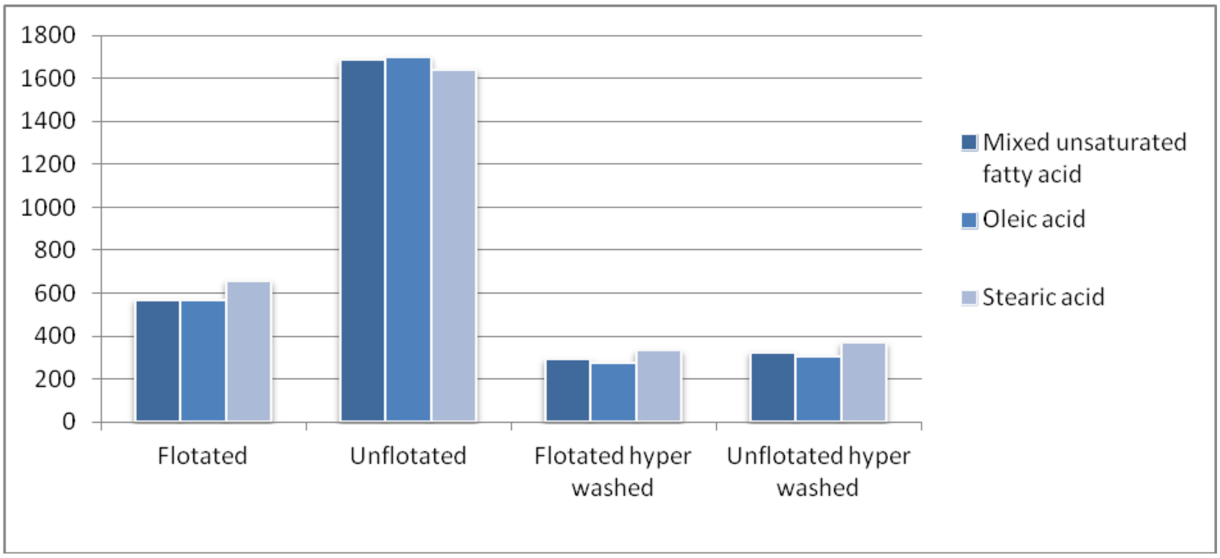

Figure 17: ERIC values for the three different fatty acid potassium soaps, using BIMPRO® as alkali source.

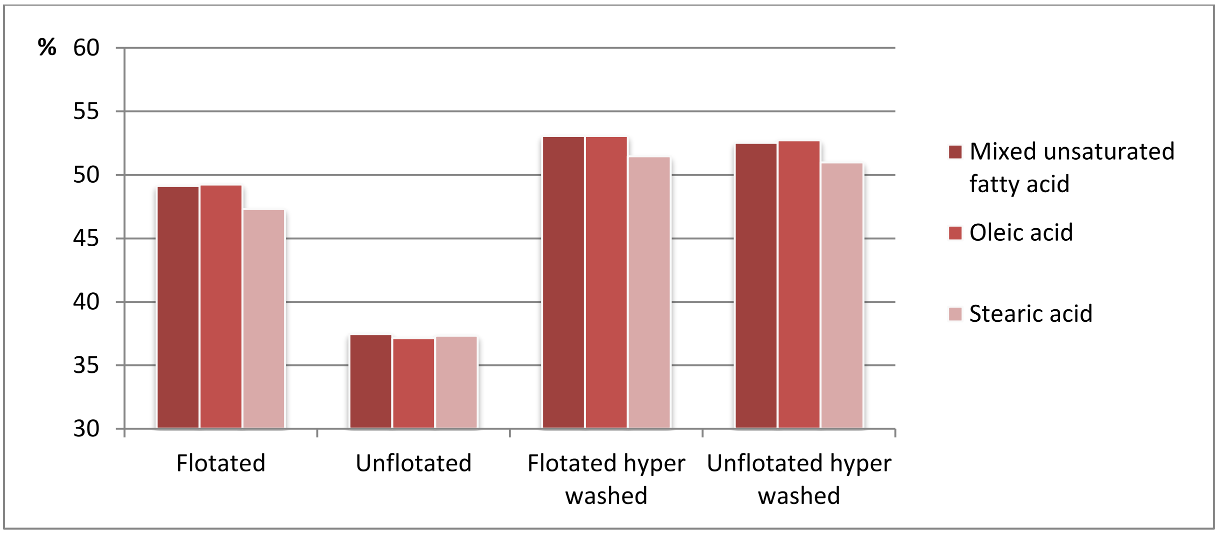

Figure 18: Brightness values for the three different fatty acid potassium soaps, using BIMPRO® as alkali source.

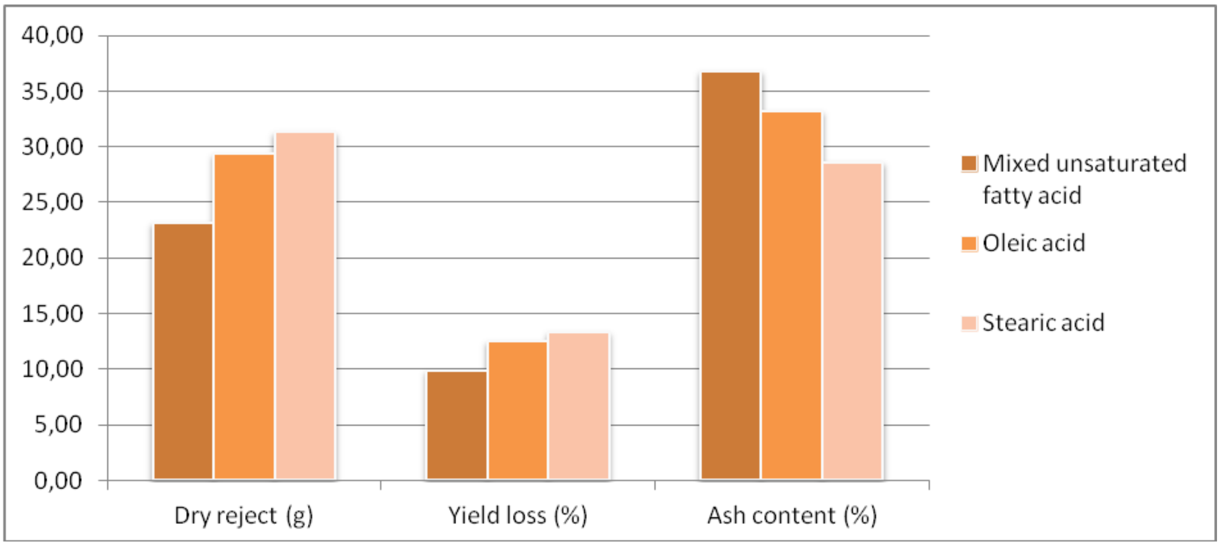

Figure 19: Dry reject, yield loss and ash content for the three fatty acid potassium soaps, using BIMPRO® as alkali source.

When using sodium hydroxide instead of BIMPRO® the difference between oleic acid potassium soap and mixed unsaturated fatty acid potassium soap was still quite small. Mixed unsaturated fatty acid showed much better ERIC and brightness results for the flotated sample and oleic acid was better for the unflotated sample, especially concerning the hyper washed results. Stearic acid is still an inferior alternative.

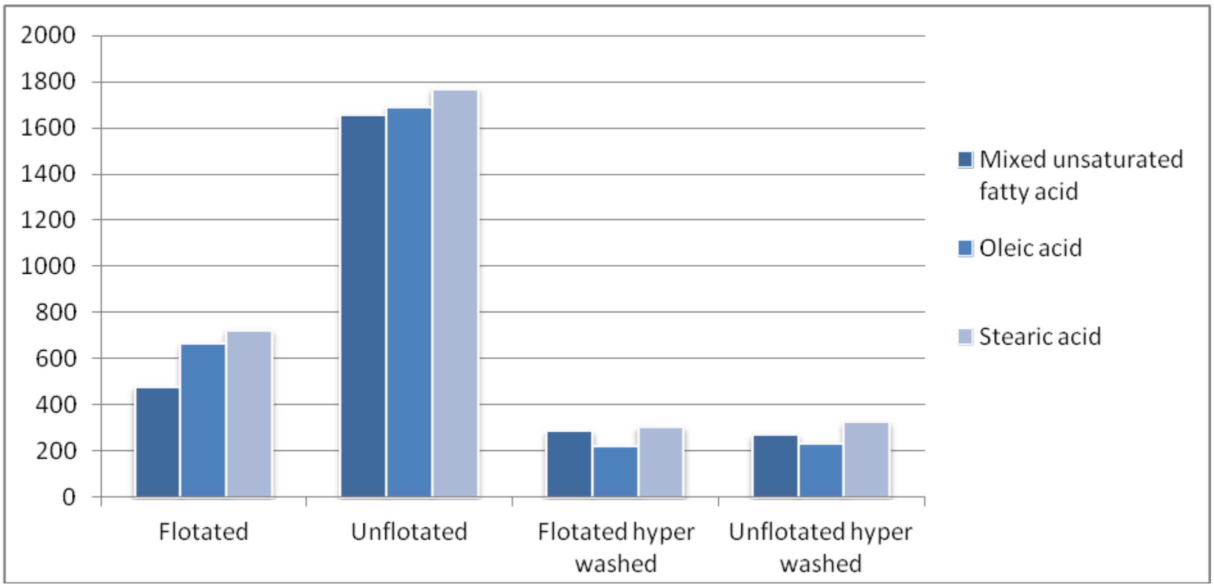

Figure 20: ERIC values for the three fatty acid potassium soaps, using NaOH as alkali source.

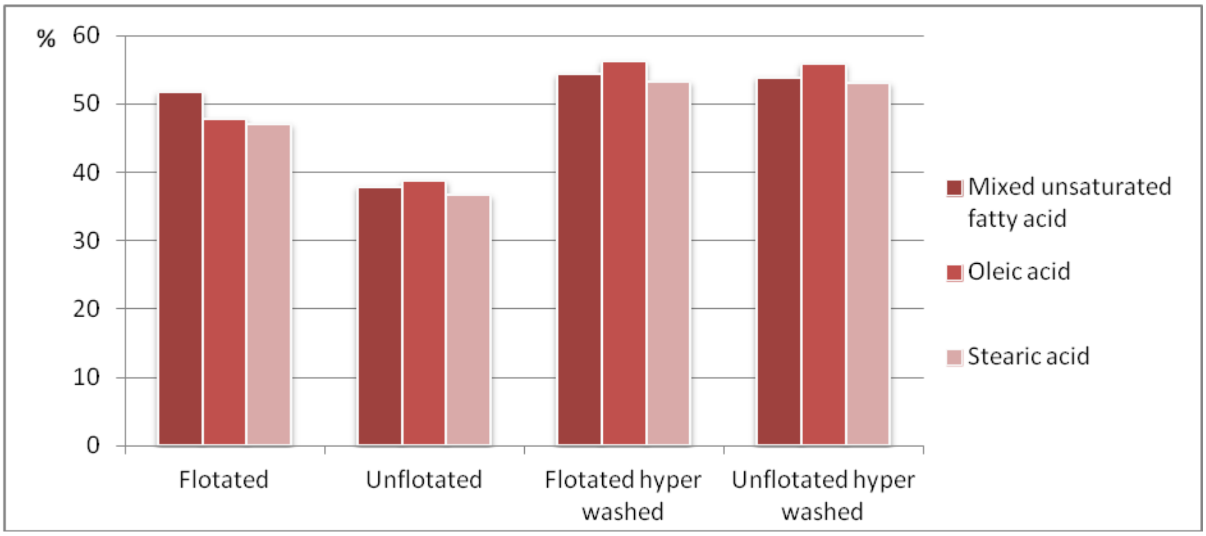

Figure 21: Brightness values for the three fatty acid potassium soaps, using NaOH as alkali source.

The results concerning the reject were found in the same range as all experiments using BIMPRO®. As can be seen in figure 19 oleic acid potassium soap gave the lowest reject values compared to the other variants using NaOH. Both the system with NaOH and mixed unsaturated fatty acid, which gave really good flotated ERIC and brightness values, and the system with NaOH and stearic acid potassium soap which instead gave poorer flotated values, gave high reject values compared to NaOH and oleic acid potassium soap.

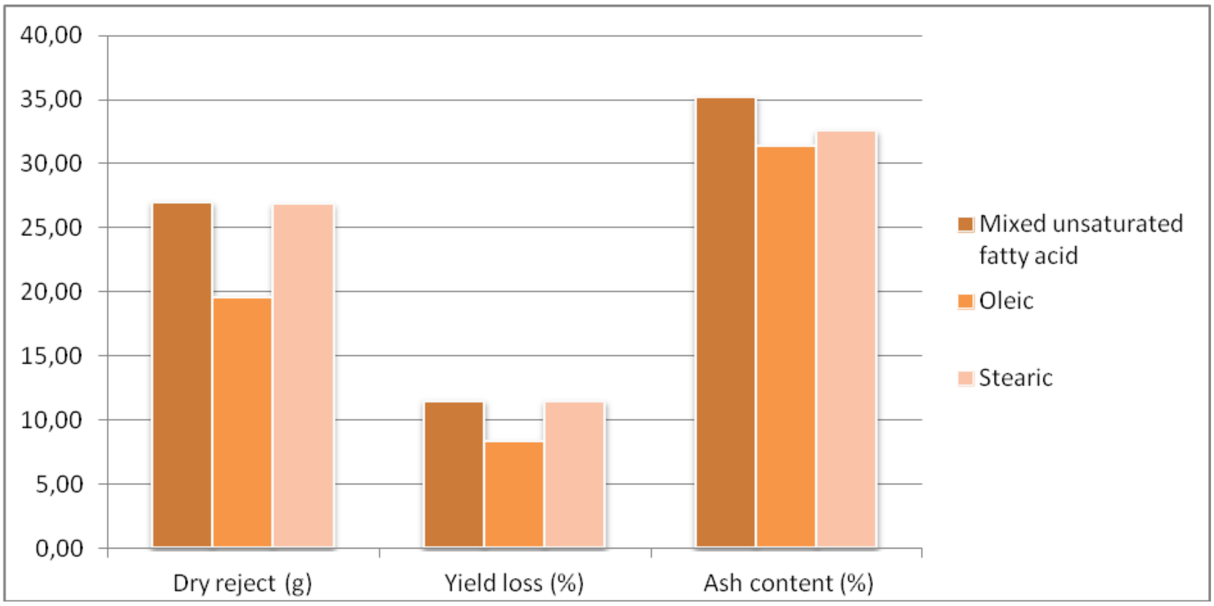

Figure 22: Dry reject, yield loss and ash content for the three fatty acid potassium soaps, using NaOH as alkali source.

4.1.2 Variation of non-ionic polymeric surfactant and oleic acid potassium soap

In order to investigate the difference between a synthetic surfactant and a fatty acid system in the pulping stage, the oleic acid potassium soap was replaced with a non-ionic polymeric surfactant in some experiments, using BIMPRO® as alkali source. There were no big differences at all found. Also experiments using both oleic acid potassium soap and a non-ionic polymeric surfactant were performed.

Four different recipes were used, the two standard recipes (with 2,5 kg/ton oleic acid potassium soap or 30 g/ton non-ionic polymeric surfactant), one with both 2,5 kg/ton oleic acid potassium soap and 30 g/ton non-ionic polymeric surfactant, and one recipe with 1,25 kg/ton oleic acid potassium soap and 15 g/ton non-ionic polymeric surfactant.

When the comparison was made the raw material, especially the ONP, was very fresh, giving very good ERIC, as can be seen in figure 23, and brightness results. This makes it unfortunately harder to see differences between the four cases since the changes are so small.

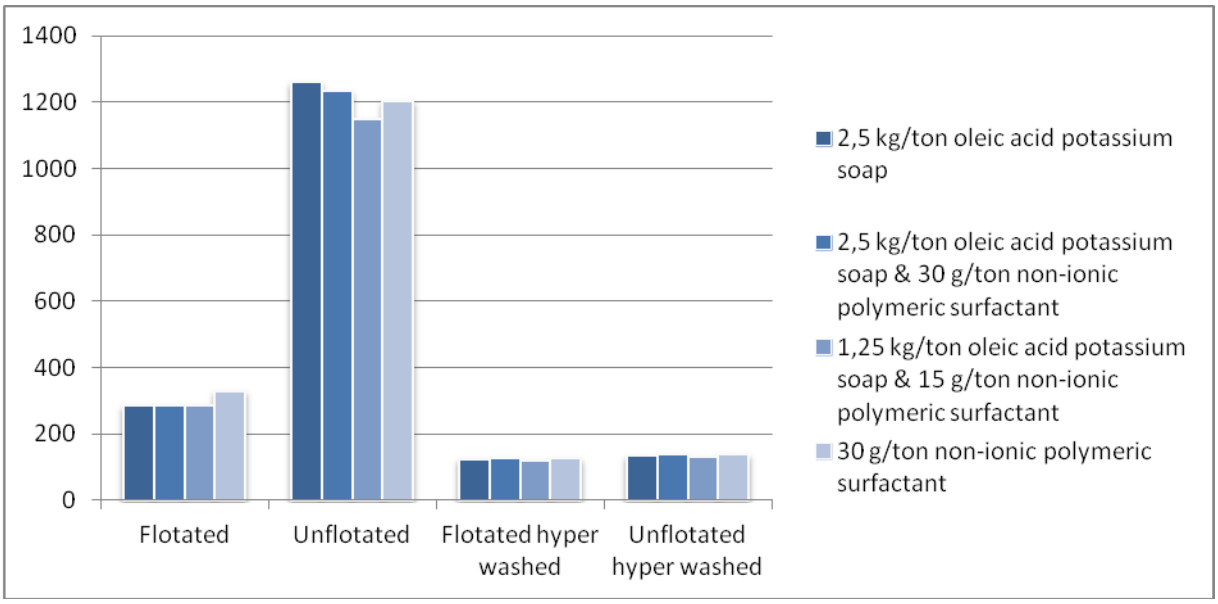

Figure 23: ERIC values from experiments with oleic acid potassium soap and/or a non-ionic polymeric surfactant.

Following the results, the flotated values seem to be better with the oleic acid potassium soap since the poorest value is from the experiment with only non-ionic polymeric surfactant. On the other hand, the three experiments with the non-ionic surfactant shows better results concerning the unflotated value compared to using only the fatty acid soap. All four experiments show very good and similar hyper washed results. The brightness results for the four experiments are found in a very narrow range in each category.

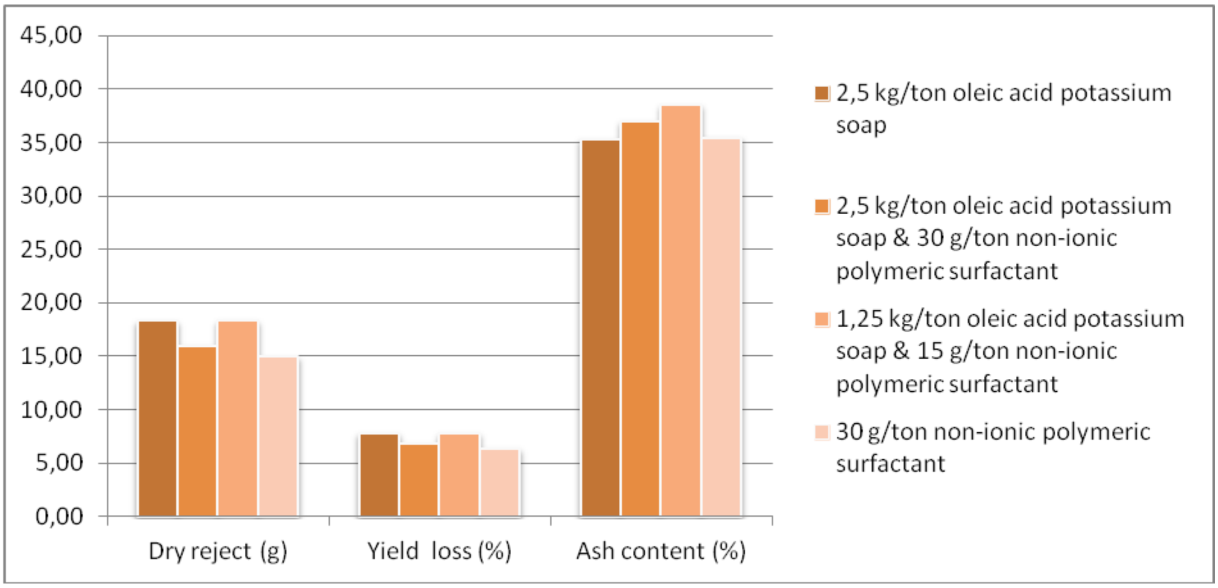

Figure 24: Dry reject, yield loss and ash content from experiments with oleic acid potassium soap and/or a non-ionic polymeric surfactant.

The results in all three reject categories in the diagram above are found in a quite narrow range. It is also difficult to see any trends, even if it can be seen that 30 g/ton non-ionic polymeric surfactant in the experiment, with or without fatty acid soap, seems to give lower reject and yield loss values.

4.1.3 Variation of the BIMPRO® dose

The BIMPRO® dose used in the standard recipe, 3 kg/ton, corresponds to the amount of NaOH that is used in the standard reference recipe, 4 kg/ton (1 kg of NaOH equals 0,728 kg of $Mg(OH)_2$ on a molar basis, i.e. 4,0 kg/ton of NaOH = 2,9 kg/ton $Mg(OH)_2$). It was investigated if better deinking performance could be acquired by increasing the BIMPRO® dose to 4 kg/ton. It is important to know that it is a difference in the age of the raw material in the two cases. When the standard recipe was used the ONP was 51 days old and the OMG was approximately 10 weeks old while the ONP was 66 days and the OMG was approximately 12 weeks old when the BIMPRO® dose was increased. This means that the experiment with high BIMPRO® dose will have a bit poorer values than if both experiments had been performed on the same day.

It is interesting that a higher BIMPRO® dose does not change the ERIC and brightness values very much. The unflotated ERIC value is even a bit poorer. As mentioned above the ageing of the ink will affect the result, and it is difficult to know by how much.

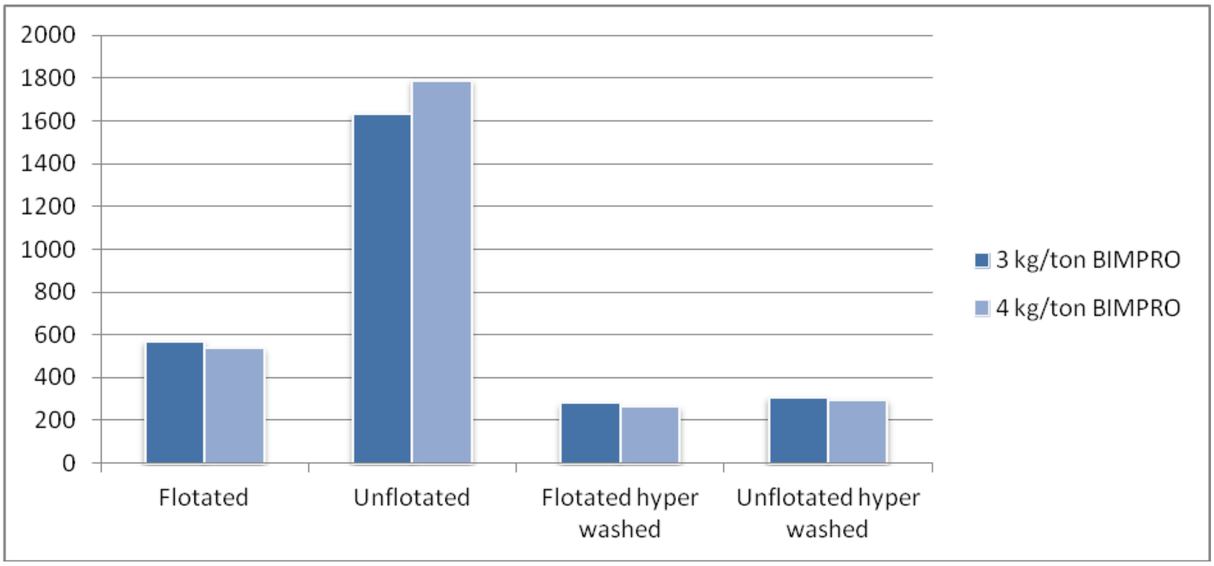

Figure 25: ERIC values from the experiments changing the BIMPRO® dose.

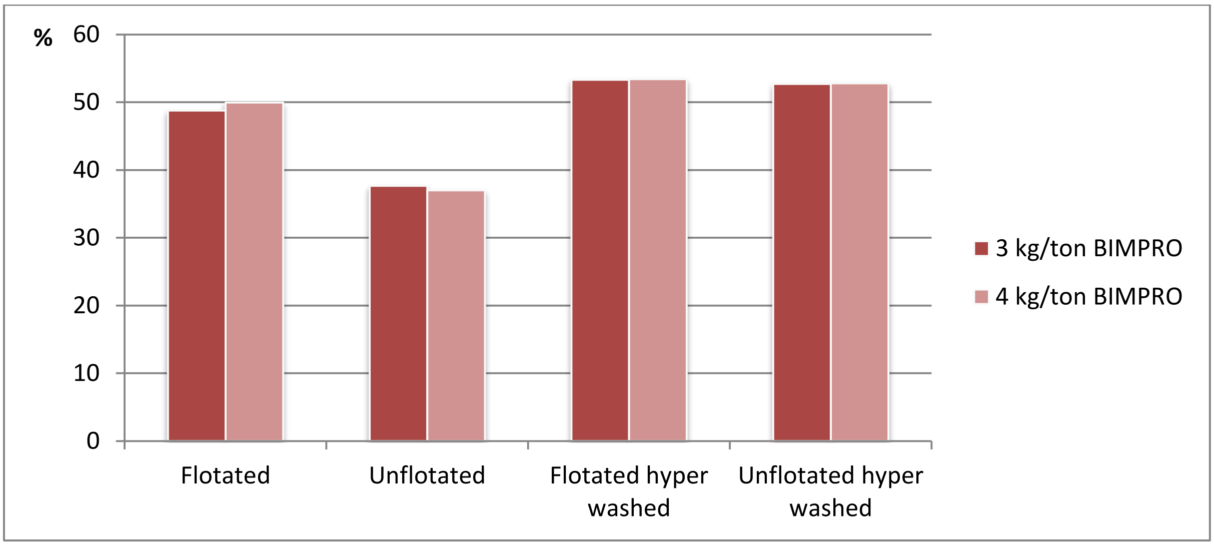

Figure 26: Brightness values from the experiments changing the BIMPRO® dose.

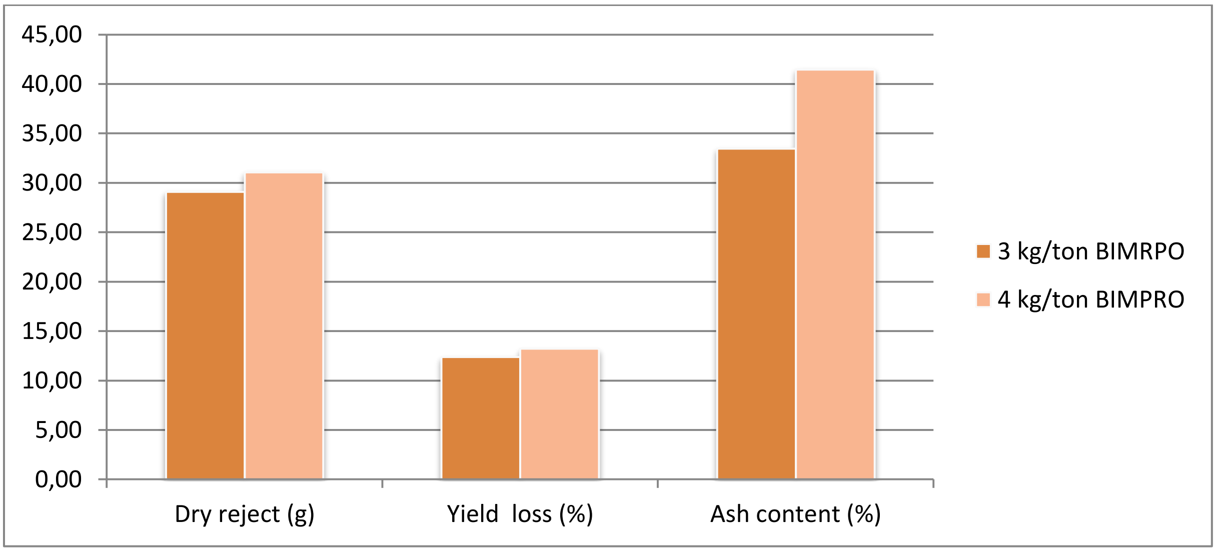

Figure 27: Dry reject, yield loss and ash content from the experiments changing the BIMPRO® dose.

There are some differences between the two experiments if evaluating the reject, yield loss and ash content results. Here, a lower dose will give a bit better values concerning reject and yield loss but the largest difference is found in the ash content. It seems like a higher dose BIMPRO® will give much higher ash content in the reject.

4.1.4 Variation of sodium silicate dose

In order to investigate the importance of sodium silicate in the flotation process three different experiments were performed varying the dose of this chemical. In all three cases the higher BIMPRO® dose was used, 4 kg/ton. The different silicate doses used were 0 kg/ton, 3 kg/ton and 5 kg/ton.

The trend is that a higher dose of silicate gives better results concerning ERIC, brightness and reject values. It also seems that there is no big difference between 3 kg/ton silicate and 0 kg/ton silicate: 3 kg/ton gives a bit better flotated ERIC and brightness values while 0 kg/ton gives better unflotated values. The results from the unflotated samples suggest that silicate does not have an important role concerning when the ink particles are detached from the fibres. The values are quite the same and the best ERIC value was actually received using 0 kg/ton silicate. The flotated ERIC values show that a higher dose of sodium silicate will help the flotation. 414 in flotated ERIC value, which is the result using the highest dose silicate, is a good result since the used raw material was old at the time for this experiments. The good result can of course also depend on the high BIMPRO® dose but the high silicate dose is definitely helping since 3 kg/ton gives 537 in flotated ERIC value.

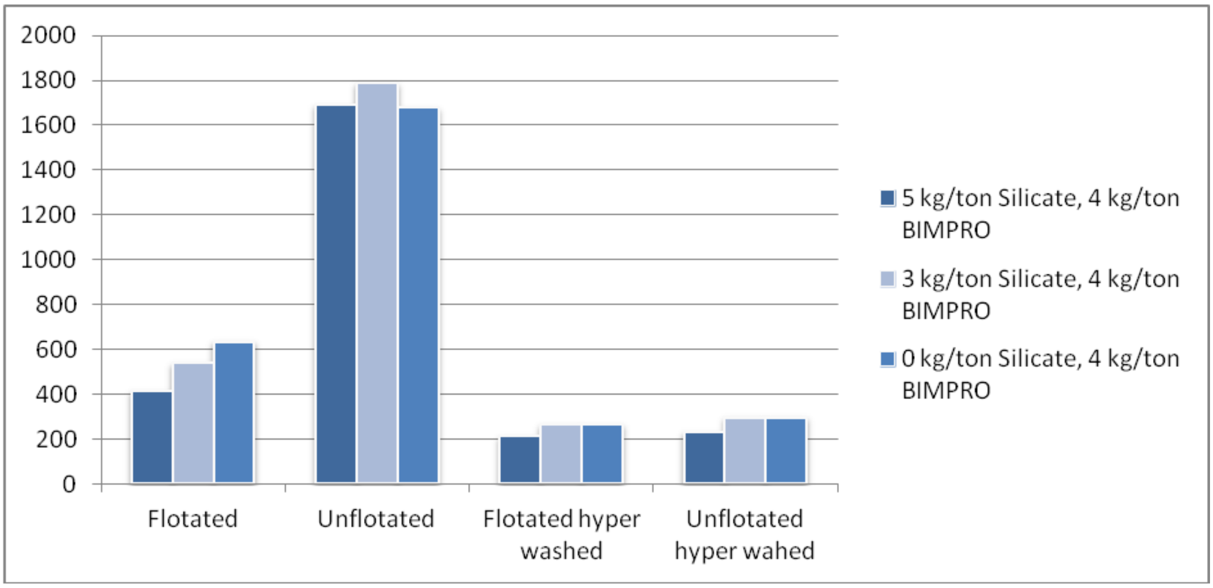

Figure 28: ERIC values from the experiments changing the sodium silicate dose.

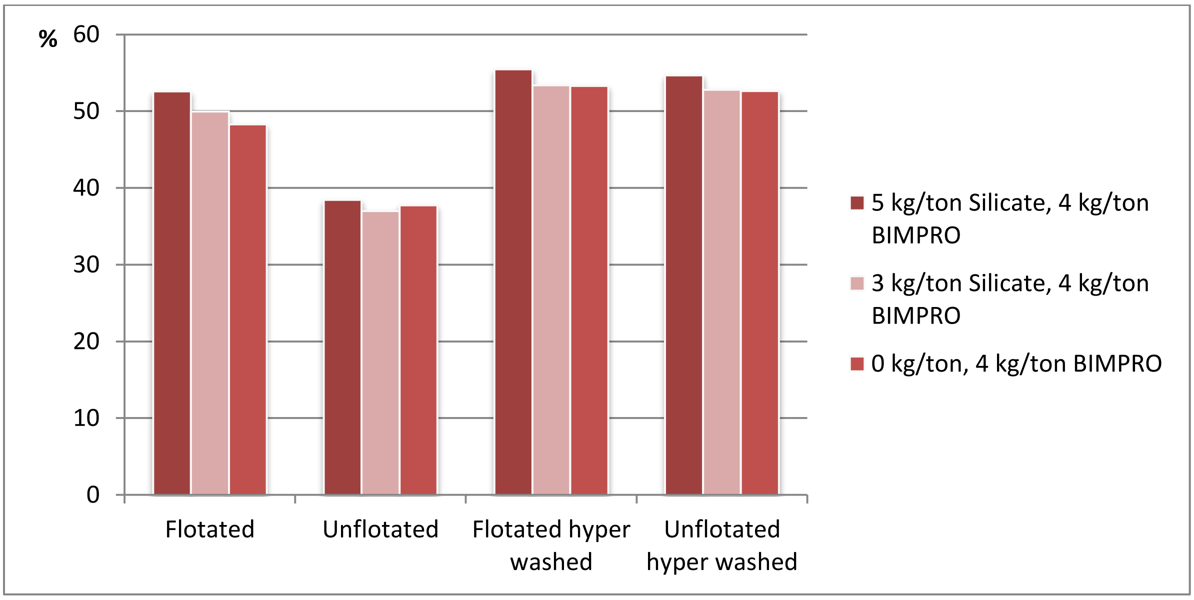

Figure 29: Brightness values from the experiments changing the sodium silicate dose.

When experimenting with the high silicate dose and a high BIMPRO® dose a very high alkalinity value was achieved: 422. The high BIMPRO® dose explains a part of it but it is also obvious that increasing the sodium silicate will increase the alkalinity in all three measuring points; after the pulper, in the unflotated sample and in the flotated sample. The values are even higher than using NaOH instead of BIMPRO®. After the flotation step the alkalinity values are in a narrow range for the three experiments, not at all as it was after the pulper.

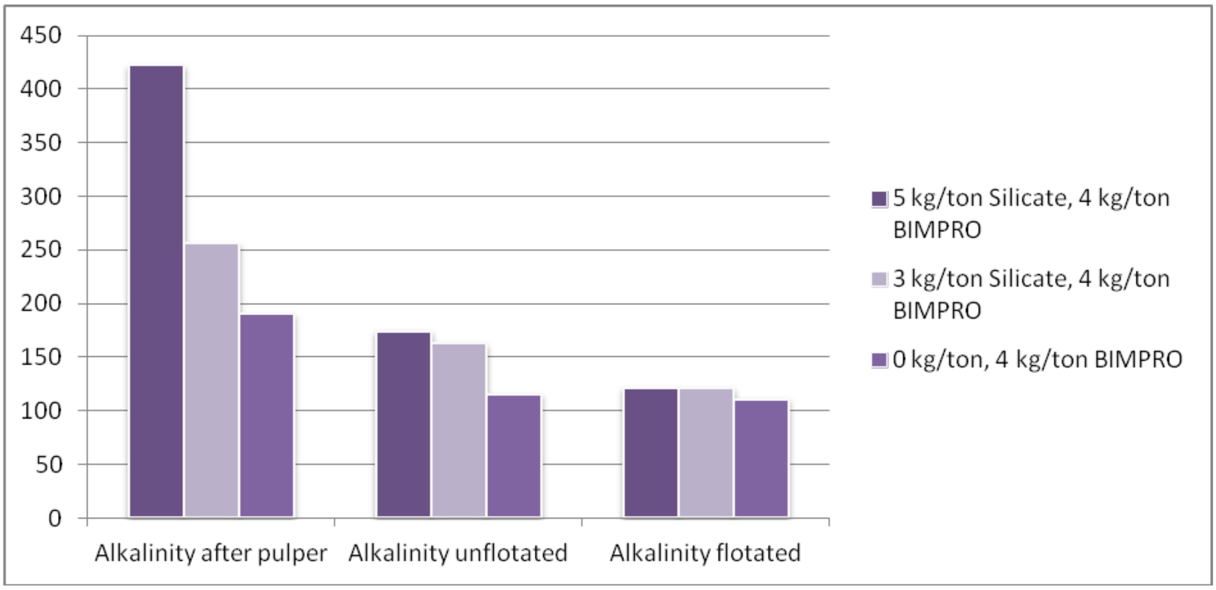

Figure 30: The alkalinity achieved from the experiments changing the sodium silicate dose.

The reject, yield loss and ash content results do not follow any specific order. 5 kg/ton sodium silicate still gives the best values but 3 kg/ton gives the poorest values which are a bit strange. However, the yield loss result follows the dry reject result meaning that if the reject is high, yield loss will also be high.

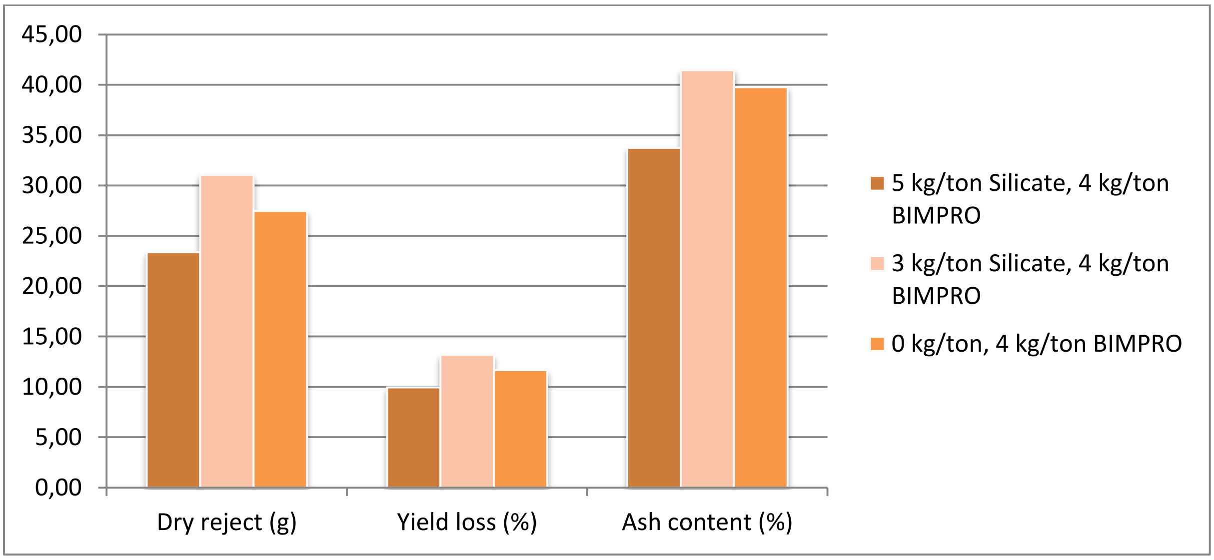

Figure 31: Dry reject, yield loss and ash content from the experiments changing the sodium silicate dose.

4.1.5 Effects of pH and alkalinity

Many parameters are interesting to follow through a deinking process. For example, hardness, pH and alkalinity are all changing depending on the chemicals used and where in the deinking process the sample is taken. In traditional flotation deinking using NaOH, pH drops from above 10 to approximately 8 in the flotation cell. Using BIMPRO® will lower the values in the whole process.

The pH of the pulp was tested at four different points in the deinking experiments; after the Kitchen Aid, after the pulper, in the unflotated sample and in the flotated sample. In the experiments using BIMPRO® almost all pH values are found to be 7,7-8,0 in the two first measuring points and 8,0-8,4 for the unflotated and the flotated samples. Thus, pH actually increases during the deinking process. There were no differences which of the three soaps that were used, or if a non-ionic polymeric surfactant is used. A higher dose of BIMPRO® increased the pH in the two first measuring points while no trend was seen when changing the amount of sodium silicate. Using NaOH instead of BIMPRO® gave higher pH values, as expected. Here, the pH was decreasing in the course of the experiment, from approximately 9 to 8,2-8,5. All pH values can be found in Appendix 6**.**

The alkalinity values were followed in three measuring points in the deinking experiments; after the pulper, in the unflotated sample and in the flotated sample. All the values can be found in Appendix 5. The alkalinity values from the first two experiments are not accurate since an ampoule fitting a much higher alkalinity range was used. From deinking experiment 3 and forward another and much better suited ampoule was used.

Some variations in alkalinity possibly related to the age of ONP and OMG were noted, but no trends could be seen.

The differences in alkalinity between the three fatty acid potassium soaps were also very small. Using sodium hydroxide as alkali source gave higher values with the three soaps.

The absolutely highest alkalinity value, 422, was achieved with a high dose of BIMPRO® and a high dose of sodium silicate. Using the high dose BIMPRO®, 4 kg/ton, gave values more like using NaOH compared to using a lower dose of BIMPRO® (3 kg/ton).

Another high alkalinity value, 217, was achieved after the pulper when no $CaCl_2$ were added to the process. One reason that has been discussed is that all $Mg(OH)_2$ from the BIMPRO® is dissolved when no calcium ions are present. The dissociated fatty acid soap helps the $Mg(OH)_2$ particles to dissolve by attach to them. It seems that one way of increasing the alkalinity, and pH, is to skip the addition of $CaCl_2$ in the beginning of the process and instead just use $Mg(OH)_2$. The role of hardness is further discussed in the next section.

4.1.6 Effect of Ca^{2+} and Mg^{2+} on the deinking performance

Some of the experiments were performed to evaluate the role of the addition of $CaCl_2$, both in the pulping step and in the flotation step. By adding $CaCl_2$ early in the process the hardness of the system is adjusted, in this case up to 10 dH. The addition of $CaCl_2$ can also be made in the flotation step, where it has the role of creating solid calcium soap flakes from the dissolved sodium or potassium soap, thus helping the ink particles to aggregate and flotate with the air bubbles.

Three experiments using the standard recipe with oleic acid potassium soap were performed in order to evaluate the effect of $CaCl_2$ additions at different points in the deinking process. In the first experiment the sodium stearate soap used in the flotation was excluded to see what happens with the flotation step without adding the soap but with $CaCl_2$ still added. In the two continuing experiments the $CaCl_2$ was skipped, once both in the early stage and in the flotation step, and once just in the early stage, while retaining the soap addition in the flotation.

Table 6: The addition of $CaCl_2$ and soap in the experiments described in 4.1.6.

	Experiment 1	**Experiment 2**	**Experiment 3**
K+ oleic soap	Pulping step	Pulping step	Pulping step
Na stearic soap	---	Flotation step	Flotation step
$CaCl_2$	Pulping step Flotation step	---	Flotation step

When not adding the sodium soap in the flotation step the flotated ERIC and brightness values are poorer compared to the standard case. The reason seems to be that no or at least too few soap flakes are created which makes it hard for the ink particles to agglomerate and float to the reject channel. The wet reject amount was very high when no soap was used in the flotation. The reject was direct from the start of the flotation step very watery, giving the high value. It seems that the foam existing in the flotation cell without addition of sodium soap become more hydrophilic, less hydrophobic stabilized, and therefore the water will follow the foam to the reject bucket. The result concerning dry reject is even lower than normal which strengthens the upcoming theory about large amount of water in the reject. The low dry reject value is also connected to the poorer flotated ERIC and brightness values; not enough ink particles have flotated to get good results.

The unflotated and the two hyper washed samples for the experiment without soap addition in the flotation gave normal results which indicate that it was only the flotation step that was working poorer with the lack of soap. The normal values of the hyper washed samples also indicate that the ink particles have detached from the fibres and that no redeposition has occurred.

The conclusion is that a soap addition is needed in the flotation step for a system using BIMPRO® as the alkali source on a 70:30 ONP:OMG mixture. This was also confirmed in an earlier master thesis at BIM Kemi AB (37) where it was evaluated if the sodium stearic soap could have been replaced by a potassium oleic or mixed unsaturated fatty acid soap in the flotation, but the result was negative. It is possible that the higher hydrophobicity of the saturated stearic fatty acid as compared to the more hydrophilic, unsaturated oleic-type of fatty acids is favourable for flotating the hydrophobic ink particles. However, as noted, in the pulper step the effect stearic and oleic acid seems to be quite the opposite.

The next experiment was containing sodium soap in the flotation step but no $CaCl_2$ was added in the whole process. As in the case without sodium soap in the flotation described above, the flotated ERIC and brightness values are poorer without addition of $CaCl_2$, due to the lack of formed calcium soap flakes. However, the unflotated ERIC and brightness values are good. It could mean that no calcium (or magnesium) ions are needed in the first stages of the process, it is enough with a dissociated fatty acid not yet precipitated. As described above the alkalinity value after the pulper was high, 217 while the flotated and unflotated alkalinity values are normal.

Without adding $CaCl_2$ the reject amounts are low which is opposite to without sodium soap, when the wet reject was watery. This reversed tendency could be explained since there is both sodium soap, calcium (mainly from the OMG raw material) and magnesium ions present in the flotation step, enough to make hydrophobic soap flakes. The foam in the flotation was good and dark in the beginning confirming that the ink was following the foam to the reject channel, but the lack of calcium ions is the reason to the poorer flotated ERIC and brightness values; the amount of soap flakes were not enough for the whole flotation process.

The results of the unflotated and the hyper washed samples are in the normal range which, as in the case of no added sodium soap, indicating that the detachment process has worked, in contrast to the flotation step.

This conclusion was the reason to perform the following experiment; no addition of $CaCl_2$ in the beginning of the process but adding both $CaCl_2$ and sodium soap in the flotation step. When this experiment was performed the raw material was 12 days older which, considering ageing of ink, could affect the results.

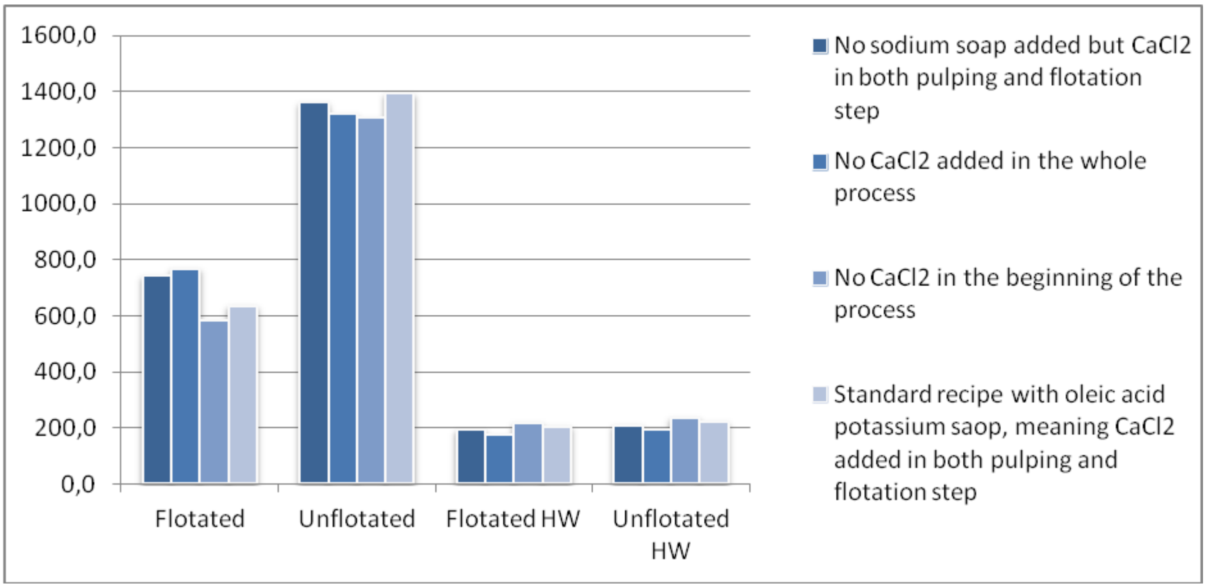

Figure 32: ERIC values from the experiments evaluating the importance of adding $CaCl_2$ and sodium soap.

The flotated ERIC value in this experiment turned out to show a promising result. It was significantly better than the other two results, and also better when using the standard recipe (adding $CaCl_2$ both in the pulper and in the flotation step), which actually was using 14 days newer raw material than in the studied experiment. It seems that better flotated values can be achieved if magnesium ions alone are used in the beginning of the experiment. The hyper washed values are in the same range as from the other experiments, just a bit poorer, which could depend on the older raw material.

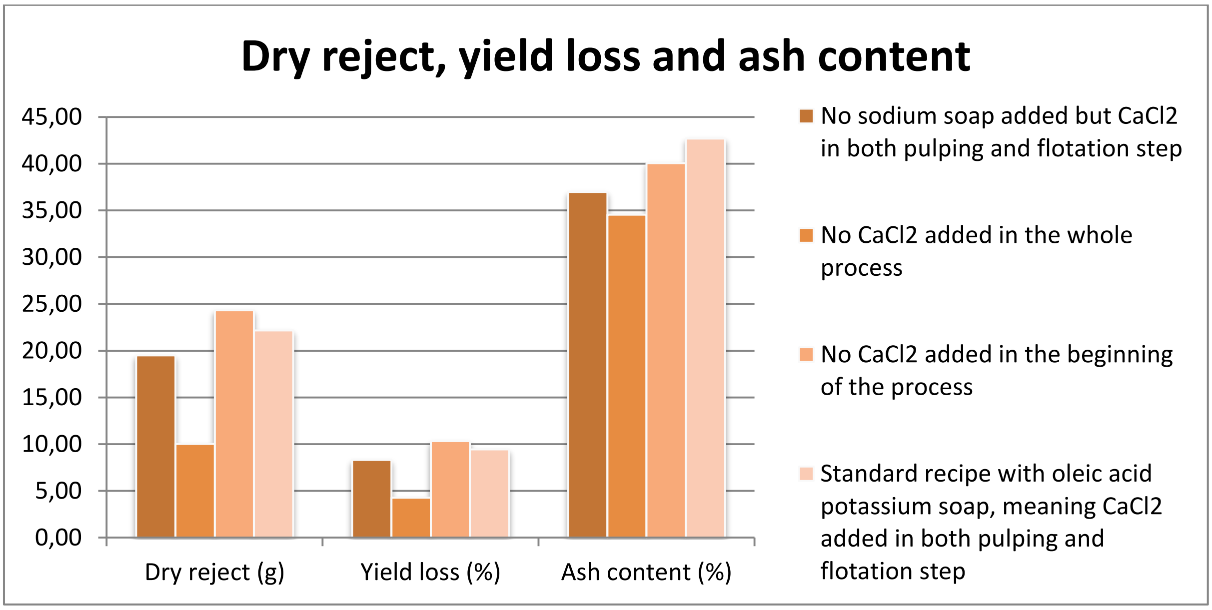

Figure 33: Dry content, yield loss and ash content from the experiments evaluating the importance of adding $CaCl_2$ and sodium soap.

The results concerning the rejects are more widely distributed. The really low dry reject value, 10,0 g, might be connected with the poorer flotated ERIC result; not enough ink particles have been remove from the pulp.

4.2 Ageing of ink

Some experiments were performed in order to study the influence of ageing of ink on the deinking performance. Two reference recipes with BIMPRO® were used; one containing oleic acid potassium soap and the other one containing a non-ionic polymeric surfactant in the pulping step. Since the two recipes showed similar trends, only the results for the oleic acid recipe are shown here, however all values can be found in Appendix 10. The old newsprint (ONP) was between 2 and 51 days old while the old magazines (OMG) were between 1 and 12 weeks old.

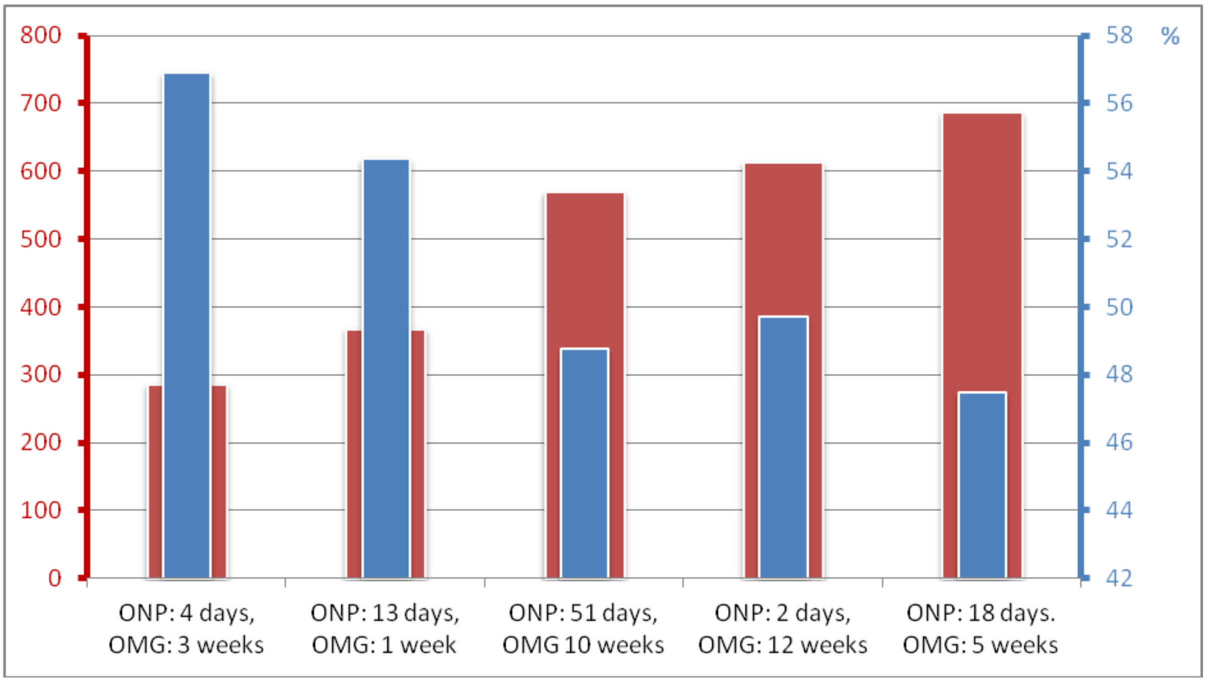

Figure 34: Flotated ERIC values using oleic acid potassium soap.

As can be seen in the diagram above, the flotated values change a lot with ageing raw material. The best ERIC value is 285 and was achieved when the ONP was only a couple of days old and the OMG was approximately three weeks old. 285 is the best flotated ERIC value during this project and a brightness of 56,9 % is almost the best brightness value. The next value in the diagram shows that every day the ONP is ageing will change the result. 13 days old ONP and only 1 week old OMG gives poorer values, 367 in ERIC and 54,4 % in brightness. This is still good values but it is interesting that ONP seems to have much bigger influence on the results than OMG.

That conclusion is however not true for the next three cases. Here, the ERIC and brightness values are much worse than the first two, even if the ONP in two of the cases are quite new. The poorest value may depend on a too low temperature in the flotation step due to a malfunctioning thermometer in this very experiment. It is interesting that the ERIC and brightness results from the experiment with 51 days old ONP and 10 weeks old OMG are similar to the results from the experiment with 2 days old ONP and 12 weeks old OMG. The reason might be that the OMG is now so old that it determines the result much more than before compared to ONP. Maybe the values will not change so much from approximately 600 in ERIC and 49 % in brightness if making experiments on even older ONP and OMG.

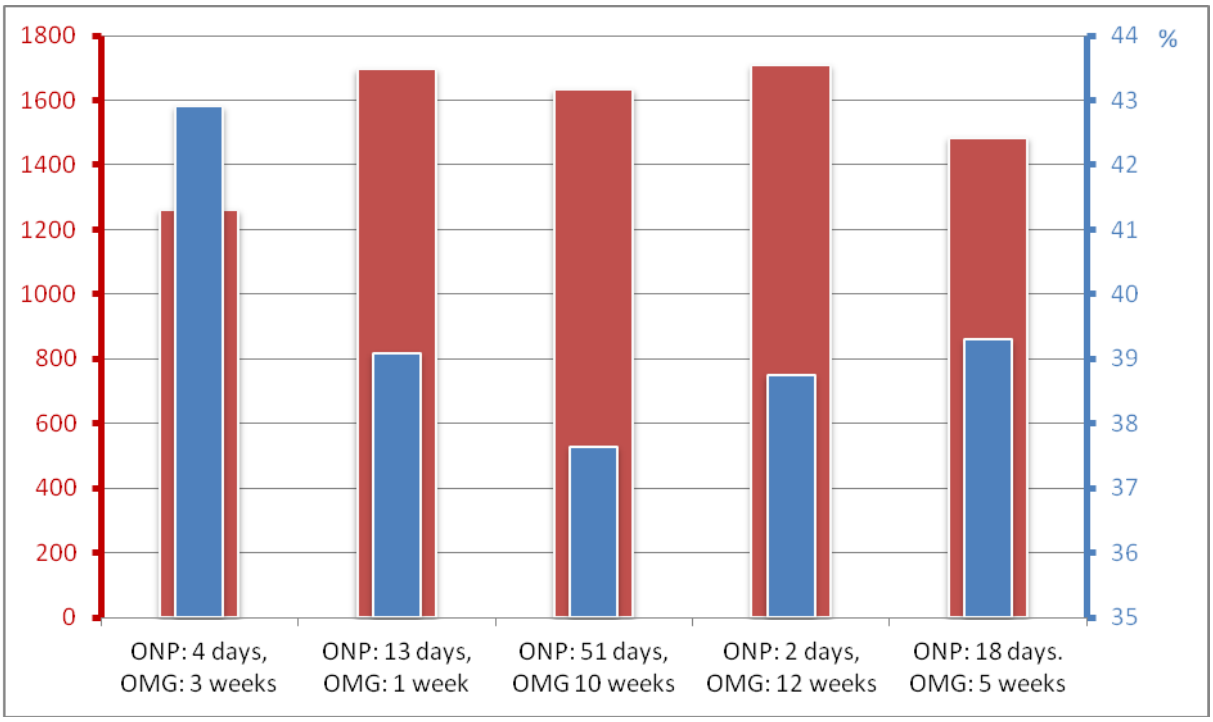

Figure 35: Unflotated ERIC values using oleic acid potassium soap.

The unflotated values are a bit more difficult to explain. Still 4 days old ONP and 3 weeks old OMG gives the best values; especially its brightness value is very good. The next experiment, 13 days old ONP and 1 week old OMG, gave as described before good flotated values but the unflotated values were not as good. One reason could be that the sheet formation of unflotated samples is more difficult giving a bigger uncertainty in the results.

The hyper washed results followed the same trends as the standard ERIC and brightness values, see table in Appendix 9. The amount of wet reject (also table in Appendix) also increases with increasing age of the ONP/OMG raw material. Thus, the ageing process affects not only the ink detachment but also the flotation efficiency.

4.3 Agglomeration kinetics

4.3.1 Evaluating visible precipitation

The use of the Hach Turbidimeter gave a very wide range of values. A clear solution often gave values of 0-3 NTU, for example distilled water 0-1 NTU, but then no, for this project, useful trends could be found. Solutions with visible precipitation between the fatty acid soap and the calcium or magnesium ions gave lower NTU values than a mild opaque solution. Therefore the focus was on the visibility tests. Almost all of the solutions were analysed several times the same day they were prepared but also the morning after.

Differences in visual precipitation behaviour were found in almost every solution and some results were very interesting. It seems that calcium ions more easily precipitate with mixed unsaturated fatty acid potassium soap than with oleic acid potassium soap. When evaluating magnesium it was the opposite; the system with magnesium ions and oleic acid potassium soap gave precipitation while no precipitation is found using mixed unsaturated fatty acid. These results are without addition of silicate or hydrogen peroxide.

The precipitation differs not only in amount but also in shape and where in the solution it is mostly found. In the system using mixed unsaturated fatty acid potassium soap and calcium ions the precipitation seems to consist of small, almost spherical particles in all the solution but with an increase of particles at the bottom and on the water surface. The particles seem to be found in a quite narrow size range. The solution was mildly opaque. The precipitation from magnesium ions and oleic acid potassium soap gave bigger agglomerates, more as “clouds”. They had many different shapes and sizes and were found in the whole solution with no increase at the bottom or at the water surface. The solution was opaque in the beginning of the tests but when the precipitation started the solution became transparent. The differences can be seen in figure 36. When stirring the two different solutions the agglomerates were destroyed and much smaller particles appeared in the solution. A difference between the two systems after stirring; when the solution stopped moving the solution with mixed unsaturated fatty acid and calcium ions started to create bigger particles while it took longer time for the magnesium system to create its agglomerates again.

When adding sodium silicate and/or hydrogen peroxide the precipitation acted differently in some of the cases. When adding sodium silicate to oleic acid potassium soap and calcium chloride suddenly gave that system precipitation, and even very fast. In the first experiment it only took 15 minutes, in the next 1-2 hours. When using the same system but in the beginning also adding hydrogen peroxide the solution only becomes very opaque. A solution containing mixed unsaturated fatty acid potassium soap, calcium ions and sodium silicate will not differ in precipitation compared to without sodium hydroxide. Addition of hydrogen peroxide will not affect the result either.

The amount of oleic acid potassium soap was changed, 40, 50 and 60 mg/l and was tested with $CaCl_2$ but no precipitation was found in the three cases during 6 hours. However, when adding sodium silicate in the beginning precipitation was found in the three solutions after 1-2 hours.

Three different concentrations of magnesium chloride were used in oleic acid potassium soap solutions. 0,5 mM gave no precipitation while 5 mM gave precipitation faster than 1 mM magnesium chloride.

Table 7: The visible precipitation for the different experiments.

Potassium soap	**$CaCl_2$ or $MgCl_2$**	**Silicate**	**H_2O_2**	**pH at start**	**Precipitation**
50 mg/l oleic	5 mM $CaCl_2$	No	No	9,05	Opaque
50 mg/l mixed unsaturated fatty acid	5 mM $CaCl_2$	No	No	9,07	Morning after*
50 mg/l oleic	5 mM $MgCl_2$	No	No	9,07	Morning after*
50 mg/l mixed unsaturated fatty acid	5 mM $MgCl_2$	No	No	9,04	Opaque
50 mg/l oleic	5 mM $CaCl_2$	0,50 g	No	10,04	15 minutes
50 mg/l mixed unsaturated fatty acid	5 mM $CaCl_2$	0,51 g	No	9,87	Morning after
50 mg/l mixed unsaturated fatty acid	5 mM $CaCl_2$	0,52 g	5,00 g	9,79	Morning after
50 mg/l oleic	5 mM $CaCl_2$	0,53 g	5,01 g	9,85	Very opaque
40 mg/l oleic	5 mM $CaCl_2$	0,50 g	No	9,89	1-2 hours
50 mg/l oleic	5 mM $CaCl_2$	0,51 g	No	9,87	1-2 hours
60 mg/l oleic	5 mM $CaCl_2$	0,52 g	No	9,89	1-2 hours

40 mg/l oleic	5 mM $CaCl_2$	No	No	9,05	No**
50 mg/l oleic	5 mM $CaCl_2$	No	No	9,00	No**
60 mg/l oleic	5 mM $CaCl_2$	No	No	9,04	No**
50 mg/l oleic	0,5 mM $MgCl_2$	No	No	9,07	No
50 mg/l oleic	1 mM $MgCl_2$	No	No	9,07	390 minutes
50 mg/l oleic	5 mM $MgCl_2$	No	No	9,08	90 minutes
50 mg/l oleic	5 mM $MgCl_2$	0,51 g	No	9,86	120 minutes
50 mg/l mixed unsaturated fatty acid	5 mM $MgCl_2$	No	No	9,01	Opaque
50 mg/l oleic	5 mM $MgCl_2$	0,51 g	5,00 g	9,75	120 minutes

* The tests were not checked until the morning after. ** The solutions were only controlled in 375 minutes.

The pH of the solutions was tested several times during the experiment. It was adjusted to pH 9 using sodium hydroxide in all experiments except when silicate and/or H_2O_2 due to an already high enough pH. The values were in all cases decreasing with time.

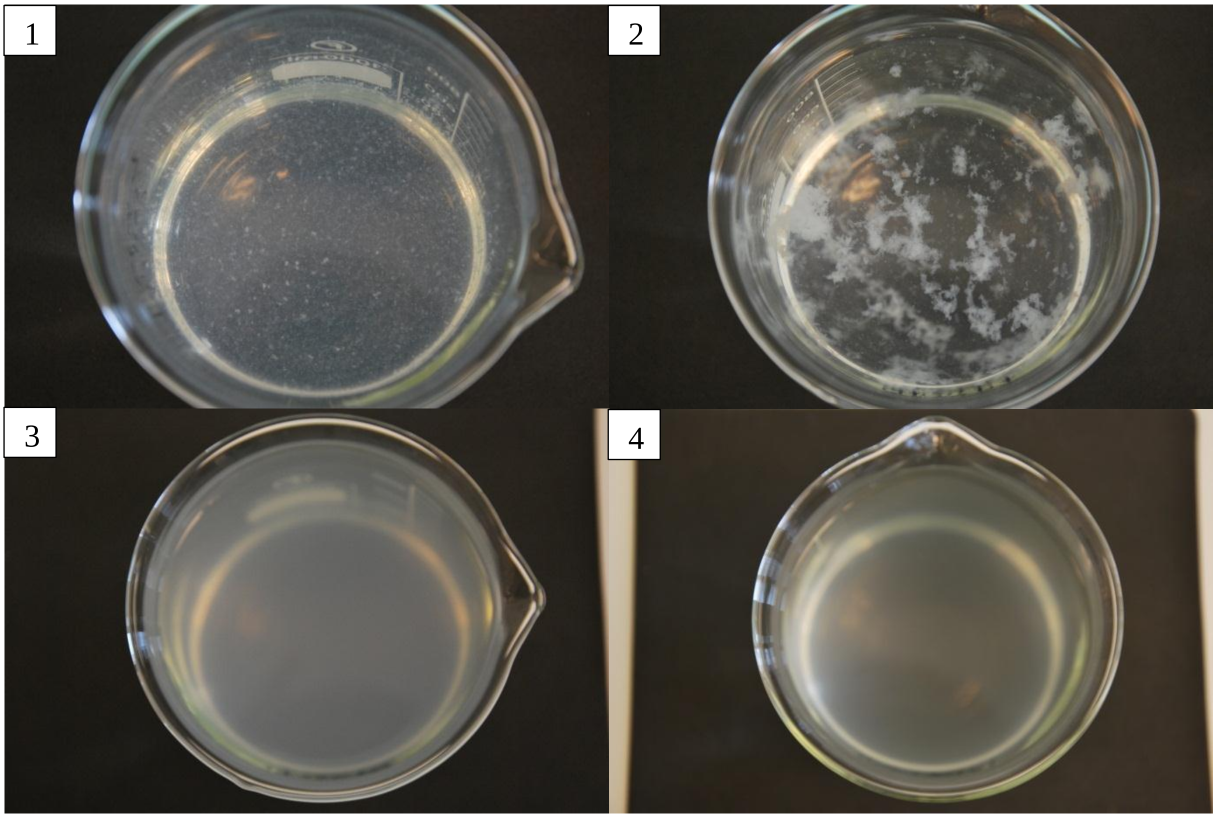

Figure 36: Pictures of four of the tested solutions. Number 1 is showing the precipitation of mixed unsaturated fatty acid and calcium ions, number 2 is showing the precipitation of oleic acid and magnesium ions, beaker number 3 is containing oleic acid and calcium ions while number four contains mixed unsaturated fatty acid and magnesium ions.

4.3.2 Results using Turbiscan online

By using a Turbiscan online the transmission of the tested samples could be evaluated. A decrease in transmission means precipitation of soap particles scattering light. In some experiments a minimum value in transmission was found, where after the transmission increased. Since transmission and scattering of light of particles in this size region depends on both their shape and size according to the MIE theory (38), it is not totally clear if the increase in transmission is the result of a change in particle size it may merely be a result of larger particles moving to the surface of the measurement cell not further contributing to the signal. Many different experiments were tested were changing the concentration of $CaCl_2$ and/or

$MgCl_2$ while the concentration of the fatty acid potassium soap used, oleic acid or mixed unsaturated fatty acid, was the same; 50 mg/l.

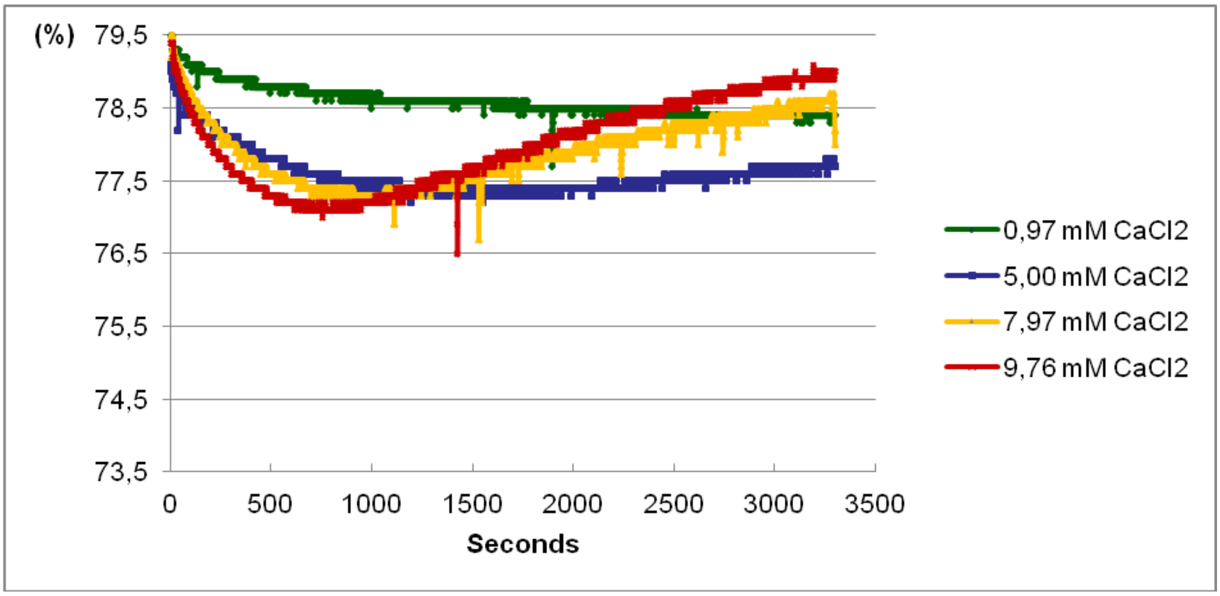

Figure 37: Experiments evaluating the effect of $CaCl_2$ concentration in an oleic acid potassium soap solution, using a Turbiscan Online.

The first tests were evaluating the precipitation between oleic acid potassium soap and calcium ions. The trend was that a higher concentration of calcium chloride gave more precipitation. In the three experiments with the highest concentration a minimum value of transmission was found, earlier in time and lower transmission with higher concentration of calcium ions. Even if the transmission increased, precipitation could be seen in the solution. In solutions containing $CaCl_2$ the precipitation was found in the whole solution as small particles with, as it looked, almost the same size. It was also precipitation at the water surface and these particles agglomerated to bigger flakes, compared to the particles in the solution.

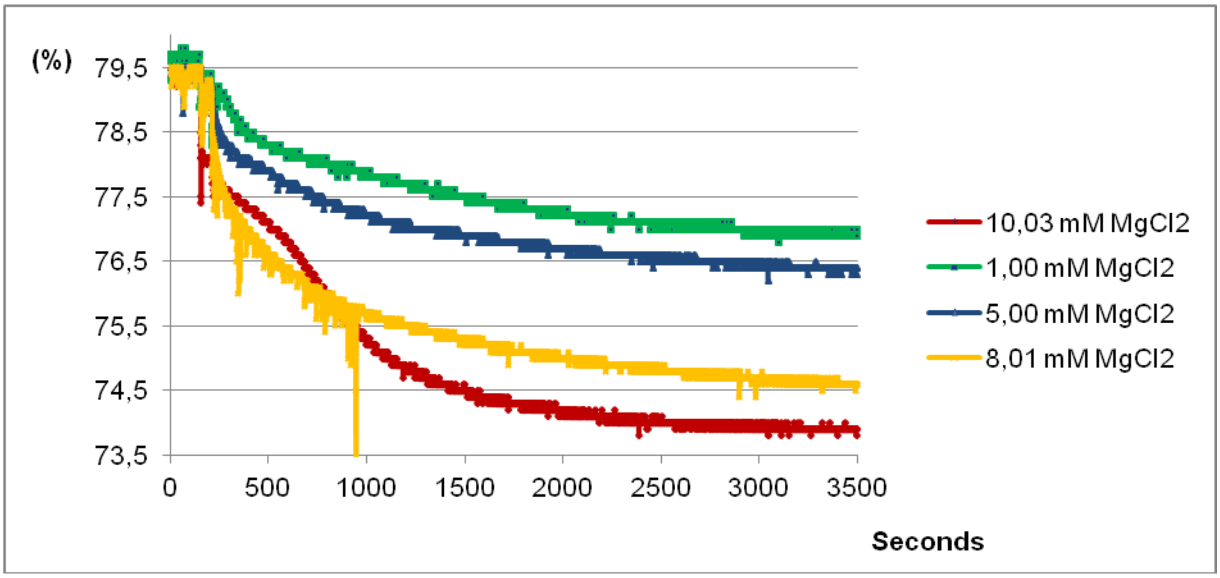

Figure 38: Experiments evaluating the effect of $MgCl_2$ concentration in an oleic acid potassium soap solution, using a Turbiscan Online.

Solutions with oleic acid potassium soap and magnesium ions gave not the same results as with calcium. Here no minimum was found, independent of the concentration of magnesium ions. As in the case of calcium ions, a higher concentration gave a lower transmission value. Using magnesium ions gave a bigger difference in transmission compared to using calcium ions, which after 3500 seconds gave 0,5-2 % difference. The systems with magnesium ions gave 2,5-6 % difference after 3500 seconds, and seem to increase. Precipitation was found evenly distributed in the solution with no increase at the water surface.

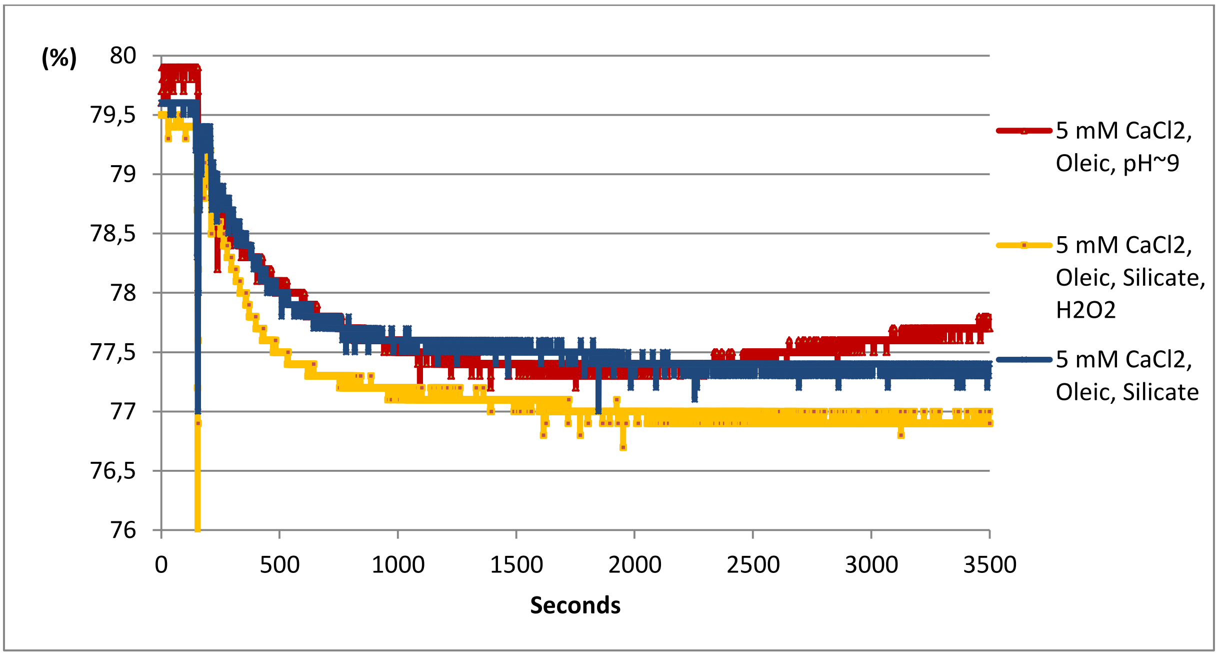

Figure 39: Evaluating the role of sodium silicate and hydrogen peroxide in a solution containing calcium ions and oleic acid potassium soap, using a Turbiscan Online.

If adding sodium silicate to a system containing oleic acid potassium soap and $CaCl_2$ no big differences occur, the only change is that no minimum is found with silicate. When adding both silicate and hydrogen peroxide to the system the result is very similar to the one with sodium silicate, just less than 0,5 % lower precipitation. It is visible precipitation in both cases and it is occurring earlier and become larger, especially on the water surface, than without addition of silicate and/or hydrogen peroxide.

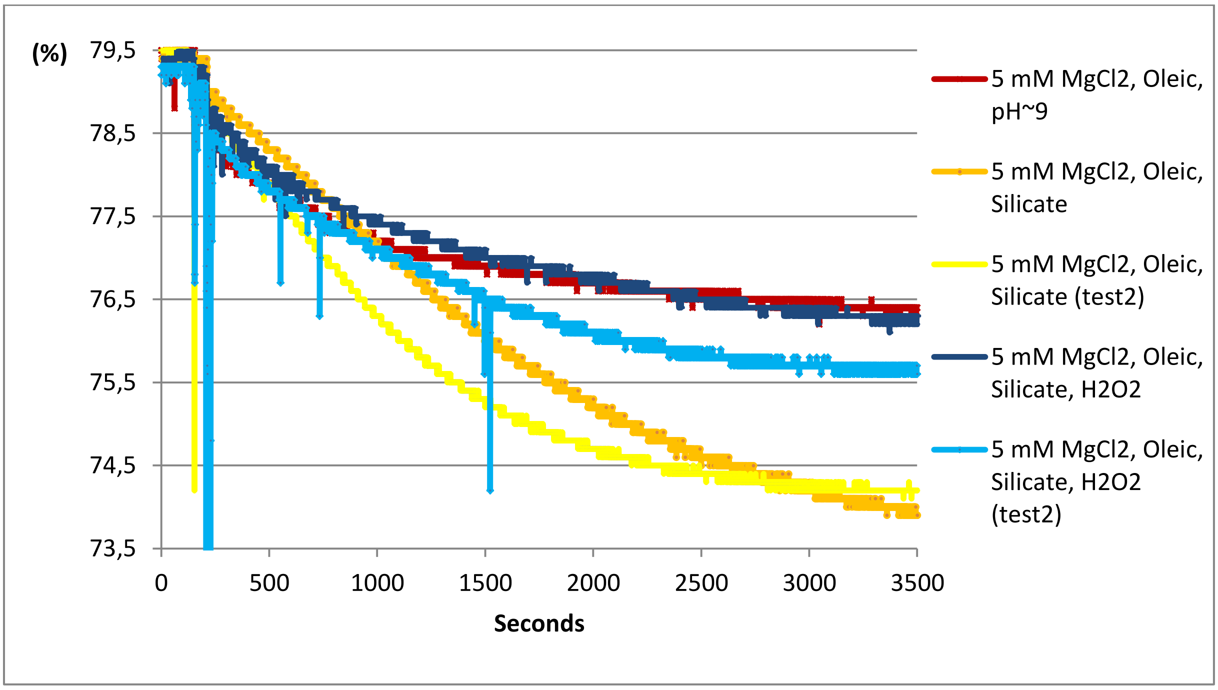

Figure 40: Evaluating the role of sodium silicate and hydrogen peroxide, in a solution containing magnesium ions, using a Turbiscan Online.

The transmission is decreased if sodium silicate is added to a system containing of oleic acid potassium soap and magnesium chloride. However, when hydrogen peroxide is added to the solution the decrease in transmission disappears. It seems like the silicate is focusing on stabilizing the hydrogen peroxide instead of be a part of the precipitation of soap flakes.

Without addition of sodium silicate and hydrogen peroxide precipitation was found in the whole solution after approximately 1000 seconds. When adding sodium silicate the solution was opaque a longer time and precipitation was not found until after 2000 seconds. When also adding hydrogen peroxide to the solution, precipitation was, by eye, visible after approximately 1000 seconds, more alike without any sodium silicate addition.

Since addition of sodium silicate and/or hydrogen peroxide gives a higher pH, the role of pH was evaluated. pH was adjusted to 8, 9 and 10 in two systems; one containing oleic acid potassium soap and calcium chloride and one system containing oleic acid potassium soap and magnesium chloride.

When using the oleic acid and calcium ions no big difference can be found. All three pH values gives almost the same curve, with a minimum of 77-77,5 % and a value after 3500 seconds of 77,3-77,8 %. The curves from the measurements with pH adjusted to 8 and 9 are almost identical while a little lower transmission is found when pH is adjusted to 10. It was also more visible transmission with higher pH.

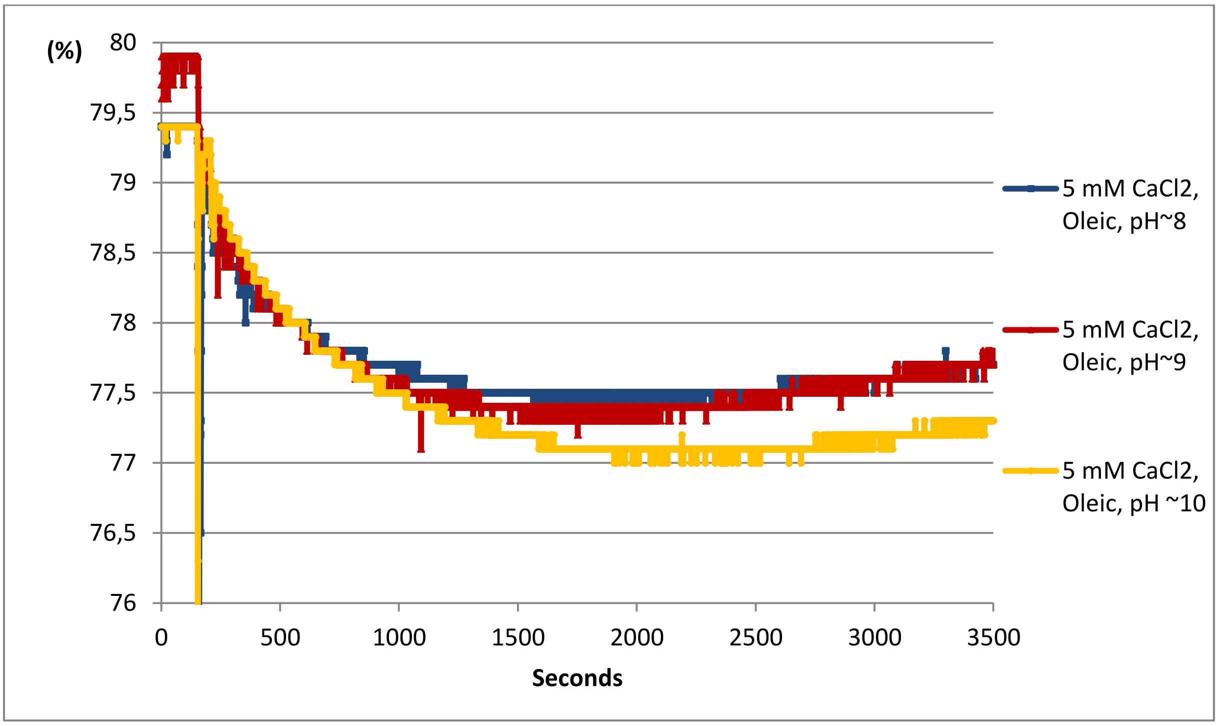

Figure 41: The transmission of a system containing calcium ions and oleic acid potassium soap, and the effect of pH.

The system with oleic acid potassium soap and magnesium ions showed much more difference in transmission when changing the pH. The solution with pH 10 gave much lower transmission values than with pH 8 and 9 which were following each other. When evaluating visible precipitation it was clear that the solution with pH 10 gave much more precipitation than the other two solutions. It had precipitation in the whole solution after only 600 seconds and after 1000 seconds particles were found at the water surface. The amount increased with time but the particles at the surface did not agglomerate to flakes as with calcium ions.

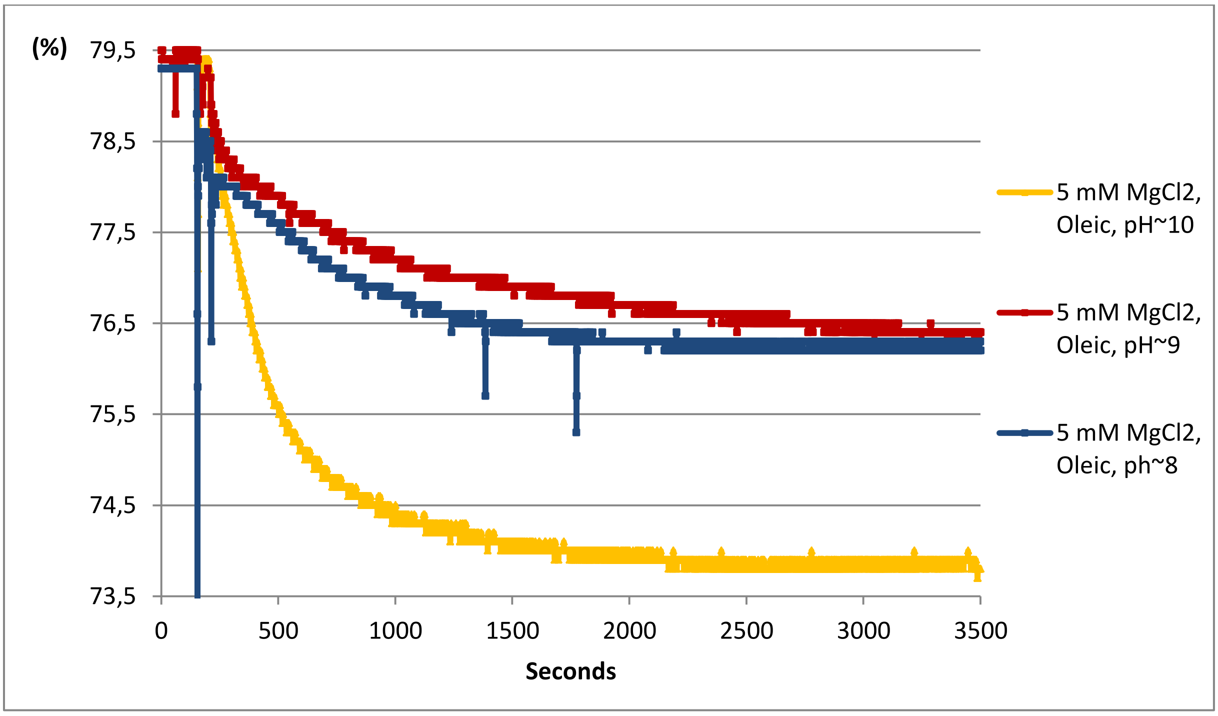

Figure 42: The transmission of a system containing magnesium ions and oleic acid potassium soap, and the effect of pH.

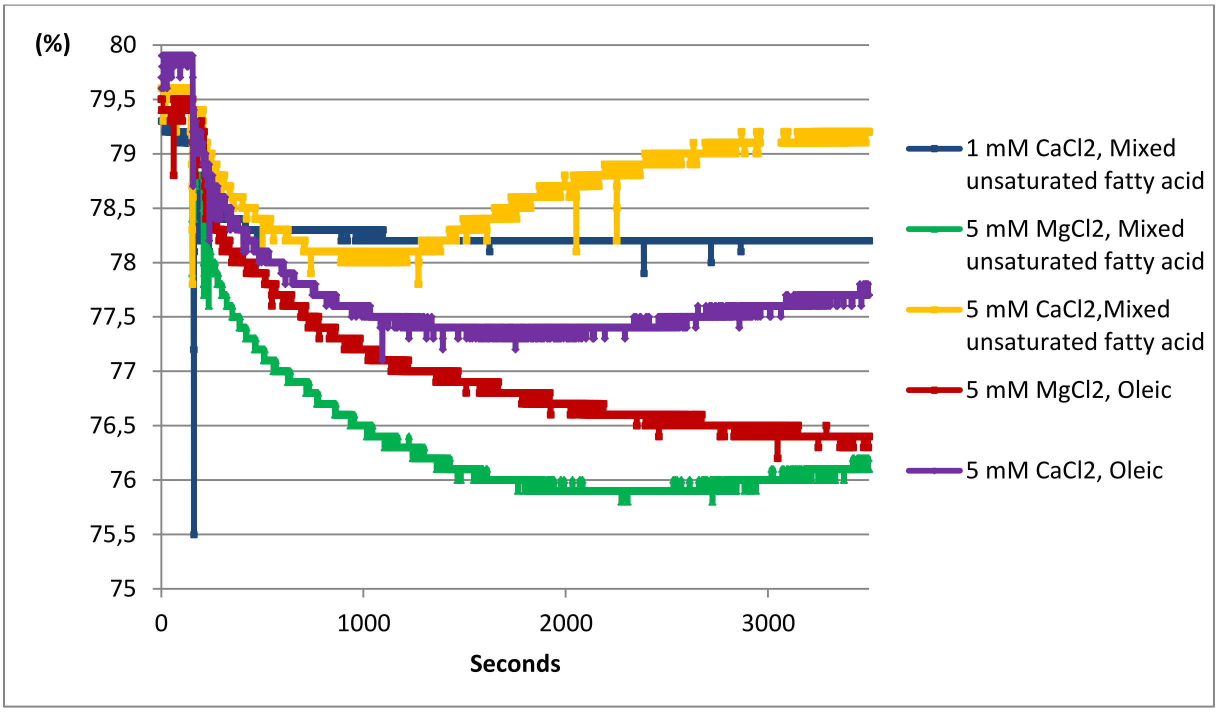

Figure 43: The differences in transmission between oleic acid and mixed unsaturated fatty acid potassium soap.

The differences in precipitation between using oleic acid potassium soap and mixed unsaturated fatty acid potassium soap was evaluated with $MgCl_2$ and $CaCl_2$, individually. Mixed unsaturated fatty acid gave lower transmission values with magnesium ions than with calcium ions, the same trend as with oleic acid. However, the solution containing mixed unsaturated fatty acid and magnesium chloride got a minimum in transmission, which no solution with oleic acid and magnesium chloride has got. There was less precipitation with mixed unsaturated fatty acid and magnesium than with oleic acid and magnesium, and the precipitation was containing of very small particles in the whole solution.

The solution containing mixed unsaturated fatty acid potassium soap and calcium chloride got less change in transmission than oleic acid and calcium ions, and the minimum was found earlier. The end value after 3500 seconds is only 0,4 % lower in transmission than the start value. Visible precipitation was found both in the solution and on the water surface. The solution with mixed unsaturated fatty acid potassium soap and 1 mM $CaCl_2$ was tested since the 5 mM $CaCl_2$ gave high transmission values in the end. The transmission decreased approximately 1,5 % and no precipitation could be seen, the solution was only mild opaque.

When using BIMPRO® in the deinking processes both calcium ions and magnesium ions can precipitate with the soap. No information has been found evaluating this mixture of ions. This was tested in this master thesis.

Four different solutions were arranged; 1 mM of both $CaCl_2$ and $MgCl_2$ in oleic acid potassium soap, 1 mM of both $CaCl_2$ and $MgCl_2$ in mixed unsaturated fatty acid potassium soap, 2,5 mM of both $CaCl_2$ and $MgCl_2$ in oleic acid potassium soap and finally 2,5 mM of both $CaCl_2$ and $MgCl_2$ in mixed unsaturated fatty acid potassium soap.

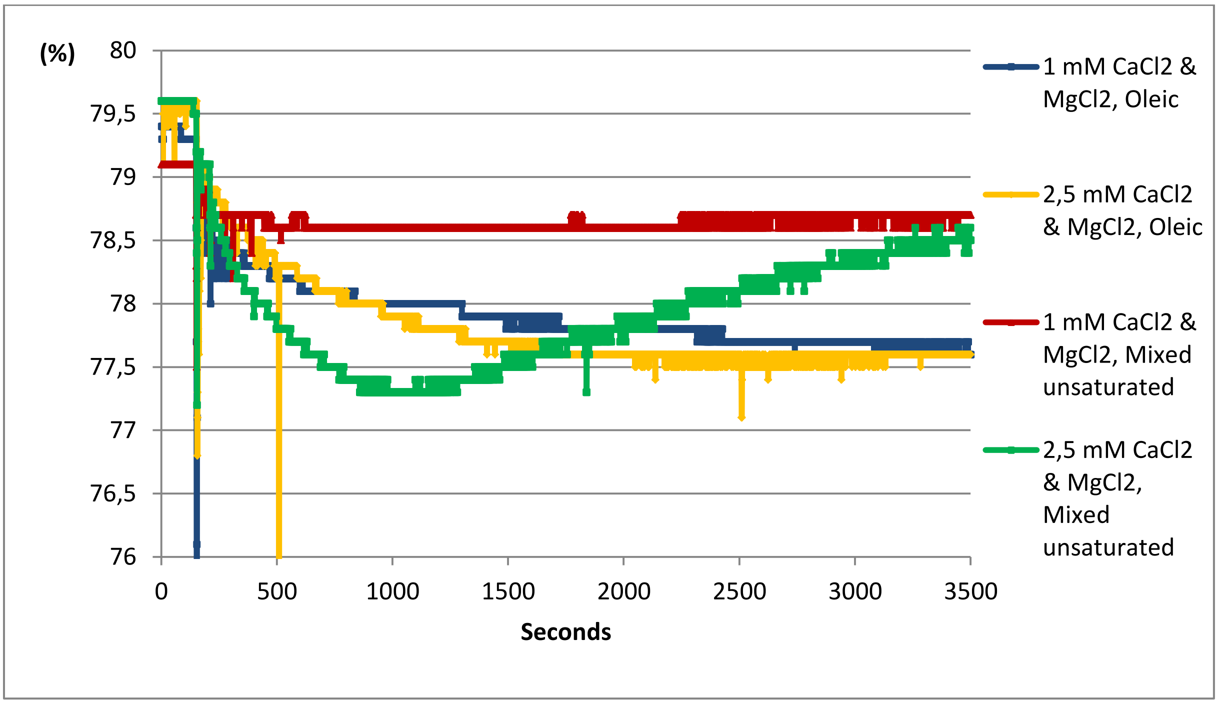

Figure 44: The transmission of solution containing a fatty acid potassium soap and both calcium and magnesium ions.

As can be seen in figure 44, the transmission results had more similarities with solutions containing only calcium ions compared to only magnesium ions, giving the conclusion that in a mixed system calcium ions are favourable considering precipitation to soap flakes.

The visible precipitation was also, in the systems with both 2,5 mM $MgCl_2$ and $CaCl_2$, more alike systems containing only calcium ions and a fatty acid potassium soap. It was precipitation in the whole solution but also a significant amount on the water surface. At the surface the agglomerates were formed more as flakes than particles. The systems containing 1 mM $MgCl_2$ and 1 mM $CaCl_2$ showed just opaque solutions, no particles or flakes.

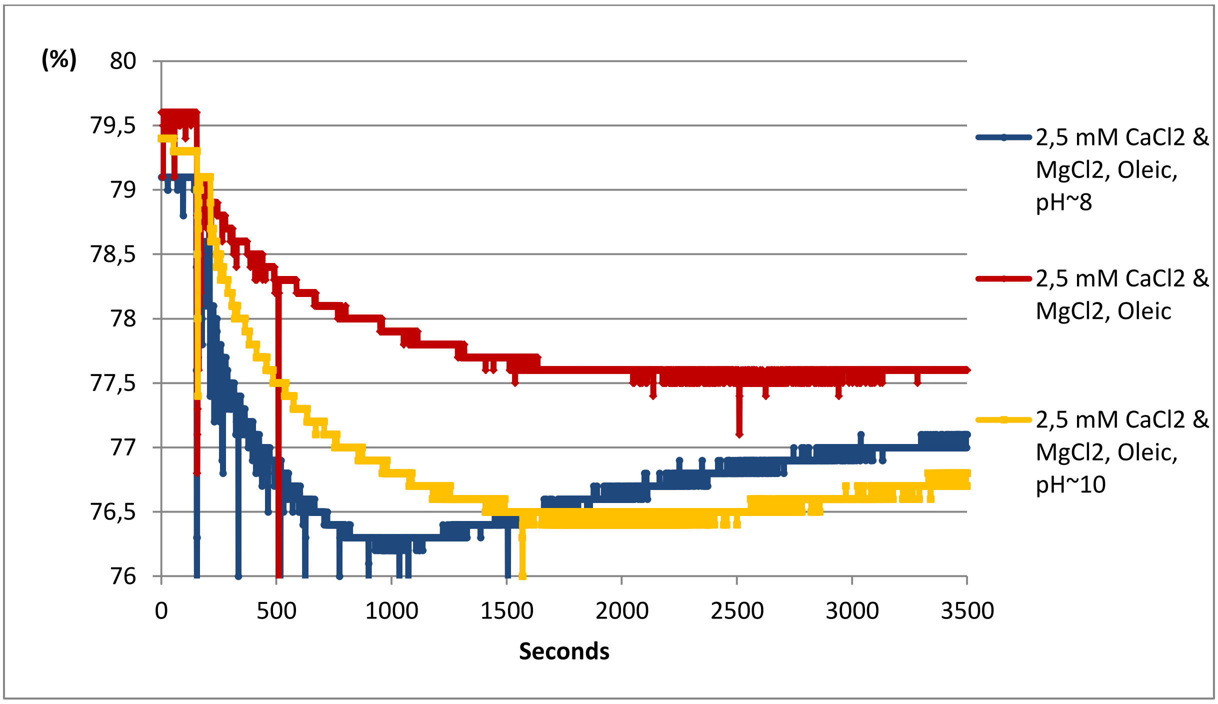

Figure 45: The transmission of a system containing oleic acid potassium soap and both calcium and magnesium ions, and the effect of pH.

As in the experiments concerning addition of calcium ions and magnesium ions individually, the role of pH was evaluated in a mixed system. Solutions with both 2,5 mM $MgCl_2$ and $CaCl_2$ in oleic acid potassium soap were used and pH was set to 8, 9 and 10. No distinct trend could be found but minimums were found in all three cases, showing more resemblance with calcium systems than with magnesium addition. There were no significant differences concerning visible precipitation between the three pH adjusted solutions.

4.3.3 Particle size measurements

Since the agglomeration experiments gave interesting results showing differences in precipitation depending on which soap and which metal ion used, the particle size distribution of four solutions were evaluated, see table 8.

Table 8: The four solutions used in particle size measurements.

Potassium soap	**$CaCl_2$ or $MgCl_2$**	**Precipitation**
50 mg/l oleic acid	5 mM $CaCl_2$	Opaque
50 mg/l mixed unsaturated fatty acid	5 mM $CaCl_2$	Yes
50 mg/l oleic acid	5 mM $MgCl_2$	Yes
50 mg/l mixed unsaturated fatty acid	5 mM $MgCl_2$	Opaque

The solutions were prepared as described in 3.5.3 and was left over the night. The next morning two of the four solutions showed precipitation while the other two were opaque. The solutions are found in figure 36**.**

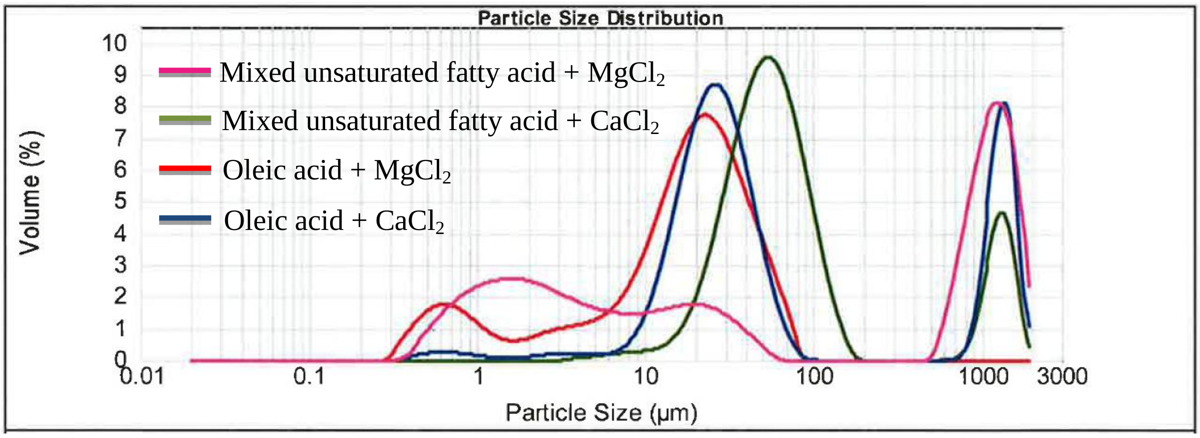

Figure 46: The particle size distribution of four different solutions. The peaks at approximately 1000 µm arise from air bubbles and should be excluded in the comparison.

With this quick test some preliminary conclusions could be drawn. A difference in particle size distribution was found between the solutions containing $MgCl_2$ or $CaCl_2$, the trends independent on which potassium soap that was used. In the two cases containing calcium ions a distinct peak was found, with oleic acid at approximately 25 µm and with mixed unsaturated fatty acid at approximately 55 µm. Using magnesium ions instead two smaller peaks with distribution in between was found. When using oleic acid potassium soap the largest peak is found almost at the same place as with calcium ions but there is also a smaller peak at approximately 0,6 µm. The system with mixed unsaturated fatty acid and magnesium ions are showing two not especially distinct peaks, at 1,5 µm and 20 µm. All solutions were stirred before analysed and the stirrer during the experiment was set to 1950 rpm.

This preliminary particle size distribution analysis show that it seems to be differences between the four solutions but no trend can be found concerning size distribution for systems giving precipitation. However, more experiments have to be done to get more statistic results.

4.2.4 Surface tension measurements

The results from the surface tension measurements were compared to an article (35). The difference between their arrangement and the one in this project was that they used a sodium oleate system compared to potassium fatty acid soap. The concentration, 50 mg/l, was the same in both cases, and the pH was set to approximately 9.

The first curve shows the results after adding $CaCl_2$ to the oleic potassium soap system. It is following the results from the article quite good. One more difference, except the difference in soap systems, is that the chemicals used in this experiment are industry products, which may have some impurities and will due to that fact give slightly lower surface tension.

The result shows that addition of $CaCl_2$ will increase the surface tension of the solution. A fast increase in the beginning is followed by more stable values between approximately 49-52 mN/m. Except 0 mM $CaCl_2$, three concentrations of $CaCl_2$ were tested, where a higher concentration gave a slightly higher surface tension, even if the results for 5 mM and 8 mM do not differ much. The results show that the soap system is less surface active after approximately 1000 seconds.

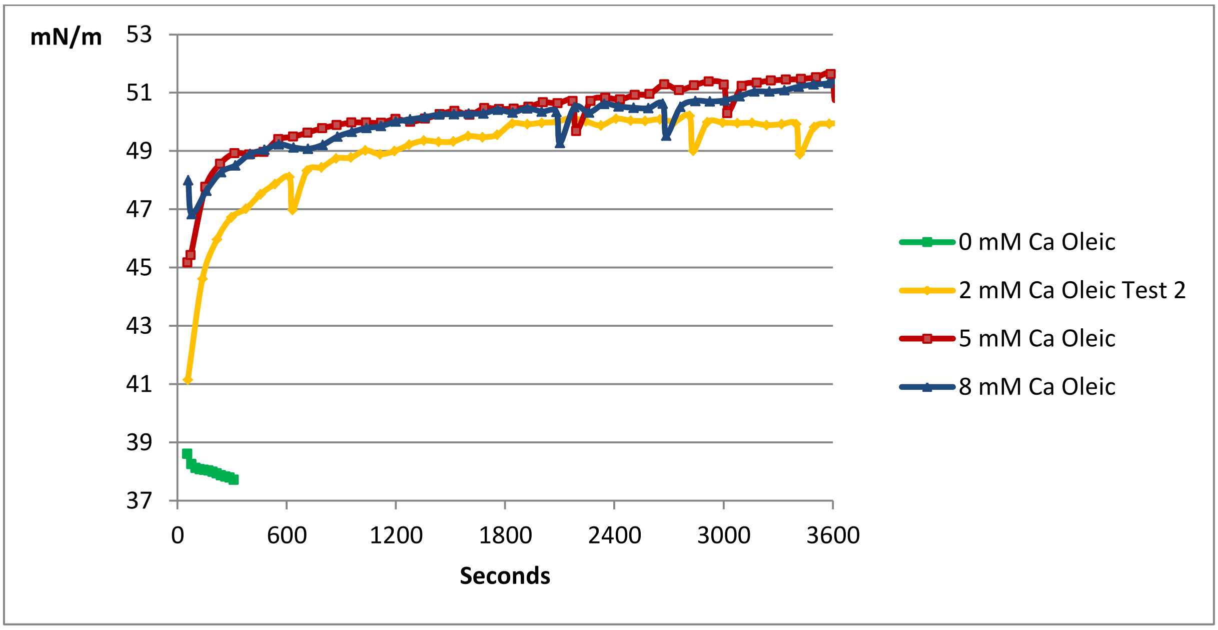

Figure 47: The surface tension of solutions containing oleic acid potassium soap and calcium ions.

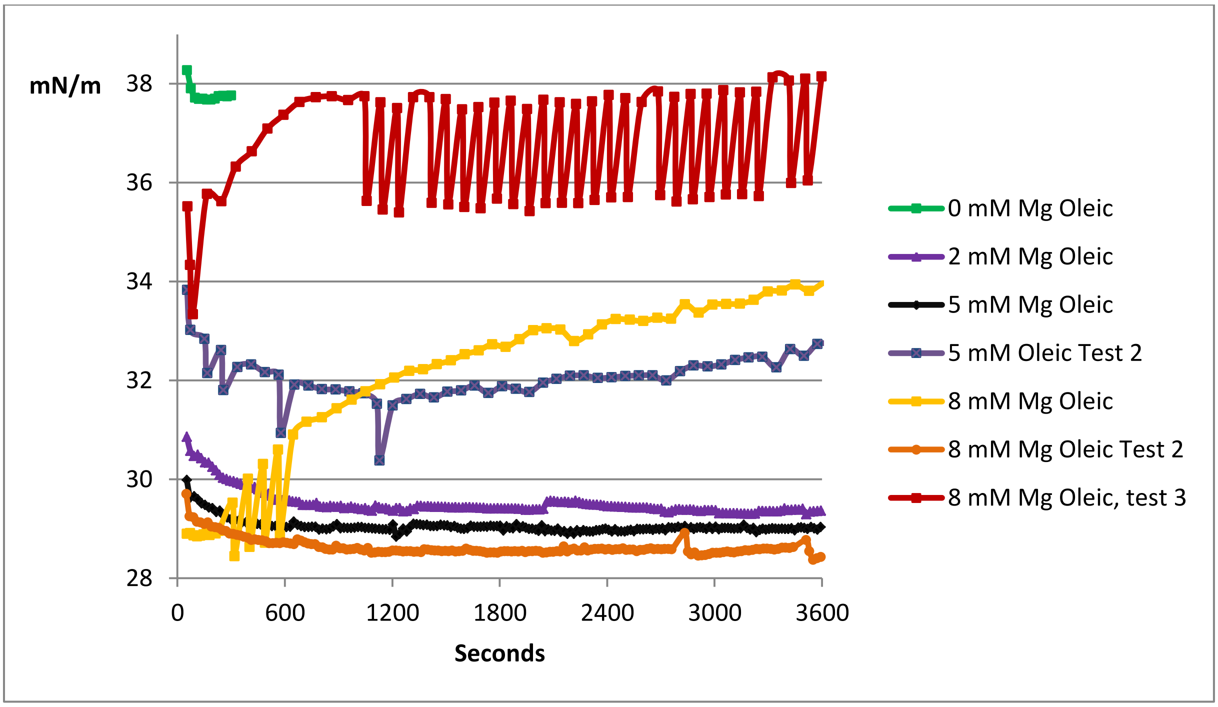

Figure 48: The surface tension of solutions containing oleic acid potassium soap and magnesium ions.

The results from the experiments with $MgCl_2$ in the oleic potassium soap are more spread compared to the results with calcium. Several tests were done with the same concentration of $MgCl_2$ and they gave various results. But the trend is quite easy to decide; adding $MgCl_2$ to the solution will decrease the surface tension. The surface tension of the oleic potassium soap is approximately 38 mN/m while the value decreases to between 29-39 mN/m with addition of $MgCl_2$. There is no trend concerning the concentration of $MgCl_2$ as it was with $CaCl_2$, since a concentration of 8 mM $MgCl_2$ both gives the highest and the lowest values in the experiments. One reason that might explain that some of the experiments gave strange results is the setup of the experiment, as described in 3.5.3

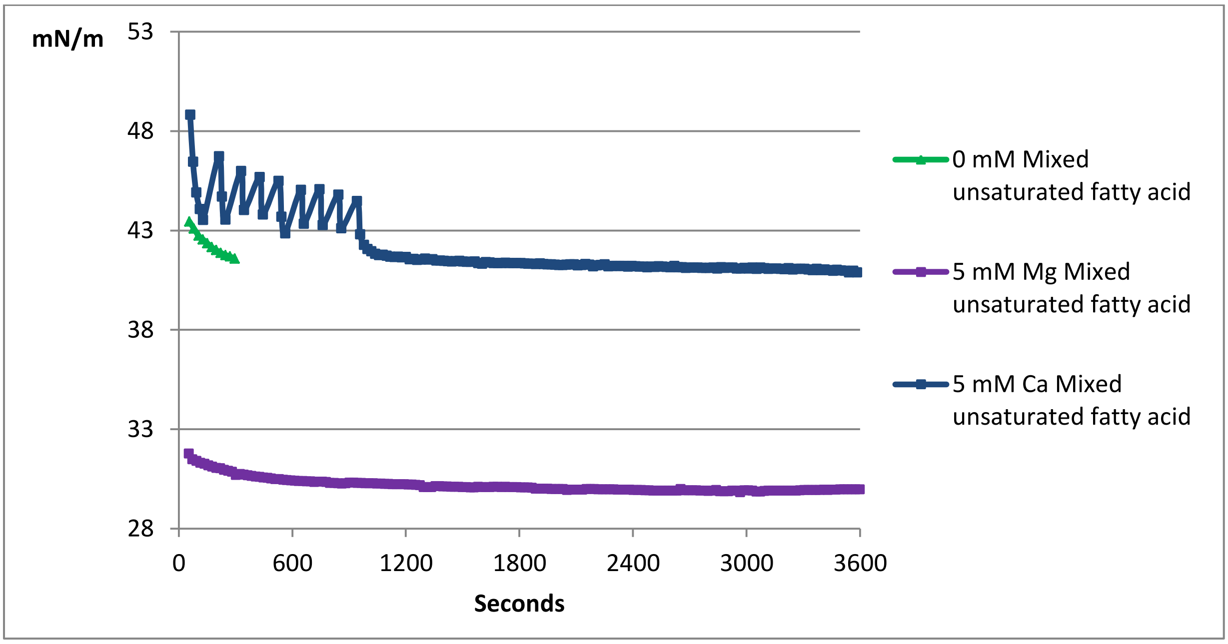

Figure 49: The surface tension of solutions containing mixed unsaturated fatty acid potassium soap and magnesium or calcium ions.

A few tests were performed with mixed unsaturated fatty acid potassium soap instead of oleic potassium soap. The result shows that mixed unsaturated fatty acid potassium soap also seems to follow the trends that calcium ions give an increase in surface tension while addition of magnesium ions decreasing the surface tension.

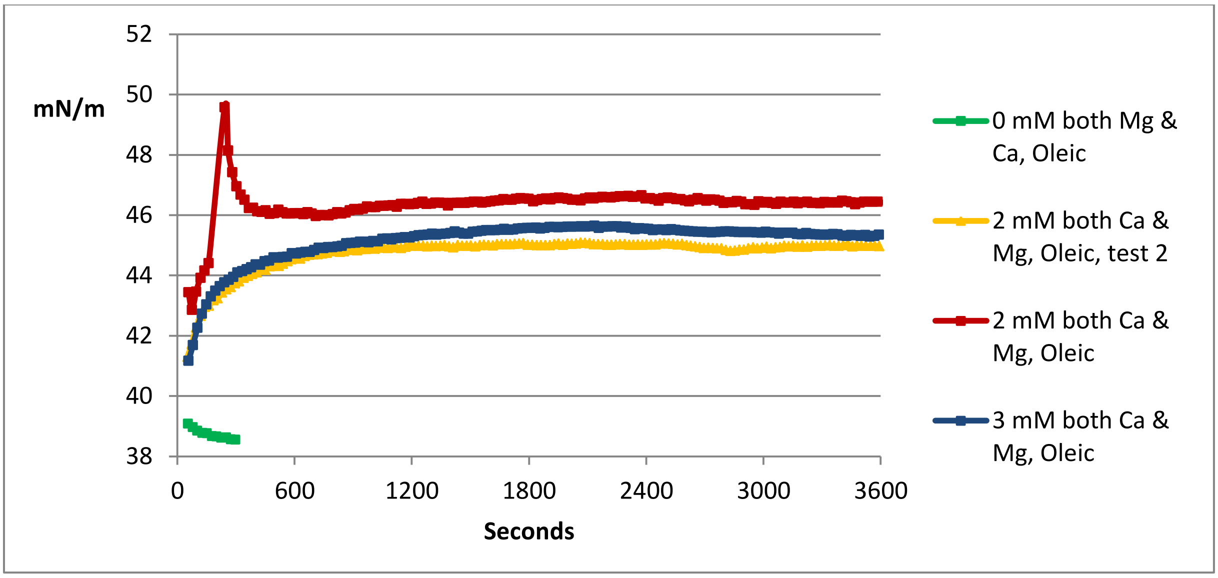

Figure 50: The surface tension of solutions containing oleic acid potassium soap and both calcium and magnesium ions.

The last surface tension measurements were concerning what happens with the surface tension if both $CaCl_2$ and $MgCl_2$ are added to the measured solution. In each test, the same amount of the two salts was used. The result shows distinct that a mixture solution will have the characteristics of $CaCl_2$ in oleic potassium soap solution: the surface tension will increase and find a more stable value after approximately 1000 seconds, as in the case of $CaCl_2$. The values of all mixture measurements are a bit lower than with pure $CaCl_2$, meaning that $MgCl_2$ seems to have some effect of the result, but definitely not as much as $CaCl_2$

5. Conclusions

With the results from the deinking experiments several conclusions can be drawn. Both oleic acid potassium soap and mixed unsaturated fatty acid potassium soap showed promising results when using BIMPRO® as alkali source. Mixed unsaturated fatty acid potassium soap could also be an interesting alternative if using sodium hydroxide as alkali source. Using a non-ionic polymeric surfactant instead of a fatty acid soap gave similar values and is considered an interesting alternative to a soap.

Since many parameters are affecting the deinking process the role of each one separately is hard to analyse. No distinct trends considering which alkalinity values are most favourable could be found. The same conclusion can be drawn about hardness. The pH values were found in a quite narrow range in all BIMPRO® experiments and the results suggests that pH 8 is needed before the flotation step, to avoid poorer unflotated values. The temperature in the process was never adjusted, except once in the flotation step. It showed that the temperature needs to be at least 45 °C in the flotation step to not lose in ERIC and brightness results, and reject values.

The ageing of ink is an important factor to consider. Experiments showed that just some days older ONP and OMG gave poorer results, but no trend could be found evaluating if aged ONP or aged OMG was making biggest decrease in ERIC and brightness results. Using oleic acid potassium soap or a non-ionic polymeric surfactant gave similar results when compared to each other.

When excluding the addition of calcium chloride in the pulping step and just adding calcium chloride before the flotation step, the flotated ERIC and brightness results become better. This is an interesting approach and it seems as the magnesium ions works better alone in the pulping step.

The first tests concerning agglomeration, when evaluating visible precipitation, showed that calcium ions more easily precipitate with mixed unsaturated fatty acid potassium soap than with oleic acid potassium soap. When evaluating magnesium it was the opposite; the system with magnesium ions and oleic acid potassium soap gave precipitation while no precipitation was found using mixed unsaturated fatty acid.

The results from the Turbiscan online measurements showed that magnesium ions and oleic acid or mixed unsaturated fatty acid potassium soap gave lower transmission than calcium ions and fatty acid soap. When evaluating a system containing both magnesium ions and calcium ions the conclusion is that the solution behaves more as a pure calcium system than a magnesium system.

The same conclusion is drawn considering surface tension. Addition of calcium ions to an oleic acid or mixed unsaturated fatty acid potassium soap solution will increase the surface tension. Addition of magnesium ions will instead decrease the surface tension of the fatty acid soap system. A mix of calcium and magnesium ions will increase the surface tension of the fatty acid soap system, showing characteristic behaviour for calcium ions.

6. Future work

The most interesting result from the deinking experiments is the one suggesting that no calcium ions are needed in the pulping stage to ensure proper deinking if BIMPRO® is used as the alkali source. Continued work evaluating semi-neutral deinking with BIMPRO® should focus on finding a “perfect” amount of magnesium ions in the pulping stage, with or without calcium ions.

Turbiscan Online and surface tension measurements both showed that calcium ions decide how a mixed system with magnesium ions would perform with respect to agglomeration of potassium fatty acid soaps. However, in this master thesis the reasons have not been fully evaluated or explained. Since this is very important to understand when working with semi-neutral deinking based on magnesium chemistry, this should be further investigated.

Performing the same measurements but adding ink particles would give even more information about the influence of soap agglomeration on the deinking efficiency, e.g. if there is an optimal size for the soap/ink particle aggregates in semi-neutral deinking that differs from alkali deinking. Also, the behaviour of calcium and magnesium ions in the flotation step would be interesting to investigate further, since this thesis has focused on the chemistry in the pulping step.

7. Acknowledgements

First of all, I would like to thank my fantastic supervisor Helena Wassenius for all help during this master thesis, always very supportive and enthusiastic. Also, thanks for giving me the opportunity to perform my master thesis at BIM Kemi AB, and for all the laughs during our Friday afternoon meetings.

I would like to thank Krister Holmberg for the expertise during this master thesis and thanks for giving me the opportunity to perform the master thesis at the division of Applied surface chemistry for BIM Kemi AB.

Thanks to Rickard Svensson for helping me, and learning me, the laboratory parts of the deinking experiments.

Thanks to Jan Hagnell, Oscar Sävinger, Johan Berglund, Katayon Nedjabat, Anders Önneby and Joakim Åberg for helping me with different parts of the laboratory work.

Thanks to Romain Bordes for helping me with the surface tension measurements.

Thanks to Mikael Rasmusson, Chris Bonnerup, Peter Wållberg, Mikael Perdin, Heino Kuusk, Reine Borg and Mattias Jarnedal for great inputs and discussions about the master thesis, and also about the lokalfotboll in the Göteborg region.

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Appendix

Appendix 1 - Recipe deinking experiments

First of all the old newsprint (ONP) and old magazines (OMG) have to be arranged. Remove staples and loose advertisements and cut the paper in small pieces, approximately two times two cm.

Start to pour three times 2,75 litres of tap water in three beakers, and put them in a water bath adjusted to 53 °C. Put 0,4 g of $CaCl_2$ in each beaker to adjust the water hardness to approximately 10 dH.

Use the Kitchen Aid bowl and weigh in a total of 250 g of paper. In all experiments a mix of 70 % ONP and 30 % OMG are used, therefore 175 g ONP and 75 g OMG are weighed.

When the water is heated and hardness adjusted, weigh in 1417 g in a separate beaker.

Next step is to weigh the chemicals to be used in the experiment. Start to adjust the hydrogen peroxide concentration as described in Appendix 3. The standard recipe can be found below. If NaOH is used instead of BIMPRO® the amount is 2,22 g, which correspond to 4 kg/ton (dry). The fatty acid potassium soap is often used, otherwise a non-ionic polymeric surfactant.

Chemical	**g/250 g paper**	**Kg/ton paper**
BIMPRO® 7101 X	1,82926	3 (dry)
Na_2SiO_3	0,75 (45 % concentration)	3 (wet)
H_2O_2	15 (10 % concentration)	6 (dry)
Fatty acid potassium soap	0,625	2,5 (dry)
Surfactant (diluted 1:100)	750 µm	30 g/ton (dry)

Use two small beakers for the chemicals, one for the hydrogen peroxide and one for the remaining chemicals. Use approximately 100 g of the 1417 g water in each beaker to easily get all chemicals to the Kitchen Aid bowl.

Add the majority of the water to the Kitchen Aid followed by the chemicals. Use some of the 1417 g of water to rinse the two beakers used for chemicals and add that part of the water to the Kitchen Aid bowl too.

Start the Kitchen Aid on speed two for 20 minutes.

After 20 minutes, add 2333 g of water to the bowl and measure the pH of the pulp. Cover the Kitchen Aid bowl and place the bowl in a water bath for 45 minutes. The temperature of the water bath is 53 °C which will give a temperature in the middle of the bowl of approximately 48 °C.

The next step is to divide the pulp into two equally sized batches, approximately 2000 g each. To each batch 900 g of water is added and the batches are individually mixed in a Hobart mixer for three minutes. A sample of approximately 150 g pulp is collected after the mixer and by using suction filter the liquid phase is used to measure pH, alkalinity and hardness.

To the next step, the flotation, some preparations have to be done. A bucket used to collect the reject has to be weighed and put in position under the reject channel. Also, two spray bottles are weighed. One of the bottles contains hot tap water and is used to clean the cell wall and the paddles from ink and fibres. The other one is filled with distilled water and is used to help the reject to reach the reject bucket.

There are also added both a soap and $CaCl_2$ to the flotation step and these have to be prepared as well. The used soap is from Hylte and has to be melted before usage while the $CaCl_2$ only has to be weighed in some tap water.

Chemical	**g/250 g paper**	**Kg/ton paper**
Hylte soap	8,92857	2,5 (dry)
$CaCl_2$	2	0,5

The pulp is then transferred to the Voith flotation cell. The cell is filled with hot tap water, between 45 °C and 55 °C, to the 23,5 dm^3 mark before it was started. The first thing to do is to collect a sample of 2 dm^3 of unflotated pulp.

The cell is then filled up to the 23,5 dm^3 again, with hot tap water. Hylte soap and $CaCl_2$ is poured in to the cell before the flotation is started.

The flotation is going on for 6 minutes, start a timer at the same time as the operation switch is moved to the left, to air inlet. Use the two spray bottles during all six minutes. After six minutes, take out a flotated sample, 2,5 dm^3. Do not forget to flush the valve before the sample is collected.

The collected samples are now divided as followed:

- 3 times 300 ml of unflotated sample are used to make 3 sheets. A very small amount of poly(ethyleneimine) are used in each case to make the samples stick together better.
- 1000 ml of unflotated sample are hyper washed, see Appendix 2. 3 times 300 ml are used to make 3 sheets.
- 3 times 350 ml of flotated sample are used to make 3 sheets.
- 1000 ml of flotated sample are hyper washed, see Appendix 2. 2 times 350 ml are used to make 2 sheets.

In each case the sheets are made by using suction filter, grade 4 on the filter and a diameter of 12,5 cm of the funnel. These filters are named with the date, which flotation of the day it is and what kind of sample it is. Another filter is then placed above the sheet.

This will give 11 sheets that are pressed 2 minutes using 4 bar. After the press the filter without text is flipped to prevent it from stick to the sheet, making it hard to analyse. They are then dried for 60 minutes before they are ready to be used for ERIC and Brightness measurements.

The reject bucket is weighed with the reject. By using the value of the weight of the bucket without reject, and by consider the amount of used distilled water from the spray bottle used in the flotation step, the wet reject amount is acquired. The reject is then separated from the liquid by suction filter. This gives a cake of reject which is put in an oven over at least one night in approximately 100 °C. The cake is now the amount of dry reject from the flotation and the yield loss can be calculated as

$$Yield\ loss\ (\%) = \frac{Dryied\ reject}{Dry\ weight\ of\ ONP+OMG} \times 100$$

In this master thesis the value of dry weight of ONP and OMG is 235 g, since 15 g of the started 250 g are following the unflotated sample.

The ash content is calculated by using the dry reject. Approximately 1,0 g of the dry reject, without any part of the suction filter, is put in a cleaned and scaled crucible. A lid is also cleaned and put above the crucible. The crucible is then put in to the oven, an ash oven-CEM, for 2 hours in 550 °C. The ash content is calculated as follows:

$$Ash\ content\ (\%) = \frac{c-a}{b} \times 100$$

Where
a = the crucible
b = the weight of the sample
c = the weight of crucible and sample after oven.

This gives the ash content of the reject.

Appendix 2 – Hyper washing

1000 ml of both the flotated and the unflotated samples (individually) are put in a beaker with a filter in the bottom. Some tap water is poured in the beaker and a propeller is started, at 1500 rpm. When starting the propeller more tap water is added in the same speed as the water is leaving in the bottom. 10 litres of water is added before the hyper washing is finished.

The beaker is opened above the filter and the fibres above the filter are collected. The fibres are diluted with 1000 ml of tap water and are used for sheet formation.

Appendix 3 – Hydrogen peroxide concentration

The concentration of the hydrogen peroxide used in the deinking experiments has to be determined every morning, due to decomposition.

- Add 20,0 g distilled water to a 250 ml E-flask. Add approximately 1,00 g hydrogen peroxide solution, note the exact amount.
- Load the dispensers for H_2SO_4, ammonium molybdate and KI
- Add 5 ml H_2SO_4, 8 drops ammonium molybdate, 5 ml KI and 5 drops of starch indicator.
- Titrate the solution with 0,1 M sodium thio-sulfate until the solution is colourless.

Use the following formula to calculate the hydrogen peroxide concentration:

$$c_{[H2O2]} = \frac{c_{[thio-sulfate]} \cdot V_{[thio-sulfate]} \cdot M_{[H2O2]}}{2 \cdot m_{[H2O2]}}$$

where $M_{[H2O2]}$ = 34,01 g/mol

Appendix 4 – The standard recipes

Standard recipe using oleic acid potassium soap:
Pulper:

- 1,829 g BIMPRO®
- 0,625 g oleic acid potassium soap
- 0,75 g sodium silicate
- 15 g hydrogen peroxide

Flotation:

- 8,929 g sodium soap
- 2,0 g $CaCl_2$

Standard recipe using a non-ionic polymeric surfactant:
Pulper:

- 1,829 g BIMPRO®
- 0,0075 g non-ionic polymeric surfactant
- 0,75 g sodium silicate
- 15 g hydrogen peroxide

Flotation:

- 8,929 g sodium soap
- 2,0 g $CaCl_2$

If using sodium hydroxide as alkali source:
Pulper:

- 2,22 g NaOH
- 0,625 g oleic acid potassium soap
- 3,125 g sodium silicate
- 20 g hydrogen peroxide

Flotation:

- 8,929 g sodium soap
- 2,0 g $CaCl_2$

Appendix 5 – All deinking experiments, chemical additions

Flotation ID	CaCl2 (g)	BI 7101 Standard (g)	NaOH (g)	K+ soap (g)	Non-ionic surfactant (µl)	H2O2 (g)	Sodium silicate (g)	CaCl2 (g)	Sodium soap (g)
110211-flot2	1,2	1,83		0,62 (mixed)		19,12	0,76	2,0	8,92
110213-flot2	1,2	1,83		0,63 (oleic)		18,80	0,76	2,0	8,92
110215-flot2	1,2	1,83		0,63 (stearic)		18,80	0,75	2,0	8,93
110216-flot1	1,2	1,83		0,63 (mixed)		19,12	0,75	2,0	8,92
110217-flot2	1,2	1,83		0,63 (oleic)		19,25	0,76	2,0	8,90
110221-flot1	1,2		2,22	0,62 (mixed)		25,01	3,14	2,0	8,92
110222-flot1	1,2		2,22	0,62 (oleic)		25,24	3,13	2,0	8,92
110228-flot1	1,2		2,23	0,62 (stearic)		25,24	3,14	2,0	8,92
110301-flot2	1,2	2,43		0,63 (oleic)		19,19	1,25	2,0	8,92
110304-flot1	1,2	2,43		0,64 (oleic)		18,84		2,0	8,92
110304-flot2	1,2	2,43		0,62 (oleic)		18,83	0,76	2,0	8,92
110307-flot1	1,2	1,84		0,63 (oleic)		18,81	0,75	2,0	8,92
110307-flot2	1,2	1,83		0,63 (oleic)	750	18,80	0,76	2,0	8,93
110308-flot1	1,2	1,83		0,31 (oleic)	375	18,10	0,76	2,0	8,92
110308-flot2	1,2	1,82			750	18,08	0,76	2,0	8,92
110321-flot1	1,2	1,83		0,63 (oleic)		19,40	0,75	2,0	8,93
110323-flot1	1,2	1,86		0,63 (oleic)		18,34	0,77	2,0	8,93
110323-flot2	1,2	1,83		0,64 (oleic)		18,32	0,75	2,07	8,92
110325-flot1	1,2	1,84		0,63 (oleic)		18,63	0,76	2,0	
110325-flot2		1,83		0,62 (oleic)		18,63	0,75		8,93
110406-flot1		1,84		0,64 (oleic)		18,63	0,75		8,92
110406-flot2		3,66		0,64 (oleic)		19,60	0,74	2,05	8,93
110429-flot1	1,2	1,85		0,64 (oleic)		19,78	0,75	2,0	8,93
110429-flot2	1,2	1,83			750	19,78	0,77	2,0	8,93
110510-flot1	1,2	1,83		0,63 (oleic)		19,91	0,75	2,0	8,93
110510-flot2	1,2	1,83			750	19,84	0,76	2,0	8,93

Appendix 6 - The results of alkalinity, hardness and pH

Flotation ID	BIMPRO® or NaOH?	K+ soap	Surfactant?	Alkalinity after pulp.	Alkalinity unflotated	Alkalinity flotated
110211-flot2	BI 7101 standard	Mixed unsaturated fatty acid	No	70	45	65
110213-flot2	BI 7101 standard	Oleic	No	95	70	85
110215-flot2	BI 7101 standard	Stearic	No	99,2	89,2	73,2
110216-flot1	BI 7101 standard	Mixed unsaturated fatty acid	No	104,8	80,4	85,6
110217-flot2	BI 7101 standard	Oleic	No	112	79,6	76,8
110221-flot1	NaOH	Mixed unsaturated fatty acid	No	236	120	93
110222-flot1	NaOH	Oleic	No	190	150	127,2
110228-flot1	NaOH	Stearic	No	168	130,4	110,4
110301-flot2	BI 7101 standard	Oleic	No	422	174	121
110304-flot1	BI 7101 standard	Oleic	No	190	115,2	110,8
110304-flot2	BI 7101 standard	Oleic	No	256	162,4	121,2
110307-flot1	BI 7101 standard	Oleic	No	171	92,4	88,8
110307-flot2	BI 7101 standard	Oleic	Yes	162	82	76
110308-flot1	BI 7101 standard	Oleic	Yes	206	85,2	94,8
110308-flot2	BI 7101 standard	No	Yes	186	93,2	76,8
110321-flot1	BI 7101 standard	Oleic	No	96,8	72,8	60,8
110323-flot1	BI 7101 standard	Oleic	No	94,4	65,6	58,8
110323-flot2	BI 7101 standard	Oleic 2.0	No	91,2	69,2	74
110325-flot1	BI 7101 standard	Oleic	No	90,4	69,2	58,8
110325-flot2	BI 7101 standard	Oleic	No	216,8	74	85,6
110406-flot1	BI 7101 standard	Oleic	No	165	73,2	73,6
110406-flot2	BI 7101 standard	Oleic	No	215	90	69,6
110429-flot1	BI 7101 standard	Oleic	No	95,6	102,4	61,2
110429-flot2	BI 7101 standard	No	Yes	104,4	60,8	60,4
110510-flot1	BI 7101 standard	Oleic	No	100	88,4	79,2
110510-flot2	BI 7101 standard	No	Yes	110	104	87,2

Flotation ID	BIMPRO® or NaOH?	K+ soap	Surfactant?	Hardness after pulper	Hardness unflotated	Hardness flotated
110323-flot1	BI 7101 standard	Oleic	No	9,04	4,16	7,44
110323-flot2	BI 7101 standard	Oleic 2.0	No	9,36	4,04	7,20
110325-flot1	BI 7101 standard	Oleic	No	9,44	4,2	7,48
110325-flot2	BI 7101 standard	Oleic	No	7,92	3,76	3,8
110406-flot1	BI 7101 standard	Oleic	No	5,64	2,68	6,28
110406-flot2	BI 7101 standard	Oleic	No	7,72	2,68	6,2

110429-flot1	BI 7101 standard	Oleic	No	8,84	4,28	7,64
110429-flot2	BI 7101 standard	No	Yes	9,2	4,44	6,68
110510-flot1	BI 7101 standard	Oleic	No	40,96	14,92	13,00
110510-flot2	BI 7101 standard	No	Yes	36,52	15,36	12,92

Flotation ID	BIMPRO® or NaOH?	K+ soap	Non-ionic surfactant?	pH after K-Aid	pH after pulper	pH unflot.	pH flot.
110211-flot2	BI 7101 standard	Mixed unsaturated fatty acid	No	8,5	7,75	7,84	7,85
110213-flot2	BI 7101 standard	Oleic	No	8	7,7	8,13	8,22
110215-flot2	BI 7101 standard	Stearic	No	7,75	7,78	8,05	7,97
110216-flot1	BI 7101 standard	Mixed unsaturated fatty acid	No	7,81	7,86	8,14	8,16
110217-flot2	BI 7101 standard	Oleic	No	7,78	7,95	8,09	8,15
110221-flot1	NaOH	Mixed unsaturated fatty acid	No	8,95	8,3	8,36	8,24
110222-flot1	NaOH	Oleic	No	8,96	8,34	8,28	8,49
110228-flot1	NaOH	Stearic	No	8,98	8,36	8,35	8,34
110301-flot2	BI 7101 standard	Oleic	No	8,25	8,14	8,29	8,28
110304-flot1	BI 7101 standard	Oleic	No	8,19	8,24	8,47	8,4
110304-flot2	BI 7101 standard	Oleic	No	8,34	8,31	8,53	8,48
110307-flot1	BI 7101 standard	Oleic	No	8,35	8,16	8,3	8,31
110307-flot2	BI 7101 standard	Oleic	Yes	8,3	8,17	8,3	8,33
110308-flot1	BI 7101 standard	Oleic	Yes	8,33	8,31	8,42	8,4
110308-flot2	BI 7101 standard	No	Yes	8,33	8,26	8,38	8,43
110321-flot1	BI 7101 standard	Oleic	No	7,88	7,9	8,13	8,18
110323-flot1	BI 7101 standard	Oleic	No	7,9	7,98	8,13	8,22
110323-flot2	BI 7101 standard	Oleic 2.0	No	8,02	7,92	8,13	8,19
110325-flot1	BI 7101 standard	Oleic	No	7,89	8,02	8,16	8,27
110325-flot2	BI 7101 standard	Oleic	No	8,24	8,2	8,27	8,36
110406-flot1	BI 7101 standard	Oleic	No	8,15	8,06	8,17	8,19
110406-flot2	BI 7101 standard	Oleic	No	8,36	8,3	8,25	7,99
110429-flot1	BI 7101 standard	Oleic	No	7,99	8,01	8,08	8,24
110429-flot2	BI 7101 standard	No	Yes	7,95	7,98	8,06	8,23
110510-flot1	BI 7101 standard	Oleic	No	7,65	7,85	7,77	8,06
110510-flot2	BI 7101 standard	No	Yes	7,69	7,78	7,86	8,09

Appendix 7 – The ERIC results

Flotation ID	BIMPRO® or NaOH?	K+ soap	Surfactant?	Average flotated	Average unflot.	Average flot. HW	Average unflot. HW
110211-flot2	BI 7101 standard	Mixed unsaturated fatty acid	No	569,6	1686,4	292	324,3
110213-flot2	BI 7101 standard	Oleic	No	567,8	1697,1	277,5	302,1
110215-flot2	BI 7101 standard	Stearic	No	656,8	1638,8	332,3	367,9
110216-flot1	BI 7101 standard	Mixed unsaturated fatty acid	No	651,8	1642,5	316,8	349,2
110217-flot2	BI 7101 standard	Oleic	No	569,3	1632,9	279,4	308,2
110221-flot1	NaOH	Mixed unsaturated fatty acid	No	478,2	1657,4	286	271,2
110222-flot1	NaOH	Oleic	No	663	1686,4	217,9	232,8
110228-flot1	NaOH	Stearic	No	721,2	1767	304,8	324,3
110301-flot2	BI 7101 standard	Oleic	No	413,8	1691,4	210,7	230,8
110304-flot1	BI 7101 standard	Oleic	No	634,2	1676,5	263,8	295,8
110304-flot2	BI 7101 standard	Oleic	No	537,1	1788,1	264,8	295,6
110307-flot1	BI 7101 standard	Oleic	No	285	1259,4	123,9	132,6
110307-flot2	BI 7101 standard	Oleic	Yes	285,6	1231,9	125,5	139,1
110308-flot1	BI 7101 standard	Oleic	Yes	285,7	1149,2	119,7	131,3
110308-flot2	BI 7101 standard	No	Yes	328,8	1203,6	126,4	137,8
110321-flot1	BI 7101 standard	Oleic	No	686,4	1484,5	213,4	232,7
110323-flot1	BI 7101 standard	Oleic	No	635,2	1392,2	204,5	221,3
110323-flot2	BI 7101 standard	Oleic 2.0	No	559,2	1425,4	196,5	215,2
110325-flot1	BI 7101 standard	Oleic	No	741,3	1361,1	192,9	209,1
110325-flot2	BI 7101 standard	Oleic	No	767,6	1320,0	175,1	194,3
110406-flot1	BI 7101 standard	Oleic	No	581,6	1306,5	217,3	235,9
110406-flot2	BI 7101 standard	Oleic	No	494,0	1217,8	204,3	222,4
110429-flot1	BI 7101 standard	Oleic	No	613,0	1708,6	220,8	242,8
110429-flot2	BI 7101 standard	No	Yes	567,4	1692,9	219,9	240,3
110510-flot1	BI 7101 standard	Oleic	No	367,4	1695,7	168,8	189,0
110510-flot2	BI 7101 standard	No	Yes	457,0	1968,3	182,0	195,0

Appendix 8 – The brightness results

Flotation ID	BIMPRO® or NaOH?	K+ soap	Surfactant?	Average flotated	Average unflot.	Average flot. HW	Average unflot. HW
110211-flot2	BI 7101 standard	Mixed unsaturated fatty acid	No	49,11	37,45	53,04	52,5
110213-flot2	BI 7101 standard	Oleic	No	49,25	37,13	53,05	52,71
110215-flot2	BI 7101 standard	Stearic	No	47,3	37,32	51,45	50,99
110216-flot1	BI 7101 standard	Mixed unsaturated fatty acid	No	47,53	37,25	51,9	51,33
110217-flot2	BI 7101 standard	Oleic	No	48,75	37,64	53,3	52,7
110221-flot1	NaOH	Mixed unsaturated fatty acid	No	51,72	37,88	54,3	53,87
110222-flot1	NaOH	Oleic	No	47,78	38,66	56,19	55,78
110228-flot1	NaOH	Stearic	No	47,03	36,63	53,25	53,07
110301-flot2	BI 7101 standard	Oleic	No	52,58	38,46	55,47	54,7
110304-flot1	BI 7101 standard	Oleic	No	48,32	37,76	53,3	52,66
110304-flot2	BI 7101 standard	Oleic	No	49,95	37,02	53,4	52,8
110307-flot1	BI 7101 standard	Oleic	No	56,89	42,9	58,44	58,33
110307-flot2	BI 7101 standard	Oleic	Yes	57,04	43,47	58,67	58,62
110308-flot1	BI 7101 standard	Oleic	Yes	56,79	44,21	58,77	58,8
110308-flot2	BI 7101 standard	No	Yes	55,94	43,58	58,59	58,31
110321-flot1	BI 7101 standard	Oleic	No	47,48	39,30	55,47	55,21
110323-flot1	BI 7101 standard	Oleic	No	48,52	39,72	56,24	55,48
110323-flot2	BI 7101 standard	Oleic 2.0	No	49,84	40,21	56,79	56,19
110325-flot1	BI 7101 standard	Oleic	No	47,27	40,52	56,18	56,01
110325-flot2	BI 7101 standard	Oleic	No	46,66	41,00	57,17	56,63
110406-flot1	BI 7101 standard	Oleic	No	49,46	41,05	55,91	55,53
110406-flot2	BI 7101 standard	Oleic	No	51,56	42,27	56,67	56,31
110429-flot1	BI 7101 standard	Oleic	No	49,72	38,75	56,51	56,10
110429-flot2	BI 7101 standard	No	Yes	50,52	38,95	56,82	56,27
110510-flot1	BI 7101 standard	Oleic	No	54,36	39,09	58,18	57,56
110510-flot2	BI 7101 standard	No	Yes	52,33	36,42	57,39	57,20

Appendix 9 – The results concerning reject, yield loss and ash content

Flotation ID	BIMPRO® or NaOH?	K+ soap	Surfactant?	Wet reject (g)	Dry reject (g)	Yield loss (%)	Ash content (%)
110211-flot2	BI 7101 standard	Mixed unsaturated fatty acid	No	1345,4	23,14	9,85	36,77
110213-flot2	BI 7101 standard	Oleic	No	1545,4	29,34	12,48	33,19
110215-flot2	BI 7101 standard	Stearic	No	1804,4	31,30	13,32	28,60
110216-flot1	BI 7101 standard	Mixed unsaturated fatty acid	No	1413	28,73	12,22	31,55
110217-flot2	BI 7101 standard	Oleic	No	1497,6	29,10	12,38	33,46
110221-flot1	NaOH	Mixed unsaturated fatty acid	No	1410,8	27,00	11,49	35,17
110222-flot1	NaOH	Oleic	No	1112,3	19,58	8,33	31,34
110228-flot1	NaOH	Stearic	No	1402,8	26,87	11,43	32,54
110301-flot2	BI 7101 standard	Oleic	No	1105,2	23,41	9,96	33,76
110304-flot1	BI 7101 standard	Oleic	No	1251,9	27,48	11,70	39,79
110304-flot2	BI 7101 standard	Oleic	No	1445,8	31,07	13,22	41,47
110307-flot1	BI 7101 standard	Oleic	No	887,1	18,28	7,78	35,29
110307-flot2	BI 7101 standard	Oleic	Yes	622,6	15,95	6,79	36,96
110308-flot1	BI 7101 standard	Oleic	Yes	739,7	18,31	7,79	38,50
110308-flot2	BI 7101 standard	No	Yes	625	14,94	6,36	35,44
110321-flot1	BI 7101 standard	Oleic	No	1235,7	24,04	10,23	44,73
110323-flot1	BI 7101 standard	Oleic	No	1169,5	22,18	9,44	42,70
110323-flot2	BI 7101 standard	Oleic 2.0	No	1196,2	24,29	10,34	44,73
110325-flot1	BI 7101 standard	Oleic	No	1517	19,52	8,30	37,00
110325-flot2	BI 7101 standard	Oleic	No	556,5	10,04	4,27	34,56
110406-flot1	BI 7101 standard	Oleic	No	1130,3	24,32	10,35	40,07
110406-flot2	BI 7101 standard	Oleic	No	1186,5	24,83	10,57	39,93
110429-flot1	BI 7101 standard	Oleic	No	998,1	20,80	8,85	39,91
110429-flot2	BI 7101 standard	No	Yes	1142,8	24,48	10,42	38,53
110510-flot1	BI 7101 standard	Oleic	No	1049,8	22,352	9,51	39,91
110510-flot2	BI 7101 standard	No	Yes	1017,2	21,6899	9,23	38,53

Appendix 10 – The results in the ageing experiments

Table 9: Eric values

Surfactant	Age ONP (days)	Age OMG (weeks)	Average flotated	Average unflotated	Average flotated HW	Average unflotated HW
Oleic soap	51	10	569,3	1632,9	279,4	308,2
Oleic soap	4	3	285,0	1259,4	123,9	132,6
Non-ionic	5	3	328,8	1203,6	126,4	137,8
Oleic soap	18	5	686,4	1484,5	213,4	232,7
Oleic soap	2	12	613,0	1708,6	220,8	242,8
Non-ionic	2	12	567,4	1692,9	219,9	240,3
Oleic soap	13	1	367,4	1695,7	168,8	189,0
Non-ionic	13	1	457,0	1968,3	182,0	195,0

Table 10: Brightness values

Surfactant	Age ONP (days)	Age OMG (weeks)	Average flotated	Average unflotated	Average flotated HW	Average unflotated HW
Oleic soap	51	10	48,75	37,64	53,30	52,70
Oleic soap	4	3	56,89	42,90	58,44	58,33
Non-ionic	5	3	55,94	43,58	58,59	58,31
Oleic soap	18	5	47,48	39,30	55,47	55,21
Oleic soap	2	12	49,72	38,75	56,51	56,10
Non-ionic	2	12	50,52	38,95	56,82	56,27
Oleic soap	13	1	54,36	39,09	58,18	57,56
Non-ionic	13	1	52,33	36,42	57,39	57,20

Table 11: Reject, yield loss and ash content

Surfactant	Age ONP (days)	Age OMG (weeks)	Wet reject (g)	Dry reject (g)	Yield loss (%)	Ash content (%)
Oleic soap	51	10	1497,6	29,10	12,38	33,46
Oleic soap	4	3	887,1	18,28	7,78	35,29
Non-ionic	5	3	625,0	14,94	6,36	35,44
Oleic soap	18	5	1235,7	24,04	10,23	44,73
Oleic soap	2	12	998,1	20,80	8,85	39,91
Non-ionic	2	12	1142,8	24,48	10,42	38,53
Oleic soap	13	1	1049,8	22,35	9,51	32,11
Non-ionic	13	1	1017,2	21,69	9,23	32,51

Appendix 11 – Turbiscan Online experiments

Number	CaCl2 or MgCl2	Which soap (50 mg/l)	Silicate	H2O2
1	1 mM MgCl2	Oleic	No	No
2	5 mM MgCl2	Oleic	No	No
3	8 mM MgCl2	Oleic	No	No
4	10 mM MgCl2	Oleic	No	No
5	5 mM MgCl2	Oleic	0,50 g	No
6	5 mM CaCl2	Oleic	0,51 g	No
7	5 mM MgCl2	Oleic	0,52 g	5,00 g
8	5 mM CaCl2	Oleic	0,52 g	5,01 g
9	5 mM MgCl2	Oleic	0,50 g	No
10	5 mM MgCl2*	Oleic	No	No
11	5 mM MgCl2**	Oleic	No	No
12	5 mM CaCl2**	Oleic	No	No
13	5 mM CaCl2*	Oleic	No	No
14	5 mM MgCl2	Mixed unsaturated fatty acid	No	No
15	5 mM CaCl2	Mixed unsaturated fatty acid	No	No
16	1 mM CaCl2	Mixed unsaturated fatty acid	No	No
17	1 mM both	Oleic	No	No
18	1 mM both	Mixed unsaturated fatty acid	No	No
19	5 mM MgCl2	Oleic	0,51 g	5,00 g
20	2,5 mM both	Oleic	No	No
21	2,5 mM both	Mixed unsaturated fatty acid	No	No
22	2,5 mM both*	Oleic	No	No
23	2,5 mM both**	Oleic	No	No

* Adjust pH to approximately 10. ** Adjust pH to Approximately 8

Appendix 12 – Surface tension experiments

Number	**CaCl2 or MgCl2**	**Which soap (50 mg/l)**	**pH at start**
1	10 mM CaCl2	Oleic	9,3
2	2 mM CaCl2	Oleic	9,3
3	No	Oleic	9,3
4	2 mM CaCl2	Oleic	9,3
5	5 mM CaCl2	Oleic	9,3
6	8 mM CaCl2	Oleic	9,3
7	2 mM MgCl2	Oleic	9,1
8	5 mM MgCl2	Oleic	9,1
9	8 mM MgCl2	Oleic	9,1
10	5 mM MgCl2	Oleic	9,1
11	8 mM MgCl2	Oleic	9,1
12	5 mM MgCl2	Mixed unsaturated fatty acid	9,1
13	5 mM CaCl2	Mixed unsaturated fatty acid	9,2
14	1 mM both	Oleic	9,2
15	8 mM MgCl2	Oleic	9,2
16	No	Oleic	9,2
17	No	Mixed unsaturated fatty acid	9,2
18	2 mM both	Oleic	9,2
19	3 mM both	Oleic	9,2
20	2 mM both	Oleic	9,2

Appendix 13 – The apparatus and instruments

Scalers:	Mettler PJ6000	*1 decimal*
	Scaltec	*2 decimals*
	Sartorius LP3200D	*3 decimals*
Hotplate:	Yellowline MSH basic	
Pulper:	KitchenAid, Heavy Duty	
Pulper (Hobart):	Noram, Lorentzen & Wettre	
Büchner funnel:	110 mm diameter	*Whatman paper, grade 4*
	125 mm diameter	*Munktell, grade 5*
Water bath:	GFL	*53 °C*
Hyper wash:	Paper research materials, inc.	*Filter: no 125p*
	Motomatic II Electro-craft	*1500 rpm*
Press:	Rexroth Mecman Pneumatik	*2 minutes, 4 bar*
Sheet dryer:	Apparateb. Büscher	*60 minutes*
Analysis kit:	Hach comp, Universal Digital Titrator	*Alkalinity, hardness*
Ash oven:	CEM	*550 °C, 2 hours*
Turbidimeter:	Hach company 2100P	*Field kit*
Turbiscan Online:	Formulaction	
Pump (TOL):	Watson & Marlow 323	*250 rpm*
Particle size:	Malvern Instruments, Mastersizer 2000	*1950 rpm*
Surface tension:	Sigma 70	*60 minutes*