TAMK, University of Applied Sciencies
International Pulp and Paper Technology

Final Thesis

Tommi Laitinen

The Impact of Chemical Pre-treatments of Fibre Fractions on Paper Properties

Supervisor	Lic. Tech. Päivi Viitaharju
Commissioning Company	Metso Paper, Supervisor: MSc Juan Cecchini

TAMK, University of Applied Sciencies
International Pulp and Paper Technology
Tommi Laitinen The impact of chemical pre-treatments of fibre fractions on paper properties
Engineering Thesis 99 pages, 7 appendices.
Thesis Supervisor Päivi Viitaharju (Lic.Tech)
Commissioning Company Metso Paper, Supervisor: Juan Cecchini (MSc)
May 2008
Keywords retention, retention aid, fractionation, broke, paper quality

ABSTRACT

Wet end related research and development projects include lots of transportation of fibres. Transporting the fresh pulp to the trials with lots of water means high transportation costs. An option for fresh pulp transportation is to bring the fibres in dry reels and slush them at the destination. This set the first target for this study, which was to find out the differences in the properties of paper made of fresh pulp and slushed broke.

The second target was related to increasing the share of filler in paper and compensation of simultaneous loss of strength properties. Because in previous studies selective chemical treatment have improved internal bonding and tensile strength of paper significantly, the second target was to find out the impact of selective chemical treatment of fibre fractions on paper properties.

The objectives were approached with a handsheet study and with a miniformer trial. To find out the difference of furnish and the impact of chemical treatment, both studies were carried out with fresh pulp and broke, which were treated with conventional and selective chemical treatments.

Both studies provided similar differences in paper structure. Broke formed the sheets with worse formation, significantly higher air permeance, lower bulk, and worse tensile strength values than fresh pulp, but provided significantly higher opacity and internal bonding strength values. Thus, the use of slushed broke in the test trials instead of fresh pulp is restricted by these quality factors.

Selective chemical treatment provided worse formation especially with broke, higher air permeance, and slightly worse opacity values. Despite the fact that previous studies have given significantly higher internal bonding and tensile strength values with same kind of selective chemical treatment, in this study strength properties were inferior to the values of conventionally treated furnishes.

Based on low strength responses and an uneven paper structure in both studies, one option for future studies would be a use of refining of long fraction before chemical treatment. Well-fibrillated long fraction before addition of strength chemicals could increase the natural bonding ability of fibres and improve the operation of starch. In addition to that, refining could open the fibre flocs of broke before chemical treatment, which could lead into more even fines distribution and sheet properties.

Tampereen Ammattikorkeakoulu
International Pulp and Paper Technology
Tommi Laitinen Kuitufraktioiden kemiallisen esikäsittelyn vaikutus paperiominaisuuksiin.
Insinöörityö 99 sivua, 7 liitettä.
Työn valvoja Päivi Viitaharju (Tekn.lis.)
Teettävä yritys Metso Paper, Valvoja: Juan Cecchini (MSc)
Kesäkuu 2008
Avainsanat retentio, retentio aine, fraktiointi, hylky, paperin laatu

TIIVISTELMÄ

Lyhyeen kiertoon liittyvät tuotekehitysprojektit sisältävät paljon kuitukuljetuksia. Tuoremassa sisältää normaalisti paljon vettä, mikä lisää kuljetuksesta koituvia kustannuksia. Tuoremassan eräänä vaihtoehtona on kuljettaa kuitu koeajoihin kuivina rullina ja pulpperoida ne vasta määränpäässään. Tämän vaihtoehdon tutkimiseksi toinen työn tarkoituksista oli selvittää, tuoremassan ja pulpperoidun hylyn erot paperiominaisuuksien kannalta.

Toinen työn tavoitteista liittyi paperin täyteainepitoisuuden kasvattamiseen ja siitä johtuvaan lujuusominaisuuksien heikkenemiseen. Koska aikaisemmissa kuitufraktioihin kohdistuvaa kemikaalikäsittelyä koskevissa tutkimuksissa veto-ja z-suuntainen lujuus on parantunut huomattavasti, tavoitteena oli selvittää kuitufraktioiden kemiallisen esikäsittelyn vaikutus paperiominaisuuksiin ja erityisesti lujuuteen.

Työn tavoitteita lähestyttiin käsiarkkitutkimuksella ja Miniformer-koeajolla. Molempia massoja käsiteltiin tutkimuksissa sekä perinteisellä- tai fraktioihin kohdistuvalla kemikaalikäsittelyllä.

Molemmat tutkimukset tuottivat samansuuntaiset eroavaisuudet paperin rakenteeseen. Verrattuna tuoremassa-arkkeihin hylkyarkeilla oli huonompi formaatio, huomattavasti korkeampi ilman läpäisy, huomattavasti alempi bulkki, huonompi vetolujuus, mutta huomattavasti korkeampi opasiteetti ja z-suuntainen lujuus. Siten edellä mainitut laatutekijät rajoittavat hylkymassan käyttöä koeajoissa.

Verrattuna perinteiseen kemikaalikäsittelyyn, fraktioihin kohdistettu kemikaalikäsittely tuotti huonomman formaation erityisesti hylylle, korkeamman ilman läpäisyn ja aavistuksen verran huonomman opasiteetin. Vastoin ennakko-oletuksia kuitufraktiohin kohdistuva kemikaalikäsittely tuotti huonommat lujuustulokset verrattuna perinteiseen kemikaalikäsittelyyn.

Huonojen lujuustuloksien ja epätasaisen paperirakenteen perusteella eräs jatkotutkimuslinja voisi olla pitkäkuitufraktion jauhatus ennen tärkkelyksen lisäämistä. Hyvin fibrilloitunut pitkäkuitufraktio lisäisi kuitujen luonnollista sitoutumiskykyä ja parantaisi tärkkelyksen toimintaa. Edellisen lisäksi jauhatus voisi avata hylyn kuituflokkeja ennen kemikaalikäsittelyä, mikä voisi johtaa tasaisempaan hienoainejakaumaan parempiin arkkiominaisuuksiin.

PREFACE

This Engineering Thesis has been carried out at TAMK, University of Applied Sciences between 1st February and 31st May, 2008. Thesis was done for Metso Paper and it is a part of bigger research and development project related to selective chemical treatments of fibre fractions.

I would like to express my warm thanks to my supervisors Päivi Viitaharju for the guidance and professional advice during the writing process. I am most grateful to Juan Cecchini for his dedication to help me to get answers to my numerous questions. I also appreciate the time of Johanna Liukkonen for sharing her knowledge and my up and downs during the writing process.

I would like to thank all the people from Metso who have been involved in this study. Especially, I am most grateful to Riitta Tuominen and Jaana Hyypiä from Anjalankoski Fiber Technology Center for being so helpful during the handsheet study. The personnel of Anjalankoski Paper Technology Center led by Jouni Juhala made possible the Miniformer trials and deserve a great share of my acknowledgements.

Last but not least, I admire the dedication of Taru Owston who despite her soar back and sick mother checked the language of my thesis in an extremely short period before the deadline.

Finally, I would like to thank my family and friends for all the understanding and support through my studies. Even though, this project has taken most of my time during this spring, those small moments with you have been in my heart when I have been writing.

In Tampere 3rd June, 2008

Tommi Laitinen

TABLE OF CONTENTS

REFERENCES

APPENDICES

1 INTRODUCTION

Paper industry is constantly searching for cost savings by aiming at more effective use of raw materials. Optimising the use of raw material can be done e.g. by reducing the grammage or by increasing the share of filler in paper. However, the challenge for increasing the filler content is, how to compensate the decrease in strength properties of paper. Previous studies have shown that selective treatment of fibre fractions has in some cases improved significantly both tensile and internal bonding strength values. Thus, the target for this study was to find out the effect of chemical pre-treatments of fibre fractions on paper properties and especially on paper strength.

On the other hand, the object for this study was related to transportation of pulp to test trials. When fresh pulp is transported to the trials, the most of the transported material is water, which means higher transportation costs. An option for fresh pulp transportation is to bring the fibres to the trials as dry reels and slush them at the destination. This set another target for this study, which was to find out the differences between the sheet properties of paper made of slushed broke and corresponding fresh mechanical furnish.

In the selective treatment of fibre fractions, furnish is first fractionated into long and short fraction, which are then separately chemically treated. Thus, the literature part of the thesis tries to give a basic picture about fractionation of furnishes, fibre fractions, and how different fractions contribute to paper properties. Special attention is paid to short fraction i.e. fines. In addition to this, literature part addresses theory information, which is important for the understanding of retention phenomenon as a whole and the operating principles of chemical additives used in selective and conventional chemical treatments.

The objectives of the study were approached with a handsheet study and with a miniformer trial. Both trials included separate parts for fresh pulp and broke, and for conventional and selective chemical treatments. The results and the conclusions from the studies are presented separately after the literature part. The main findings and suggestions to future studies have been drawn together at the end of the thesis.

Theory part:

2 THE CHARACTER AND PROPERTIES OF MECHANICAL PULPS

2.1 Introduction of different mechanical pulp grades

In mechanical pulping, the wood lignin is softened with water, heat and mechanical stress. When mechanical loading elements are run repeatedly over the wood material at a certain speed, simultaneously the wood structure absorbs energy, which is transformed into heat, which softens the lignin that bonds fibers to each other. Softening of lignin and mechanical stress releases fiber bundles, individual fibers and fiber fragments from the wood. / 23 /

The release of fiber material from wood can be considered only a sub-process of mechanical pulping and fiber treatment continues even after release. The mechanical treatment continues until the percentage of unpulped material (i.e. shives) is sufficiently low and the pulp has achieved targeted freeness value. Mechanical pulping is not used to dissolve anything from the wood, but a small amount of water soluble extractives and other components are dissolved during the pulping process. However, the yield is still very high (96-98%) compared to chemically produced pulps. / 23 /.

Ground wood pulps

In grinding, debarked and cut-to-length spruce logs are pressed sideways against a rotating grinding stone so that the wood fibres are perpendicular to the motion of the pulping stone surface. The rotating stone transfers, through grit particles of the stone surface, energy to the wood, and the wood fibres are separated. Grinding may be intensified by means of pressure, when the pulp is called Pressure Groundwood (PGW). / 23 /

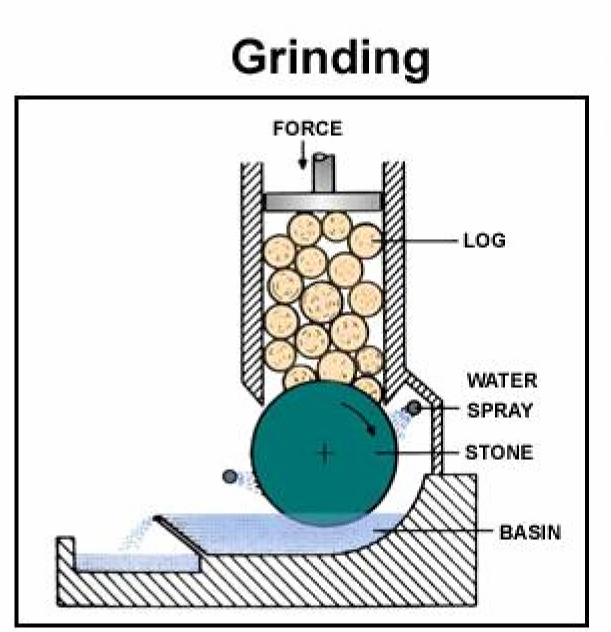

Figure 1 The principle of Ground-Wood-Pulping process / 23 /.

Refined mechanical pulps

In refining process mechanical stress is achieved by feeding spruce, or sometimes pine, chips between edge-surface refiner plates, of which one or both are rotating (figure 2). Between the refiner plates, the dimensions of the chips get smaller shrinking into the direction of outer circles of refiner plates. The surface of the plates transfers energy from the plates to the wood. The dwell time of the wood material between the refiner disks is 2 to 7 seconds. / 23 /

If the process is carried out in atmospheric pressure, the pulp is called Refiner-Mechanical-Pulp. However, normally the process is carried out in pressurised conditions with a steam pre-treatment and the pulp is called Thermo-Mechanical-Pulp (TMP). Higher temperature is aimed to affect the defibration in such a way that fibres separate longer, thus producing a pulp with better strength properties. The pre-treatment is followed by fibre separation and refining in a refiner at an overpressure of 1 to 6 bars. / 23 /

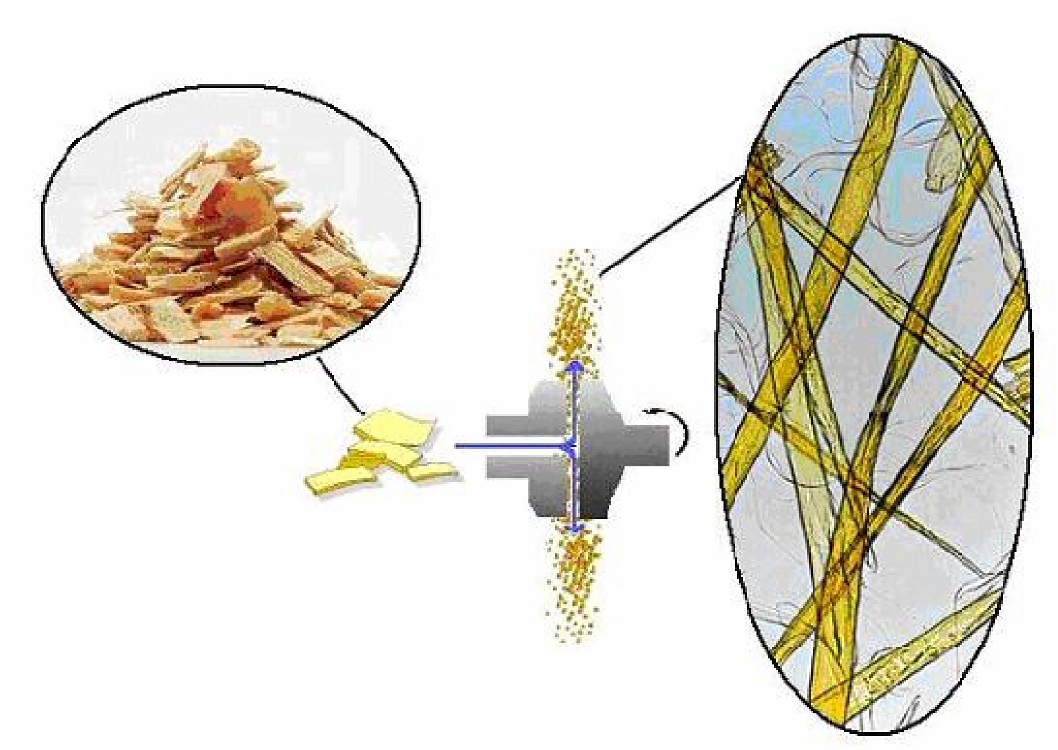

Figure 2 The principle of Refiner-Mechanical-Pulping process / 23 /.

Chemi-mechanical pulps

Chemi-mechanical pulping process is a mixture of chemical pulping and mechanical pulping. The chemi-mechanical pulping process is an application of the TMP process and the most significant difference is that there is a chemical pre-treatment of chips before pulping in the mechanical pulp refiner. There are three types of chemi-mechanical pulps:

1. Chemi-Mechanical Pulp, CMP
2. Chemi-Thermo-Mechanical Pulp, CTMP
3. Bleached-Chemi-Thermo-Mechanical Pulp, BCTMP.

Compared to mechanical pulps (TMP, RMP, GWP) chemi-mechanical pulps have:

-longer fiber length and lower amount of fines
-stiffer fibres and more bulky pulp
-better strength properties
-lower amount of shives
-pure pulp without unpleasant tastes or odours. / 23 /

2.2 Fractional composition of mechanical pulps

Circumstances in mechanical pulping affect the way the wood matrix is broken and fibres separated from each other. Shives, fibres, pieces of fibres, and fines are formed already during the fibre separation stage, thus the conditions in the very initial defibration stage determines the character of fibres. Dimensions of the particles are continuously changing during the defibration process. Both the length distribution and cross-sectional dimensions of fibres are affected when fibres are mechnanically treated. Refining affets also the properties of fines and middle fraction, due to the new material formed during the process. / 9, p. 395 /

Both the fibre length distribution and the properties of fibre fractions affect the properties of pulp. These two factors are capable of independent variation due to the variations in wood quality or pulping equipment. / 9, p. 398 /

Fiber fractions

The fiber properties of mechanical pulps are quite different than the properties of chemical pulp. While chemical pulps mainly consist of intact long fibers, mechanical pulps contain a wide variety of particle sizes like shives, intact fibers, fiber fragments, and fines. These particles can be divided into three fractions: long fibre fraction, intermediate fibre fraction, and short fibre fraction i.e fines. / 23 /

Long fiber fraction consist mainly of intact fibers and the fiber length of the fraction is equal to chemical pulps. However, the fibres are stiff and their bonding ability is poor due to their high lignin content. Intermediate fraction consist of broken fibers and fiber fragments. The fibre length of the fraction is well below that of chemical pulps being only 0.8-1.2 mm. Fines consist of short parenchyma cells, fibrils and lamella released from the secondary wall, and fragments of the primary wall and intermediate lamella. Fine particles are no longer fibrous by nature, and have a length of under 0.4 mm. / 23 /

In mechanical pulps, none of the fractions is suitable for a paper raw material alone, but together they form a usable pulp. Long fibers have the necessary length, but they have a poor bonding capacity and produce an extremely weak sheet. Intermediate fractions and fines have good bonding capabilities, but lack of required fiber length. / 23 /

Production of mechanical pulp aims at a suitable mixture of these fractions, in a way that they support each other. Long fibers form a loose matrix in the paper and smaller particles fill the pores within. A suitable particle size distribution of mechanical pulps is affected by raw materials, process and process conditions. However, when changing process conditions like loading or temperature, it is impossible to affect a single fraction only. For instance, when the amount of shives cannot be reduced without increasing the amount of fines. Thus, the pulp quality target has to be optimized based on this kind of critical property pairs. / 23 /

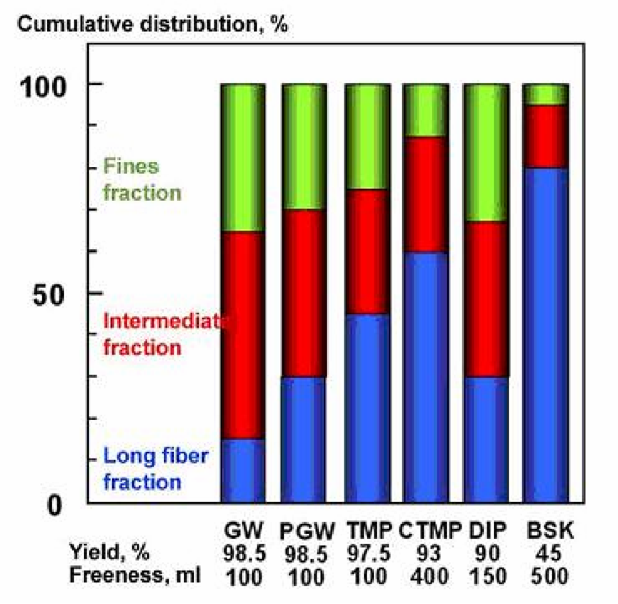

Figure 3 The effect of pulping method on fiber length distributions of given pulps / 23 /.

In PGW and TMP processes, overpressure enables the use of higher pulping temperatures, which helps the softening of lignin and fibres are released more intact from the wood. As can be seen from figure 3, the percentage of long fibers increases and the amount of fines decreases in the order SGW>PGW>TMP. Strength properties are increasing in the same order as long fiber percentage and average fiber length. The light scattering coefficient, opacity, and smoothness increase in the reverse order of strength properties. / 23 /

2.3 Fibre properties of mechanical pulps

Due to the high lignin content, mechanical pulp fibres are rigid, which limits their bonding ability and increases the coarseness of mechanical pulps. This means that chemical pulp contains almost two times more fibers per weight unit as the long fibers of mechanical pulps. Typical mechanical pulp contains a low amount of long fibers and high quantity of fines resulting in smaller average fiber length. Table 1 shows that fibre lengths of sofwood mechanical pulps are on the same level of birch sulphate pulp. / 23 /

Table 1 Average length of different pulps / 23 /.

Pulp	Average fiber length
GWP, CSF 100	0,7-1,0
PGW, CSF 100	0,9-1,1
TMP, CSF 100	1,0-1,3
Pine sulphate	2,1-2,3
Birch sulphate	0,9-1,1

Due to the short and rigid fibers, the strength properties of mechanical pulps and particularly their tear strength values are modest compared to chemical pulps (figure 4) / 23 /.

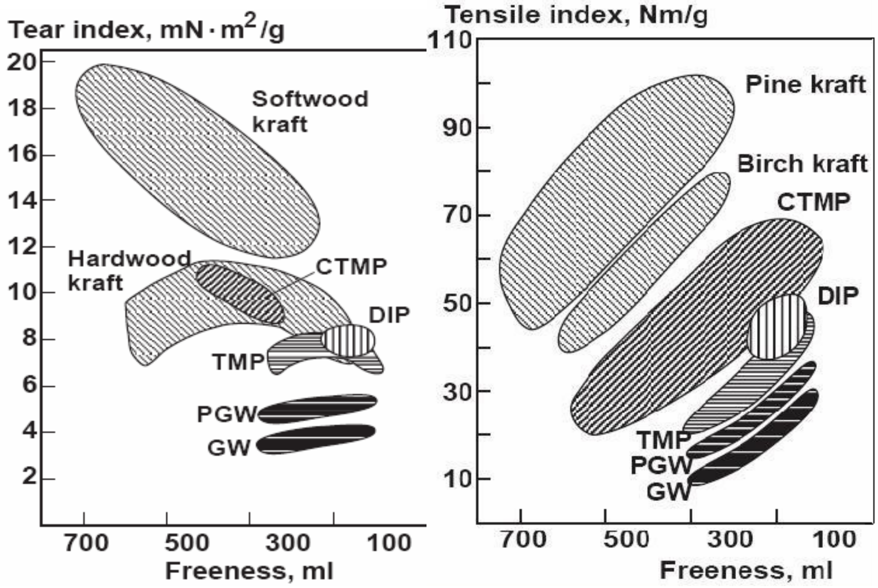

Figure 4 The differences between the strength properties of various pulps / 9, p. 411 /.

On the other hand, figure 5 shows that mechanical pulps have a high fines content, which gives a bulky structure for a paper with a higher degree of smoothness, a high light scattering coefficient, and high air permeability values / 23 /.

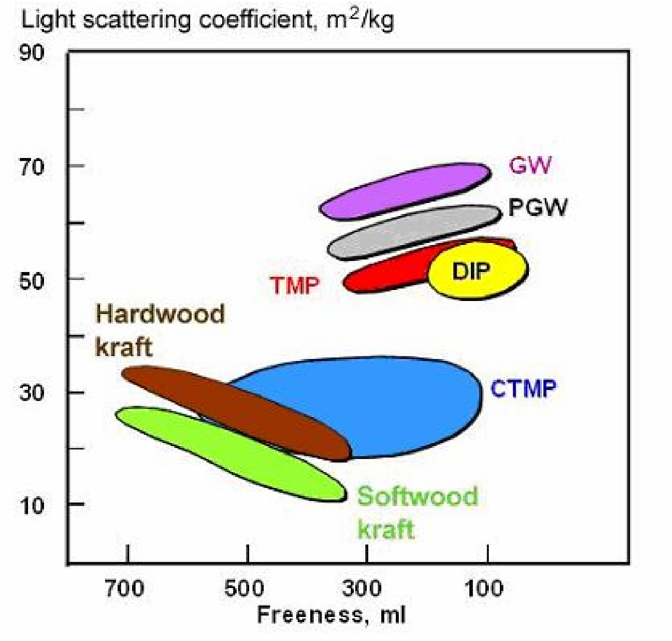

Figure 5 The relationship between pulping method and light scattering coefficient / 23 /.

As mentioned already, both the fractional composition and the properties of fibre fractions affect the pulp properties. For instance, a clear difference can be seen in tensile indexes when comparing the properties of handsheets made of TMP and SGW pulps (figure 6). The defibration stage affects both the amount and the nature of fibres and fines. It has been shown that medium and short fractions improve the bonding ability of mechanical pulp, if the long fibres have a poor bonding ability. If long fibres have been refined to the better level of bonding ability, increasing the share of short and middle fractions has a negative impact on strength properties. / 9, p. 398-399 /

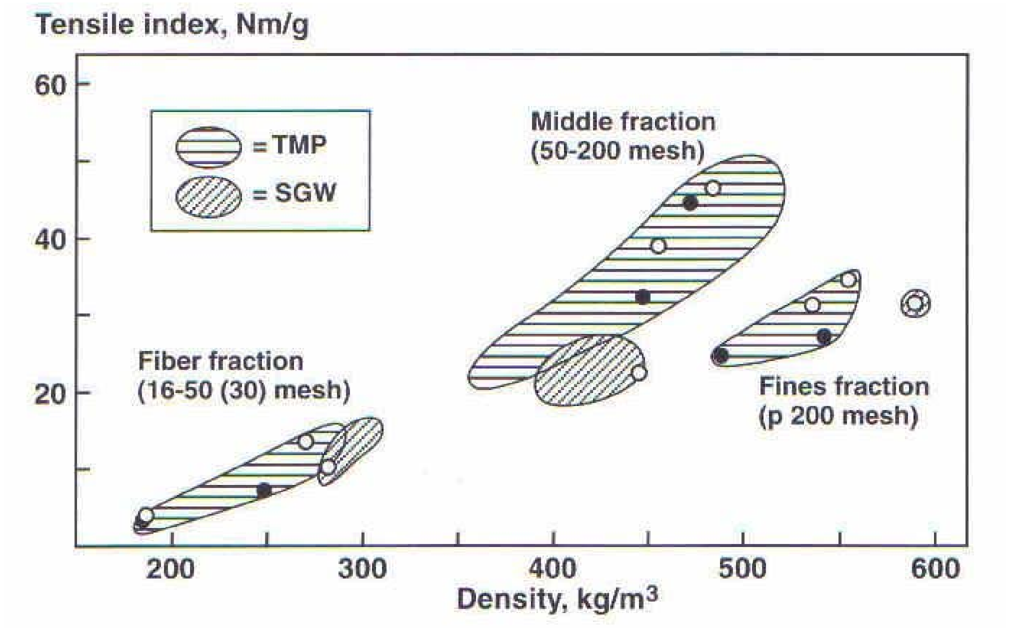

Figure 6 The effect of fibre fraction on tensile index / 9, p. 400 /.

Table 2 presents a summary of the properties of mechanical and chemical pulps and differences between them.

Table 2 The summary of fibre properties of mechanical and chemical pulps / 16, p. 60 /.

Property	**Mechanical pulps**	**Chemical pulps**
Yield of wood	High	Low
Amount of lignin	High	Low
Amount of hemicelluloses	High	Low
Degree of polymerization	High in cellulose	High
Charge in water suspension	More anionic	Less anionic
Water affinity	More hydrophobic	More hydrophilic
Long fibers per unit mass	Few	Many
Specific unit mass	Large	Small
Fines content	High	Low
Fines:		
Structure	Lamellar	Fibrillar
Bonding ability	Good	Excellent
Fibers:		
Structure	Stiff,coarse,straight	Slender,surly,kinky
Shape	Short and thick	Long and thin
Bending stiffness	High	Low
Degree of collapse	Less collapsed	More collapsed

3 FRACTIONATION

3.1 Principle of fractionation

Fractionation and further selective processing or use of furnish components provides potential to achieve raw material and energy efficiency or savings in investment costs, as the size or amount of equipment can be decreased. The principle of fractionation is to divide the feed pulp into fractions by their fibre dimensions, so that larger particles are rejected and smaller particles accepted. The fractionation occasion can be considered directing the right kind of fibres through the process and ultimately to the end use. / 12, p. 11 /

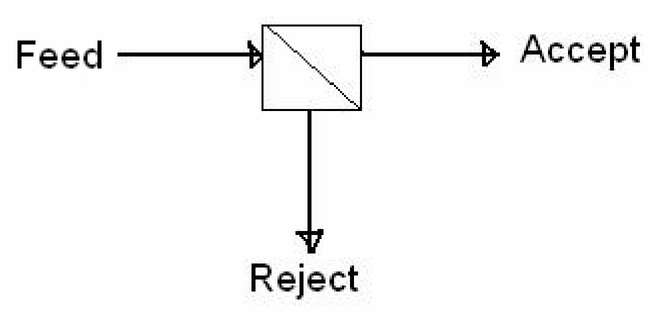

Figure 7 The principle of fractionation and names of the flows.

3.2 Fractionation equipment

Fractionation equipment and the system connections are chosen according to the required pulp and paper properties. The higher the requirements for the fractions and the end product, the more complicated the fractionation system. Previously that meant complicated cascade connections, but currently one multi-stage screen can include separate screening stages / 8, p. 270, 275 /

Separation equipment can be divided by their operating principles into four categories:

1. equipment, in which separation is done by mechanical surface (e.g pressure screens, gap washers).
2. equipment, in which the flow behaviour of the suspensions makes the separation (e.g hydrocyclones, flotation).

3. equipment, which utilise radio waves
4. other equipment (e.g selective wetting of materials). / 7, p. 18 /

However, the two first ones are the most common methods used in papermaking. The fractionation equipment and configuration of the system is dependent on the desired accept pulp quality and the raw material (pulping method, consistency etc) / 8, p. 251 /. This chapter concentrates only on pressure screening, because it was the method utilized in this study.

3.3 Pressure screens

Operating principle and structure

A pressure screen is a pressurised piece of equipment (figure 8) including a mechanical barrier, which target is continuosly separate the fibre suspension (feed) into two (accept and reject) according the particle size / 12, p. 29 /. The main parts of a pressure screen are a cylindrical screen basket or plate and a rotor and its foils, which are placed inside the basket. In addition to foil rotors, there are many other rotor types in use including solid drums with radial vanes, hemispherical bumps, and tapered surfaces. / 3, p. 232 /

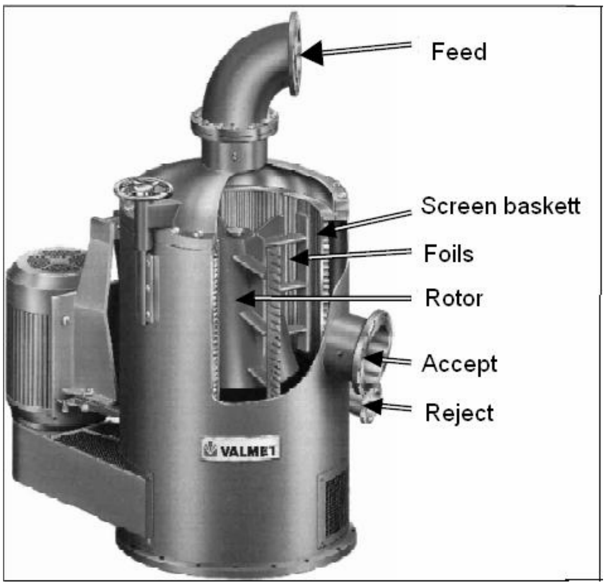

Figure 8 The cross section and the parts of Valmet TAP pressure screen / 8, p. 255 /.

Flow path through the screen can be from inside to outside, which is the most common way, or from outside to inside. Whatever the type of the rotor or flow direction, the rotor has two tasks. Like can be seen in figure 9, it keeps the pulp suspension in a tangential motion and creates suction pulses on the plate surface. Tangential velocity together with the axial flow make the flow field, which forces the accepted particles through the basket. Suction pulses on the other hand makes the backflushing, which prevents the plugging of the screen. When rotor is placed inside the screen, it makes the alignment of fibres and is more effective in clearing the screen plate surface. / 3., p. 232 /

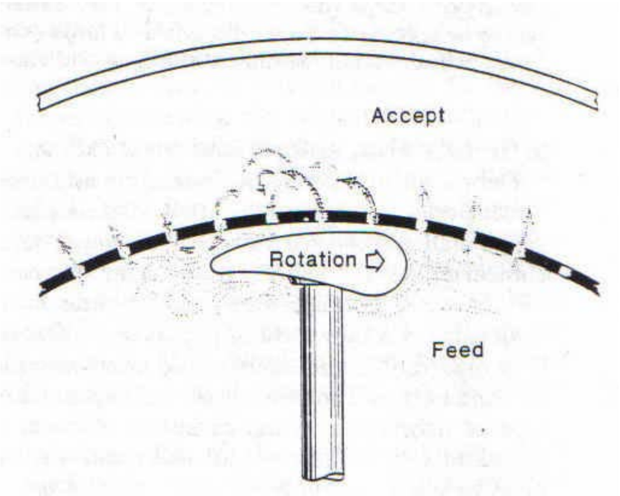

Figure 9 Flow conditions inside pressure screen / 3, p. 232 /.

It is important to make the pulsation on the screen plate surface to keep it open, but it is equally important to keep the pulsation low. Too high pressure pulse causes both fines and coarse fibres to the accept side, and too high suction pulse makes the fines come back to the reject side and eventually to the reject outlet. Figure 10 presents a comparison between the pressure curves of old-fashioned and modern rotor and their foil types. / 8, p. 267 /

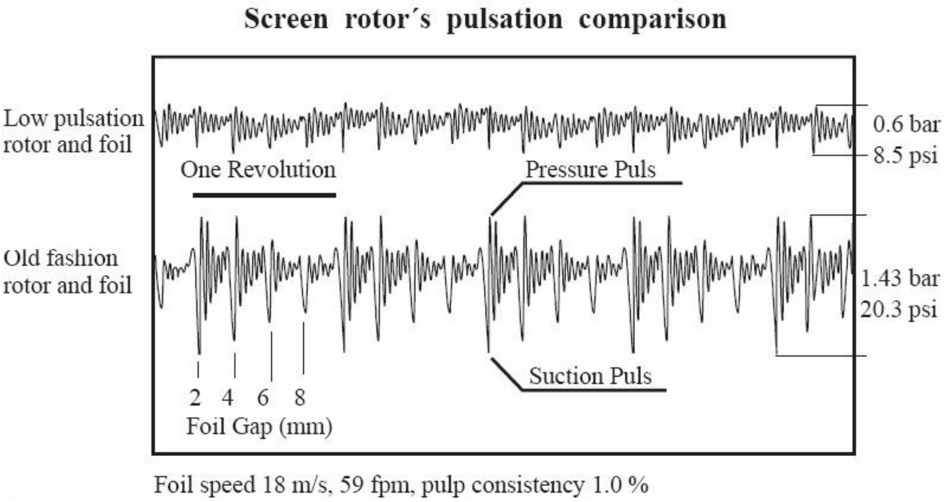

Figure 10 Comparison of the pulses caused by two different rotor types / 8, p. 267 /.

3.4 General theory about fractionation

The two most important factors to describe the performance of fractionation equipment are the capacity and the selectivity of the machine. However, they are negatively interdependent and have to be considered simultaneously. The capacity of a machine describes the amount of suspension the equipment can handle. Although the hydraulic capacity has to be taken into account, the amount of solids in suspension is the most important thing.

Thus the capacity of separation is defined as the dry mass flow rate of accept flow and it is calculated as follows:

$$\dot{m} = \dot{V} c, \qquad (1)$$

where

$\dot{m}$ is the volumetric mass flow rate (g/s),

$\dot{V}$ is the volumetric flow rate (l/s),
c is the consistency (g/l). / 12, p. 17 /

Separation efficiency is an important factor to estimate the achieved quality and further the amount of separation stages needed. The most common way to describe separation efficiency is the calculation of reject rate. Reject rate describes the quantity of rejected matter and it can be calculated based on volumetric or mass flows. Reject rate by volume RR_V is calculated as follows:

$$RR_V = \frac{V_R}{V_F} * 100\,\%, \tag{2}$$

where
V_R is the volume of the rejected matter (kg/m^3),
V_F is the volume of the feed flow (kg/m^3) / 8, p. 254 /.

Reject rate by mass RR_m takes into account that water goes preferentially to the accept side and it concentrates on the dry solid quantities. RR_m is calculated as follows:

$$RR_m = \frac{m_R}{m_F} * 100\,\%, \tag{3}$$

where
m_R is the mass of the rejected dry matter (kg),
m_F is the mass of the the dry solids in feed flow (kg) / 8, p. 254 /.

The general removal efficiency E_R is the most common way to evaluate the separation result. Removal efficiency defines the percentage of component during separation, but although it indicates the ability to reject one component, it will not tell the ability to accept others. Because of that, it does not tell the quality of accept or the degree of selective separation.

$$E_R = \frac{\dot{m}_R\,C_R}{\dot{m}_F\,C_F} * 100\ \% = RR_m\left(\frac{C_R}{C_F}\right) * 100\ \%, \tag{4}$$

where

$\dot{m}$ is the volumetric mass flow rate (g/s),

C is the content of given component (%),

RR_m is the reject rate by mass (-),

Subscript R refers to the reject fraction,

Subscript F refers to the feed. / 12, p. 20 /

Another measure, which is widely in use and describes separation efficiency is cleanliness efficiency E_c. It compares the accept quality to the feed quality and is not directly dependent on the reject rate. The cleanliness efficiency is defined as follows:

$$E_c = \frac{C_F - C_A}{C_F} * 100\ \%, \tag{5}$$

where,
C is the content of given component (%),
Subscript A refers to the accept fraction,
Subscript R refers to the reject fraction,
Subscript F refers to the feed. / 12, p. 21 /

Because consistency changes occur in all kind of separation operations, it is good to know how it is calculated. Reject thickening factor (RTF) gives an indication simultaneously about capacity and separation efficiency. Reject thickening factor is calculated as follows:

$$RTF = \frac{c_R}{c_F} = \frac{RR_m}{RR_V}, \tag{6}$$

where

RR_m is the reject rate by mass (%),

RR_V is the reject rate by volume (%),

c is the consistency (g/l),

Subscript F refers to the feed flow,

Subscript R refers to the reject flow. / 12, p. 23 /

3.4 Selective treatments of fibre fractions

3.4.1 Chemical treatment

In general, during selective treatments of fibre fractions, retention or strength aid chemicals are added separately in different fibre fractions. For instance, dry strength additive, normally starch, can be added separately into long fraction, when there has been reported improved values in internal bonding strength, tensile strength, and light scattering. Another example about fractional chemical treatments is to add polymer (PAE) into long fraction. It has been reported to increase breaking length for dry, moist, and wet paper. / 7, p. 21-23 /

3.4.2 Mechanical treatment

The most common way to mechanically treat the fiber fractions is refining. The target of chemical pulp refining is to optimize its contribution to the mechanical properties of paper. Beating loosens the structure of fiber wall (internal fibrillation) and fibre surface (external fibrillation). Fibrillation increases flexibility, swelling, and consolidation of fibre wall, which improves inter-fibre bonding and strength properties. / 16 , p. 62 /

The target of mechanical pulp refining is to make a usable pulp from poorly developed long fibres. Refining of mechanical pulps increases the internal and external fibrillation of fibres. During refining, the delamination of the fibre wall reduces the fibre stiffness and coarseness, when the outer layers of fibre wall is peeled off. The impact of mechanical pulp refining on tensile and tear strength is different. Tensile strength increases as a function of refining energy, while tear strength increases into some point and starts to decrease due to decreased strength of single fibres. / 11, p. 306 /

4 FINES AND PAPERMAKING

4.1 The definition of fines

The amount of fines and the nature of fines vary between the pulp types, but in general fines are considered to be the material which goes through the 200 or 100 mesh wire of the Bauer-McNett fractionator or similar device. The median size of fines is a few micrometers. The largest particles considered to be fines are fiber fragments and the smallest are fiber fibrils or parts of them the size being less than 1 μm / 16, p. 63 /.

The fines can be divided into two different groups called primary fines and secondary fines. Primary fines are the fines, which wood includes naturally and are released in the pulping process. They include parenchyma, ray, vessel cells, fragments of tracheids, and vessels that are broke during the pulping process. Secondary fines are developed during the refining of pulp. They are veil-like or lamellar particles produced by abrasion of fiber surface and originated mainly from S1 and S2 layers of secondary fibre wall. / 20, p. 114 /

Fines consists of cellulose, hemicelluloses, lignin, and extractives approximately in the same proportions as the other fibre fractions i.e the raw material. Because of their smaller particle size and larger surface area, fines can bind more water and swell more than fibers. Due to the same fact, the adsorption of retention aid chemicals is higher into the fines fractions / 16, p. 63 /.

4.2 Fines from mechanical furnishes

Because in mechanical pulps fines are originated partly from the lignin rich middle lamella and primary cell wall of fibers, their lignin content is higher than in fibre fractions. Due to that, lignin content of fines decreases as a function of the refining energy. The high content of hydrophobic lignin and extractives in mechanical pulp fines decreases their ability to swell in water compared to chemical pulp fines. /

Retulainen, p. 63 / Sometimes the mechanical fines are classified as slimestuff and flourstuff. Slimestuff is powdery and has a poor binding ability, while flourstuff consist of well-bonding fibrillal particles / 16, p. 63; 12, p. 59 /

In mechanical pulps, the amount of fines is considerable, which affects also the structure and properties of the end-product. The amount of fines is dependent on the defibration process and target freeness of the final pulp. The fines content in mechanical pulps grows in order TMP>PGW>SGW at the same freeness level. A fine stone GW pulp for magazine paper can include up to 50 % fines, when corresponding value for newsprint TMP is less than 25 %. / 16, p. 63 /

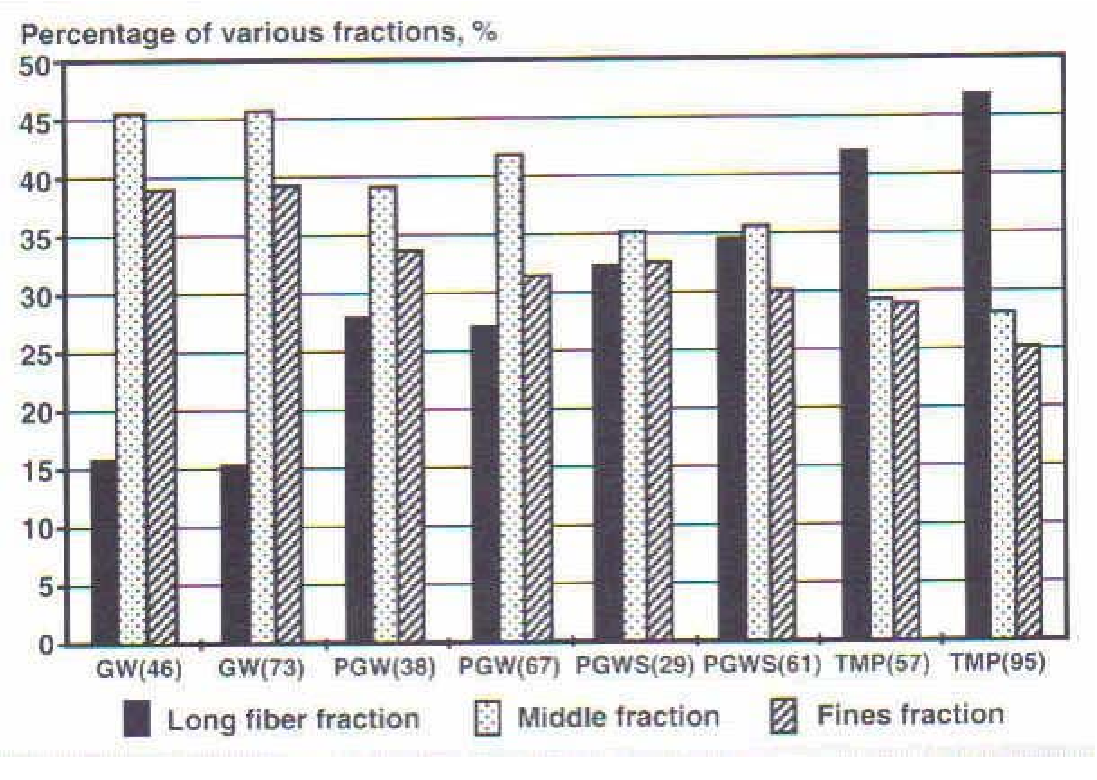

Figure 11 The share of fibre fractions in mechanical pulps / 9, p. 395 /.

4.3 Fines from chemical furnishes

In chemical pulps, the amount of fines is lower than in mechanical pulps. The content of primary fines is normally less than 2 %, but refining can increase the final fines content of pulp up to 15 %. / 16, p. 63 /

Because fines in chemical pulps are from secondary fibre wall, their hemicellulose content is higher compared to fibre fractions. Because of the smaller amount of hydrophobic lignin, the chemical pulp fines posses better swelling and bonding ability than mechanical pulp fines. / 16, p. 63 /

4.4 Other fines

In addition to the fines from wood, the paper making stock can include other particles like fillers, coating pigments from broke circulation, and ink particles and macro-stickies, if recycled fibres is used / 12, p. 58-60 /.

4.5 The impact of fines on sheet properties

Stable retention of fines is important, because they contribute to paper strenght and optical properties. Table 1 summarizes, how the increasing share of fines affect the paper properties.

Table 3 The impact of increasing fines content on sheet properties **/** 7, p. 15 /.

Property	**Effect**
Wet strength of the web	+
Sheet density	+
Shrink potential	+
Tensile strength	+
Stretch	+
Elastic modulus	+
Tear strength	-
Compression strength	+
Bending strength	+
Air permeability	- -
Characteristic bonding strength -Primary fines -Secondary fines	 - +
Light scattering -Fines from chemical pulp -Fines from mechanical pulp	 - + +
Dusting	-
+ = property improves - = property deteriorates	

4.6 The impact of fines on the process

The fibre fines affect wet end chemistry through their surface and colloid chemistry. Important characteristics are sorption capacity, swelling ability, and ion-exchange properties, which are based on chemical composition. As mentioned earlier, fines have small particle size and 5-8 times higher specific surface area than fibres. Because chemical reactions in wet end occur mainly on particle surfaces, the participation in these reactions is related to surface area, which means that fines have a dominant role in these interactions. / 20, p. 116 /

Because fibre fines retain 2-3 times more water than fibres, they swell significantly in water. This means that fines have a negative effect on machine dewatering and drainage performance. Fines may represent as much as 40-60 % of headbox dry solids, which means that fines retention is extremely important to effective material utilization. / 20, p. 116 /

Filler and pigment particles affect the wet end chemistry through their interaction with other wet end additives. Important filler characteristics for wet end chemistry are:

1. Particle size and particle size distribution.
2. Particle shape.
3. Specific surface area.
4. Degree of aggregation.
5. Surface charge.
6. Chemical composition.
7. Specific gravity. / 20, p. 116 /

5 RETENTION IN PAPERMAKING

5.1 The definitions of retention

Figure 12 illustrates the material flows on the wire section. About 98 % of the material flow coming out from the headbox goes through the wire while only 2 % stay on the wire and continue to the press section. After the wire section, the dry solid content of the web is 15-22 %. This phenomena, in which the wire retains solid material from the stock is called retention / 23 /.

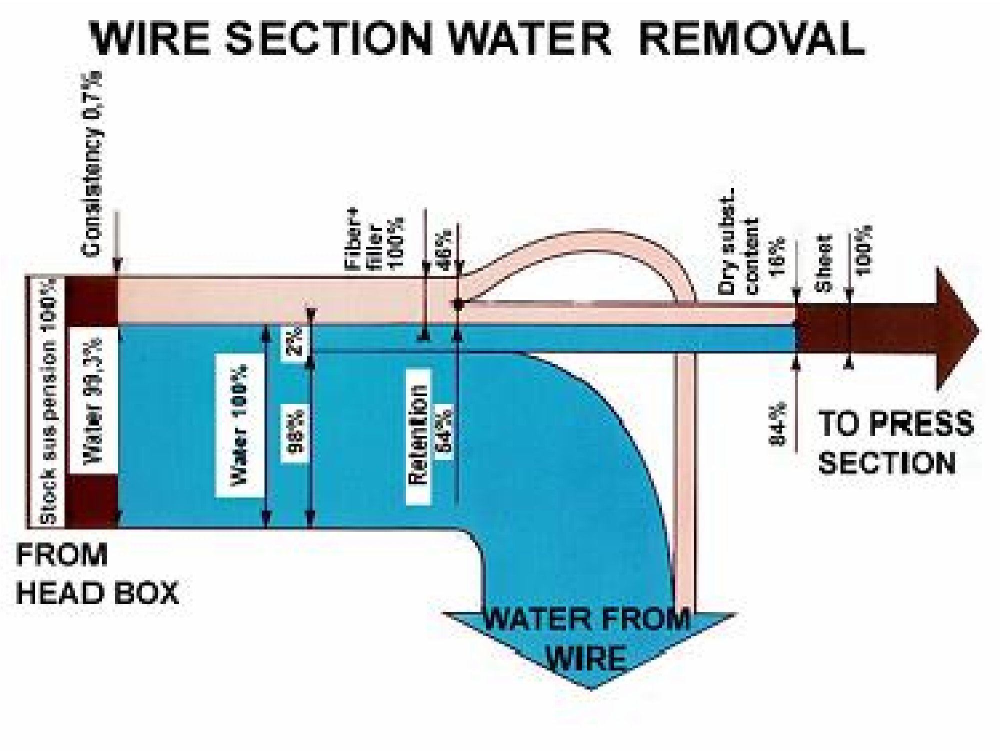

Figure 12 An example about material flows of the wire sections / 23 /.

In general, there are two types of retention: total i.e. overall retention and wire i.e. first-pass retention. Total retention means the proportion of the substance, which remains in the paper web after a run through the paper machine to the amount, which was originally added to the process. / 23 /

Wire retention indicates the proportion of the solid material, which remains on the wire to the amount, which is fed from the head box. That is to say that total retention describes the performance of the whole production process, while the wire retention is a measure for the performance of the wire section. / 23 /

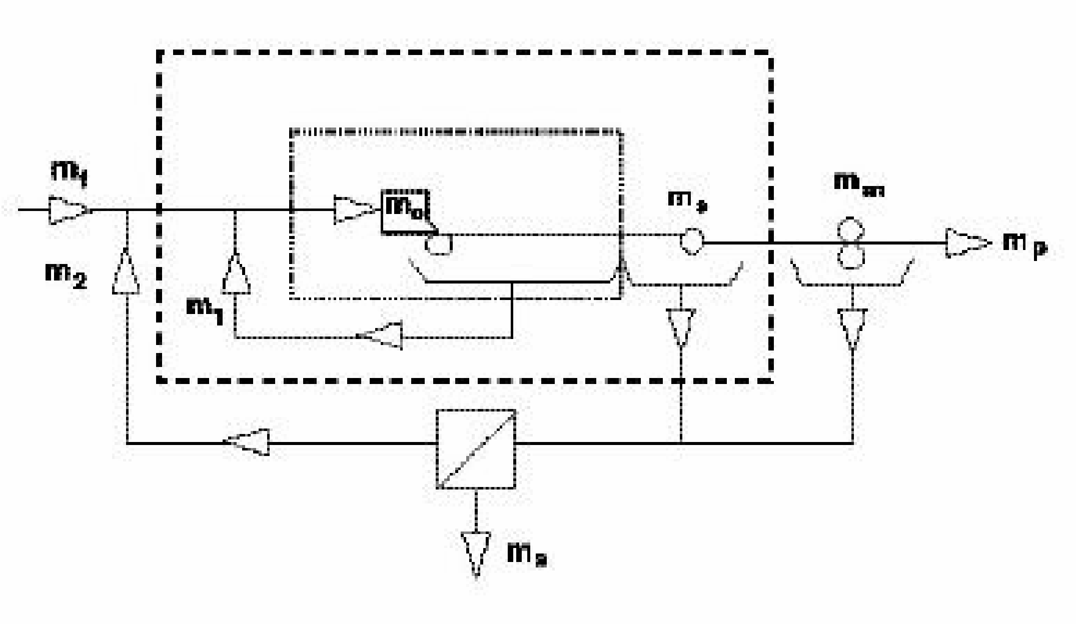

Figure 13 The massflows of short circulation / 14, p. 70 /.

Normally, when referred to retention, it means wire retention. Different retention definitions are described as follows:

- *System retention (total retention)* $SR = \frac{m_p}{m_f}$ (7)
- *Machine retention* $MR = \frac{m_m}{m_0 - m_1}$ (8)
- *First-pass retention* $FPR = \frac{m_S}{m_0} = \frac{m_0 - m_1}{m_0} = \frac{c_0 Q_0 - c_1 Q_1}{c_0 Q_0} \cong \frac{c_0 - c_1}{c_0}$ (9)

where
m represents the mass flow,
c the consistency,
Q the volume flow of the component,
and the index specifies the location in the system according to figure 13. / 14, p. 70/

There are still more specific calculation methods for first pass retention like one-pass solids retention, one-pass fiber retention, and one pass fines retention / 20, p. 113 /.

5.2 The importance of retention in papermaking

Retention should be as high as possible and before all stable. High and stable retention leads into better runnability, more even paper quality, and more efficient paper machine by improving following aspects:

- Lower white water consistency with lower recovery costs.
- Decreased cleaning demand and improved runnability because of cleaner process.
- Better control of fibre and filler distributions.
- Required filler content with minimum retention aid dosage.
- Easier and faster grade changes.
- Smaller specific water consumption makes possible to decrease the water circulation volume and improve energy efficiency / 23 /.

Total retention value includes both the retention of fibre and the retention of filler and fines. Fibre retention accounts for up to 90 % of that value. As can be seen from the figure 3, retention of particles bigger than 1.3 mm is close to 100 %. When regarding the particle sizes for fibres (2.0 mm) and fillers and fines (1-10 μm) and the size of wire opening (0.2 mm), it is obvious that wire retain fibres mechanically more efficiently. / 23 /

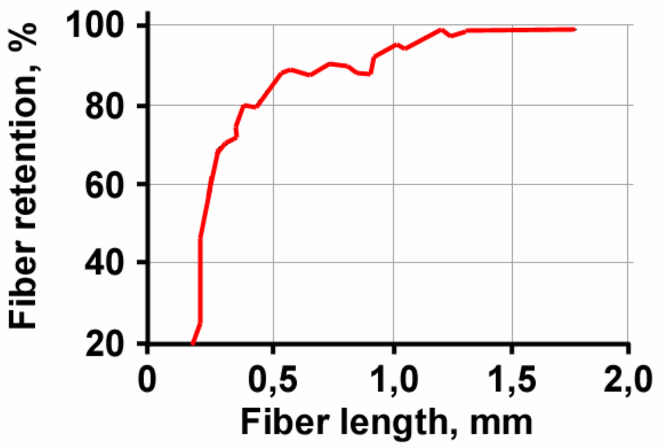

Figure 14 The effect of particle size on retention / 23 /.

5.3 Mechanical issues affecting retention

Fines retention occurs with either colloidal adsorption or mechanical entrapment. Colloidal interaction means the formation of flocs, which consist of fines only or flocs, which contain fibres and fines. Latter case includes the adsoprtion of fines onto fibres, after which they are together retained by the wire. Mechanical entrapment means catching of fines by the fibre web formed onto the wire. This phenomenom needs a certain thickness to occur and is strongly dependent on the thickness of the web i.e basis weight of the web. Mechanical entrapment can be improved by good formation of the web and larger size of the flocs. To reach a good z-directional fines distribution and avoid two-sidedness, the target is to minimize the formation of flocs containing only fines and to promote the fiber-fines flocculation. / 17, p. 17 / Following list summarizes the main mechanical issues affecting retention:

1. The size and shape of the particles being retained including type of furnish and filler.
2. The type of forming fabric initially, but later the porosity of the filtering web, which is affected by furnish components.
3. The basis weight which is being produced.
4. The machine speed i.e drainage rate at which web is formed.
5. The machinery and the way of operation including type of forming section, actions of foils and table roll / 13, p. 13 /.
6. Stock consistency, ash content, and process temperature / 2, p. 136 /.

5.4 Interactions between dewatering, retention and formation

Dewatering occurs in different zones on the paper machine:

1. In the forming zone, which is the distance between table roll and first suction box.
2. In the vacuum zone, which is the area between the first suction box and suction coach.
3. In the press section with press nips.
4. In the drying section with heat applied to the paper. / 14, p. 63 /

Two first ones are the most important one from retention and formation point of view. Water removal on the wire occurs simultaneously through filtration and thickening phenomena, which are presented in figure 15.

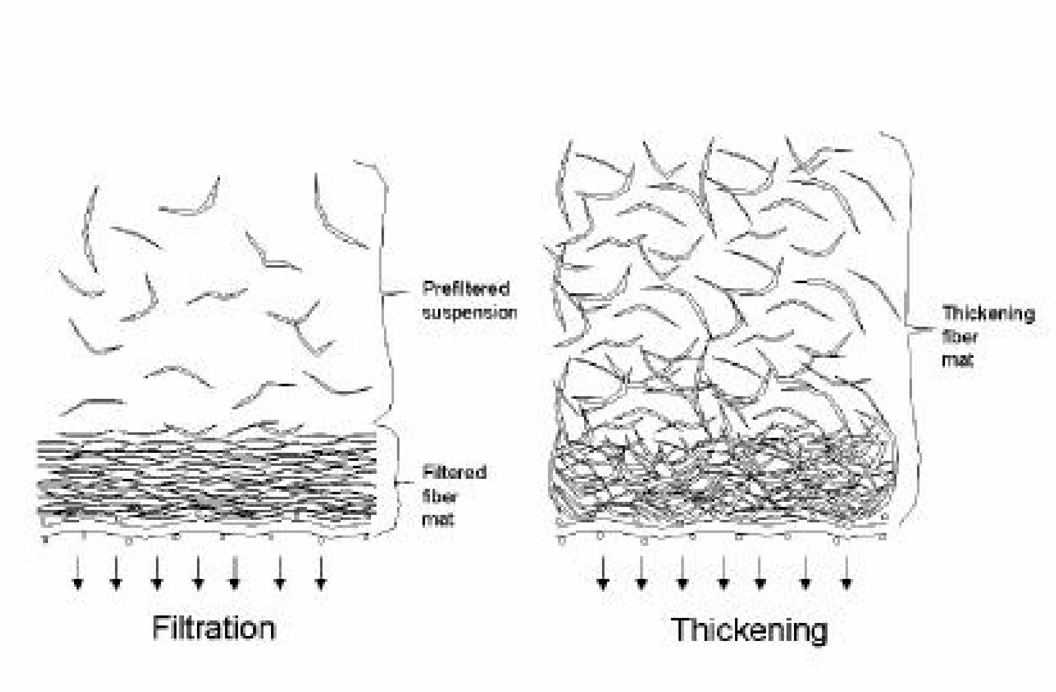

Figure 15 Filtration and thickening phenomena on the wire section / 14, p. 64 /.

Normally in papermaking, stronger flocculation i.e higher retention has a direct positive effect on drainage phenomenom on the wire. Flocculation influences the drainage by collecting the fines and colloidal substances on the fibre surfaces, thus increasing the area for water removal / 14, p. 63-65 /

As can be seen from figure 16, formation and retention are closely related to each other. In principle, when retention is increasing, formation is getting worse. The level of retention is normally adjusted with the amount of retention aid applied into the system. The upper limit for retention aid dosage is the maximum formation value, and lower limit is the minimum retention value. These values set a specific operating window, in which an optimum value has to be found to guarantee both the paper quality and the paper machine production efficiency. / 23 /

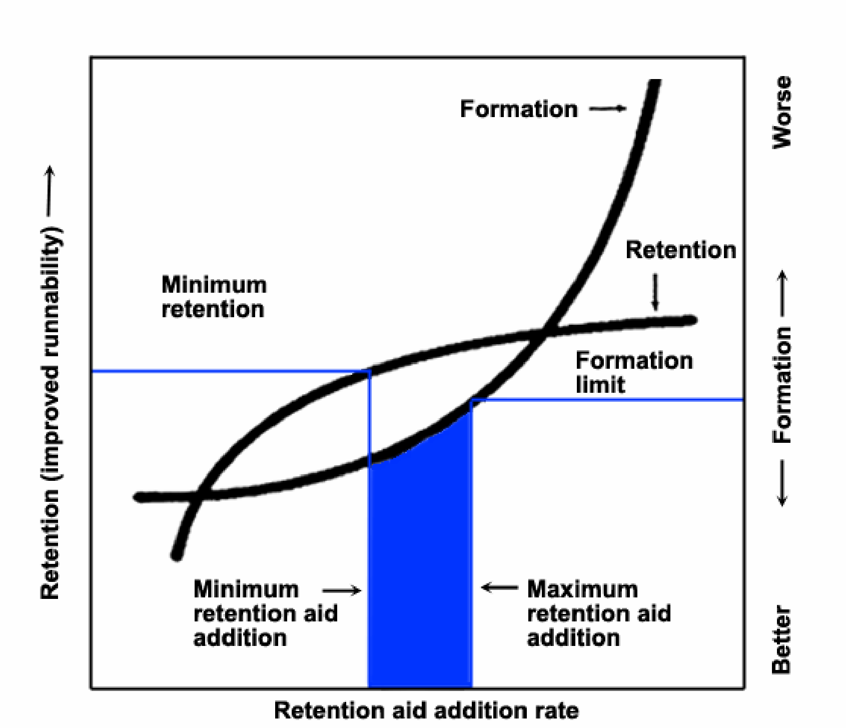

Figure 16 The operating window of retention aid additioning rate / 23 /.

5.5 The mechanisms of surface and colloidal chemistry

5.5.1 Definition of colloidal system

Colloidal system is a heterogenous system, which consists of continuous phase and several discontinuous phases. For instance, in a water-filler suspension the filler forms several discontinuous phases in the continuous water phase. The particle dimensions of colloidal material are very small (0.01-2.0 μm) compared to the continuous phase and the particles have very strong surface properties (i.e. strong negative charge). Forces between the particles are defined by the surface properties of the particles and balance among them / 5, p. 161 /.

5.5.2 Electrical double layer of suspended particles

When dispersed in a polarized liquid like water, solids take a certain electrical charge caused by the ionization of their own surface or the ions adsorbed to their surface. Chemical pulp fibres and common fillers used in paper production have normally negative charge in water suspension. / 23 /

Negative charge may arise from carboxyls and sulfonic acid groups on fibre surfaces and the adsorption of dissolved lignin and hemicelluloses on the surfaces. Mineral fillers develop their surface charge by ionization in the particle-water interface or by adsorption of charged substances like hemicelluloses, starches, polyelectrolytes etc. / 17, p. 3 /.

Figure 17 illustrates the electrical situation on the surface of a negatively charged particle in water suspension. First negatively charged surface attracts positive ions to itself. These ions are called counterions and the layer is called Stern layer. On the top of Stern layer, there is a less ordered diffuse layer or Gouy-Chapman layer. Stern layer and diffuse layer together form an electrical double layer on the surface of a particle. / 23 /

5.5.3 Z-potential of the particles

The ions of the Stern layer are held close to the particle surface by eletrostatic and Van der Waals forces and they move with the particle. The ions of Gouy-Chapman layer are not so tightly bound to the particle. Between Stern layer and diffuse layer, there is a hydrodynamic slip plane. The eletrochemical potential at the slip plane is called electrokinetic potential or Z-potential. Common surface charge measuring methods give values for the zeta-potential rather than surface charge itself. The strength of the charges and the distance over the layers define the electrostatic forces between the particles. / 17, p. 3-4; 21, p. 32 /

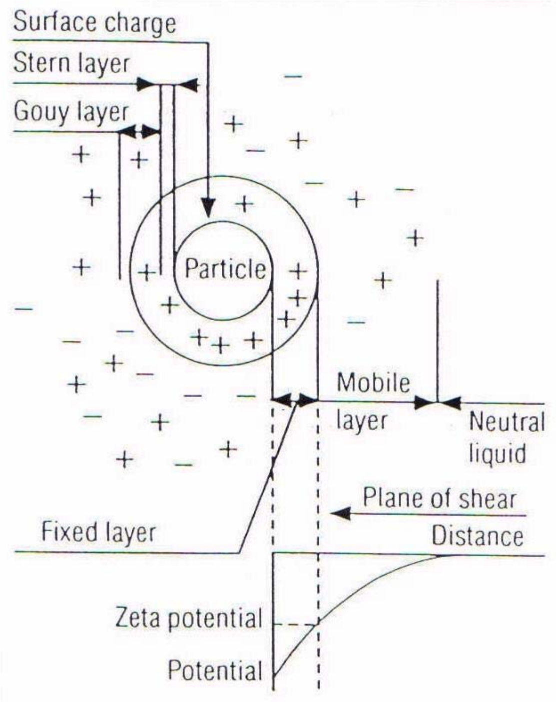

Figure 17 The electrical double layer of a particle / 15, p. 9 /

5.5.4 DLVO theory – A combination of repulsive and attractive forces

The ability of colloidal particles to remain dispersed in water solution over a period of time represents the stability of hydrophobic suspension. The stability of hydrophobic suspension is dependent on the attractive and repulsive forces between the suspended particles and the probability of particles to collide with each other. Van der Waals forces are attractive for the particles of the same chemical composition. Electrostatic forces are repulsive for the particles with the same charge and attractive for the particles with opposite charges / 17, p. 4 /

DLVO theory (Derjaguin, Landau, Verwey, and Overbeek) combines Van der Waals forces, electrostatic forces, and Z-potential into a one universal theory. DLVO theory states that the net interaction between the particles is the sum of attractive and repulsive forces:

$$V_T = V_R + V_A \tag{10}$$

where

V_T = total forces

V_R = repulsive forces

V_A = attractive forces

When the distance between the particles increases, the repulsive energy (formula 11) decreases exponentially. The repulsive force depends highly on the thickness of the electrical double layer, the size of the particle, and z-potential. For two spherical particles with identical radius, repulsive forces are calculated as follows:

$$V_R = 4\pi\varepsilon a^2 \psi_0{}^2 \alpha e^{(-KH_O)/(2a+H_O)} \qquad (11)$$

where

ε = dielectric constant of the solution

a = ionic radius

ψ_O = z-potential

α = factor dependent on the charge density and z-potential

$\frac{1}{K}$ = thickness of the double layer

H_O = distance between the spheres. / 21, p. 32-33 /

Attractive forces are also dependent on the size of the particles and distance between them. The smaller the distance and the bigger the radius, the stronger the attractive forces. Attractive forces are mainly caused by Van der Waals forces and especially so called London forces, which are calculated as follows:

$$V_A = \frac{-AR}{12h} \qquad (12)$$

where

V_A = London forces

A = Hamaker´s constant for the system under consideration

R = the radius of the particles

h = the interatomic distance between atoms in the same particle. / 21, p. 32-33 /

Figure 18 presents a combination of the attractive and repulsive potential energies. Upper dashed curve presents the electrostatic repulsion energy V_R and lower dashed curve represents Van der Waals attraction energy V_A. The solid curve is the total potential energy V_T. The depth of the minimum in total potential energy curve describes the stability of a particle-particle aggregate. The deep minimum indicates a strong aggregate and a shallow minimum a weak one. / 18, p. 25 /

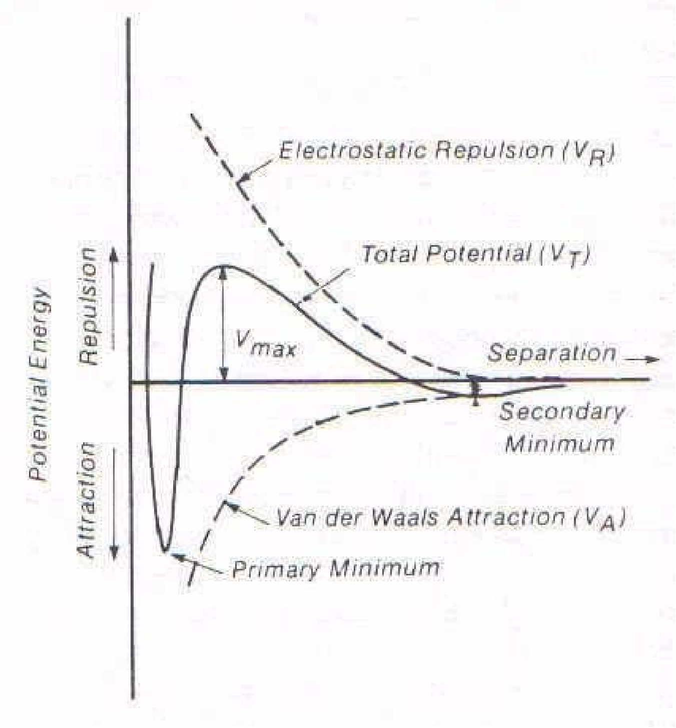

Figure 18 The effect of distance of particles (x-axes) on the interparticle interaction potential energy (y-axes) / 17, p. 4 /.

As the distance between particles decreases, the total force passes secondary minimum, in which colloidal system is stable. If the particles have enough energy to pass the maximum point $V_{\max}$, they will flocculate. Correspondingly, it is possible to break a floc with energy input high enough to help the particles to pass the maximum point. Energy input for the flocculation can be mechanical energy coming from shear forces or thermal energy caused by increased temperature. / 21, p. 33 /

5.6 The issues affecting the operation of retention aid chemicals

5.6.1 Ion exhange behavior of wood fibers

The ion exhange behaviour of wood fibres and fines defines their electrical and electrokinetic properties. These affect adsorption of dyes, aluminum, polyeletrolytes, rosin sizes, and last but not least, fibre and fines flocculation / 18, p. 16 /.

The strength of the attraction forces i.e the ability of the chemical to adsorb on cellulose molecule is dependent on its ion valence. Valences are presented from the strongest to the weakest:

$$N(CH3)_4^{+1} < Li^{+1} < Na^{+1} < K^{+1} < Ag^{+1} < Ca^{+2} = Mg^{+2} = Ba^{+2} < Al^{+3} \qquad (7)$$

Least tightly bound Most tightly bound

The higher the valence of the ion, the stronger the bond and higher the power of charge neutralizing i.e the ability to suppress the electrical double layer and decrease the charge and z-potential. For instance, Al^{+3} makes stronger bond with fibre than Ca^{+2} etc. / 18, p. 16 /.

5.6.2 Charge density of retention aid and surface charge of the particles

Because fibres and fillers are negatively charged in water suspension, the most effective polymers are positively charged, due to their natural attraction on fibres and fillers. Once the particles touch each other, other forces i.e hydrogen bonding or Van der Waals forces bond them to each other. As can be seen from the figures 19, polymer adsorption is dependent on the relationship between the charge density of the polymer and the surface charge of the particles. Figure 19 illustrates, how a low charge density polymer is attached more loosely onto the surfaces of low surface charge, which provides weak adsorption and flocculation. With a moderate charge density and surface charge, the polymer adsorption and bridging phenomena are strong. High surface charge and high charge density make polymer to adsorb as a flat layer onto particles, which leads into mosaic making phenomenon. The same kind of impact can be seen also with increasing surface charge of the particles / 18, p. 121 /

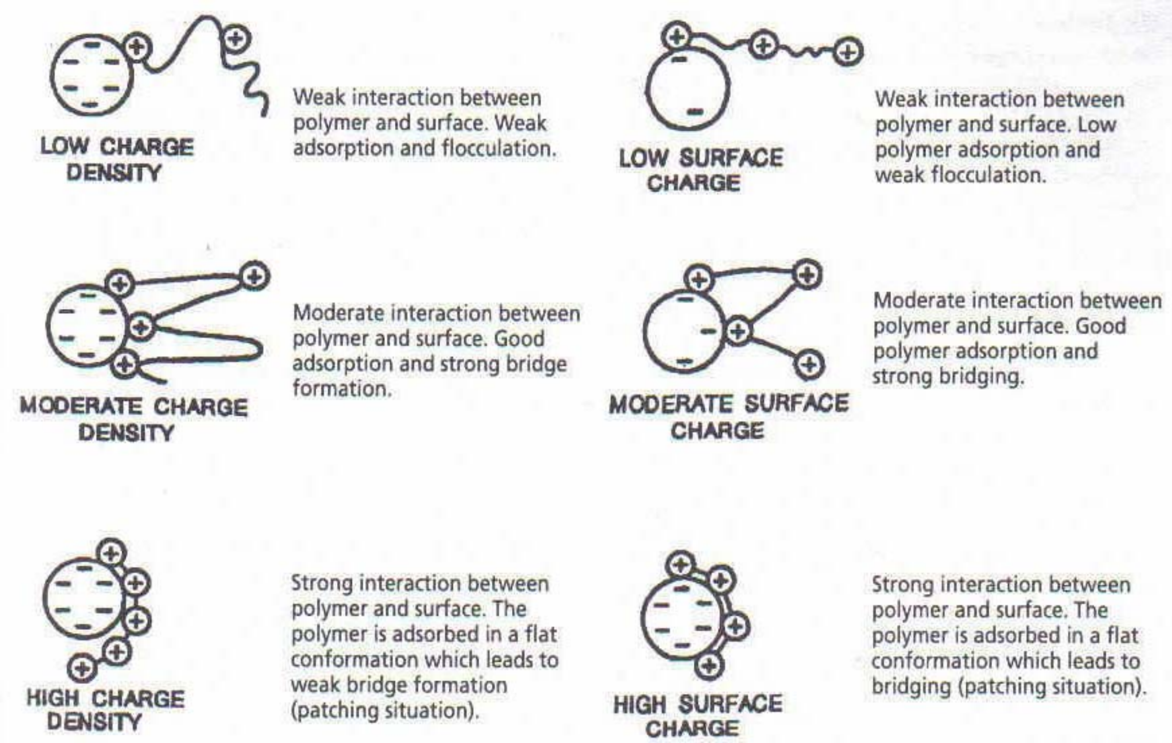

Figure 19 The effect of polymer charge density and particle surface charge on the adsorption of cationic polymer / 18, p. 121 /.

5.6.3 Molecular weight of retention aid chemical

In general, molecular weight of the polymer affects the length of the polymer chain and gives the polymer a better ability to reach particles. Molecular weight of the polymer affects the adsorption of a polymer from aqeous solution. Figure 20 shows, how the polymers with low molecular weigth reach very quickly a well-defined final level of adsorption onto the fibers, which is not dependent on the growth of the concentration / 19, p. 226 /.

The equilibrium curve varies greatly from system to system and is dependent on the chemical circumstances, polymer and fibre characteristics, and physical environment / 18, p. 27 /.

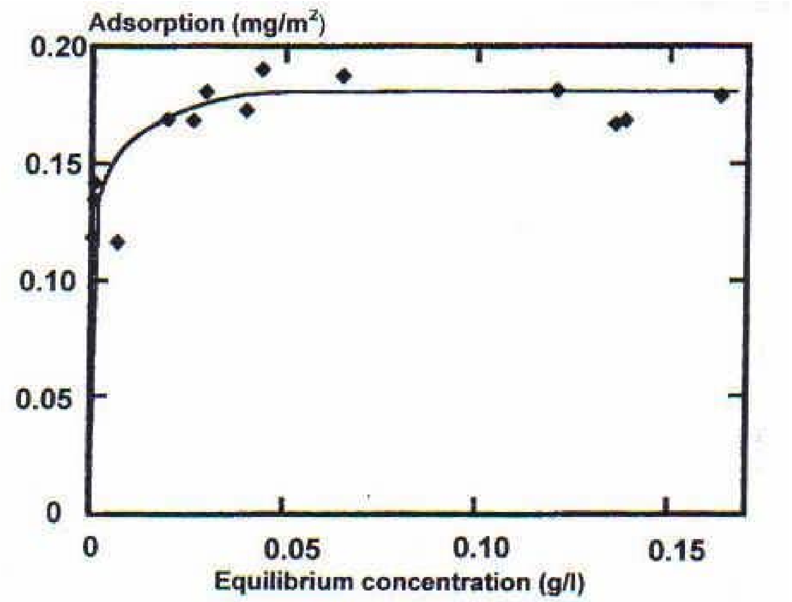

Figure 20 The adsorption of cationic polymers onto fibers / 18, p. 27 /.

When the molecular weight of the polymer is high (figure 21), adsorption increases slowly with increasing polymer concentration. Higher molecular weight increases the adsorption of the polymer, if the polymer-particle forces are not very strong. Figure 19 illustrates the phenomenon, how in the case of high charge density polymer, the molecule surfaces are covered with a flat layer of polymer and only a small amount is absorbed. Then adsorption is low and independent on molecular weight / 19, p. 227 /.

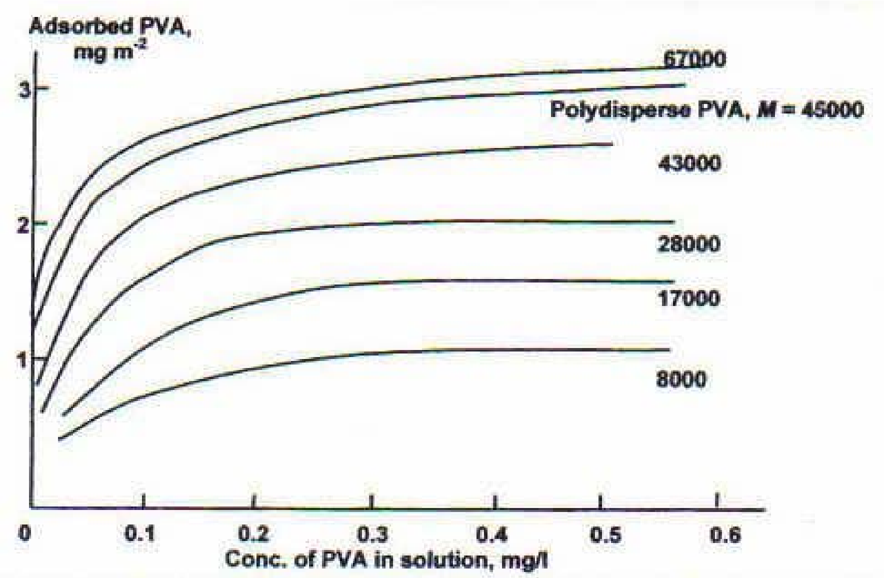

Figure 21 The effect of molecular weight on adsorption of retention aid / 19, p. 227 /.

5.6.4 Chemical conditions of media

In conventional papermaking, the bulk media between the fibers is water. In addition to the properties of fibres and chemicals, it is equally important for a papermaker to understand the basic water chemistry. First of all, water molecule H_2O is polar by its chemical nature, which gives the water molecule its tendency to make hydrogen bonds especially with the substances, which include OH^--groups. Papermaking fibers include such groups and water promotes the formation of fiber to fiber bonding by penetrating and swelling the fibre and acting as a separating lamella before it is evaporated in the papermachine drying section / 18, p. 5-6 /

Surface tension of water

Hardness of water is defined as the ”concentration of calcium and magnesium cations in water, independent of the anions present, and expressed as ppm $CaCO_3$”. Hardness is often determined by titration with disodium ethylenediamine tetraacetate (EDTA) and Calgamite indicator. The endpoint is red-blue transition / 18, p. 8-9 /.

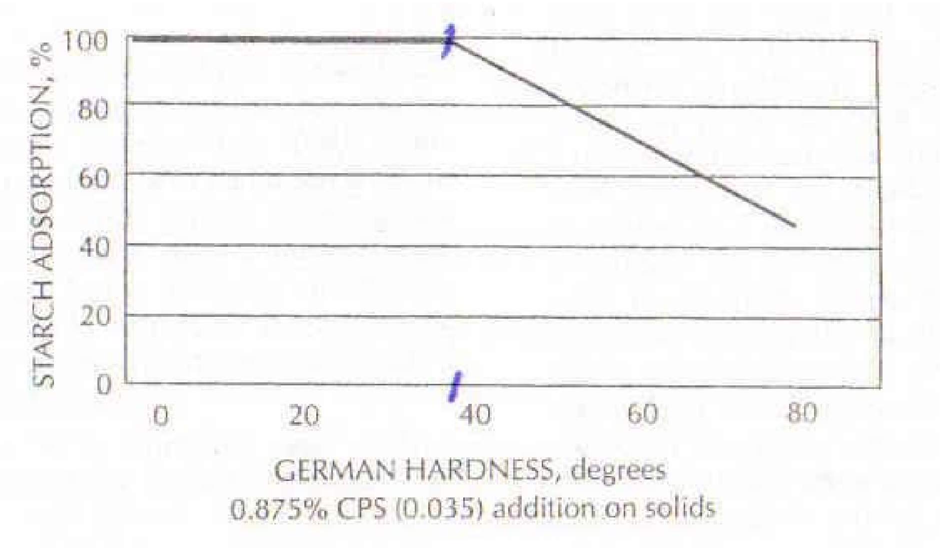

Figure 22 The effect of water hardness on the adsorption of cationic starch / 6, p. 228 /.

Figure 22 illustrates that increasing hardness of water has a negative impact on the adsorption of cationic starch and thus a negative impact on flocculation / 4, p. 228 /

When surface tension of water increases, it increases the ability of water to stand in paper pores and thus has a negative impact on dewatering / 18, 129 /.

Conductivity of the solution

Conductivity or specific conductance describes the ability of a water suspension to conduct electricity. Conductivity is mainly caused by dissolution of inorganic ions (Na^+, H^+ ,Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}) to the process . In other words, conductivity is the measure of inorganic material in process waters and purity of process water. In normal papermaking conductivity values are between 20-500 mS/m. High amounts of inorganic salts in process waters increase corrosion problems, fill the surfaces of fibres and deteriorate the adsorption of retention aid chemicals. / 22 /

On the other hand, increasing the conductivity or ionic strength of the medium decreases the size of the electrical double layers of the suspended particles. The higher the conductivity, the smaller the eletrical double layer and the closer the particles can get each other without the effect of repulsive forces. If the medium has enough high conductivity, energy maximum point can be suppressed and particles get flocculated by Van der Waals forces. This can be considered advantageous in patch and mosaic making phenomena. / 21, p. 33 /

Cationic demand

The cationic demand of a system is the amount of negative charge per unit weight or volume. The higher the cationic demand, the higher the negative charge per unit. It is measured by titrating with a special apparatus or using a colloidal titration procedure. When system is over-cationized with coagulants, it is also possible to measure anionic demand. / 5, p. 161 /

pH

In conventional papermaking pH areas, fibre charges arise from sulphonic and especially from carboxyl groups. As can be seen from the figure 23, pH has a strong effect on dissociation of the fibre charge-producing groups. Thus, variations in pH have an impact on surface charge of fibres and their electrokinetics, which causes variations in adsorption of retention aid chemicals and retention. / 18, p. 16 /

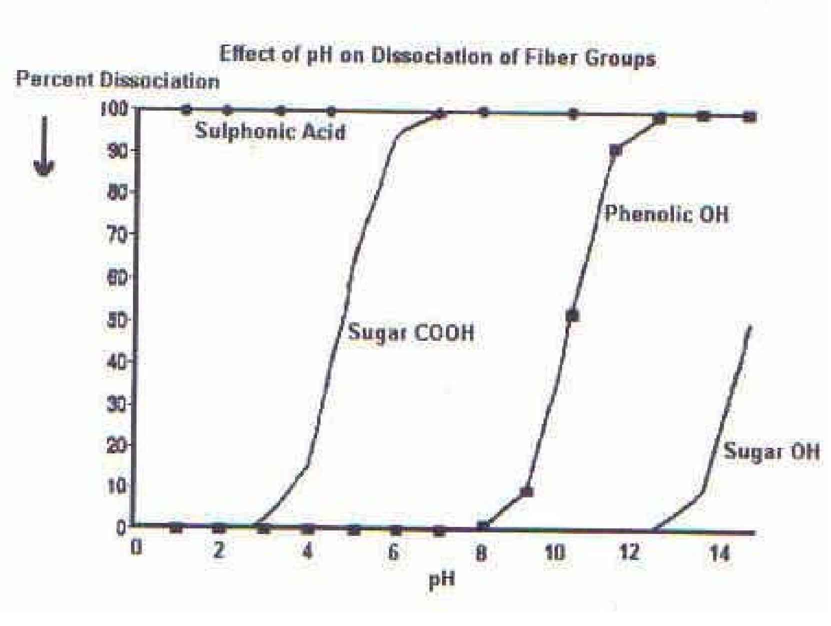

Figure 23 The effect of pH on the dissociation of fibre charge producing groups / 18, p. 16 /

When pH declines, the amount of H^+ charges increases in the stock and the charge of the fibers changes into cationic side. When pH increases, the amount of OH^- groups increase and the charge of the fibres moves into the anionic side. It is especially important to avoid pH variations from the acidic side to the alkalic side, because simultaneously the degree of ionization of carboxyl groups increases four-fold. This means that fibre surface charge magnitude and cationic demand of fibres will increase with corresponding amount, which causes heavy changes in retention. / 17, p. 8,16, and 50-51 /

Situation with pH can be seen also from other direction. It can be used as a tool to modify surface charge by changing the degree of ionization of surface carboxyls by changing pH / 17, p. 17 /.

Temperature

Chemical reactions, which take place in paper machine wet end are dependent on temperature. Temperature affects the solubility of chemicals, reaction rates, viscosity of water and dewatering speed, and functioning of most chemicals. Because temperature affects solubility of chemicals and reaction rates, variations in temperature can cause precipitation problems in paper machine wet end. / 10, p. 219 /

Interfering substances

Interfering substances or in other words anionic trash or cationic demand, consist of colloidal or dissolved anionic material, which may arise from the contaminants of fresh water, pulping or bleaching residuals, or broke (table 4). All these sources are not present at every mill. / 17, p. 41 /

Dirty process increases the cationic demand of the system i.e. the amount of polymer to achieve required first-pass-retention level. The most common practice to avoid the problem is to neutralize anionic substances with a high charge-neutralizing agent like alum or low molecular weight high charge density polyelectrolyte before the addition of cationic retention aid chemicals. / 17, p. 41 /

Table 4 Sources of interfering substances / 17, p. 41 /.

Fresh water
Calcium and water hardness
Acidity and alkalinity
Organic matter
Suspended solids
Residual chlorine
Pulping residuals
Alkanity or acidity
Sodium salts
Rosin soaps
Fatty acid soaps
Lignin compounds
Pitch
Calcium carbonate carryover in white liquor
Bleaching residuals
Alkalinity or acidity
Sodium salts
Calcium ion from calcium hypchlorite
Alkali-soluble cellulose and hemicelluloses
Lignin compounds
Broke or DIP
Starch
Adhesives
Inks
Miscellanous contaminants

5.6.5 The effect of time

The effect of time can be considered advantageous or disadvantageous depending on the chemical used and the effect targeted. Agglomerants need time to react with furnish component, but the situation is different with the flocculants, which are added as close to the headbox to reach the best possible response. / 6, p. 25 /

When cationic polymer is mixed with the fibres, polymer adsorption takes place within a couple of seconds. Figure 24 shows the Langmuir adsorption isotherm, which illustrates the adsorption of polymer versus time. Even though the shape of the curve looks the same, the equilibrium retention level vary between the systems and is dependent on the polymer and fibre characteristics, chemical circumstances, and physical environment of the system / 18, p. 27 /.

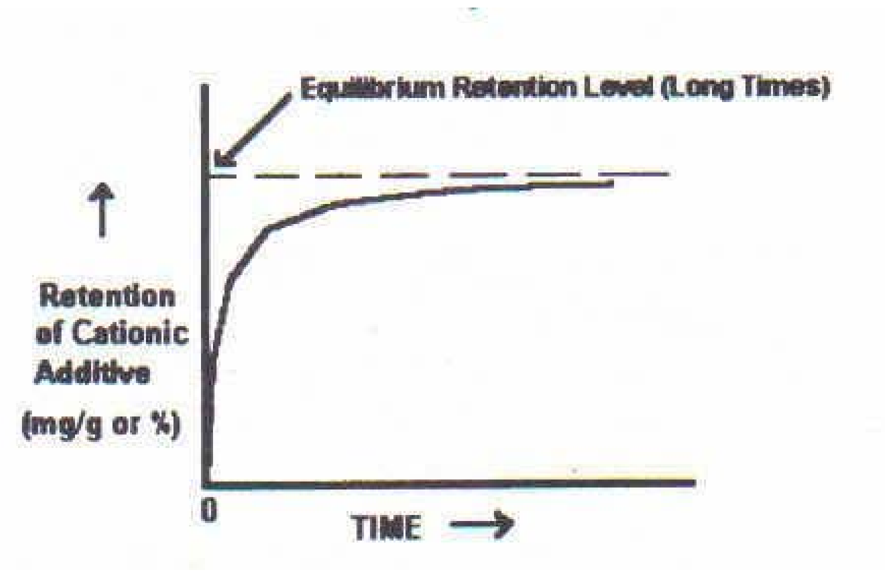

Figure 24 The dependence of adsorption of cationic polymer on time / 18, p. 27 /.

Polymer-fibre interaction vs. time

Once the polymer is mixed into the stock, the reaction with the fibres consists of three-stages. First, within a couple of seconds occurs adsorption (figure 25), which often involves contact by only s small part of the polymer chain. Polymer reconformation begins immediately after adsorption, in which previously extended particles move closer to the fibre surface and form a more flat layer onto the particle. The third stage is diffusion of the polymer into pores of the particles. Once the polymer has diffused into the pores, it no longer takes part in the electrochemical reactions on the particle surface / 18, p. 118 /.

The reconformation of polymer molecules by diffusion on the particle surfaces is relevant in the time scales of preparation and storage of e.g coating colors, printing inks, and sizing emulsions. All in all, the times involved in papermaking on a paper machine are usually very short. / 19, p. 229 /

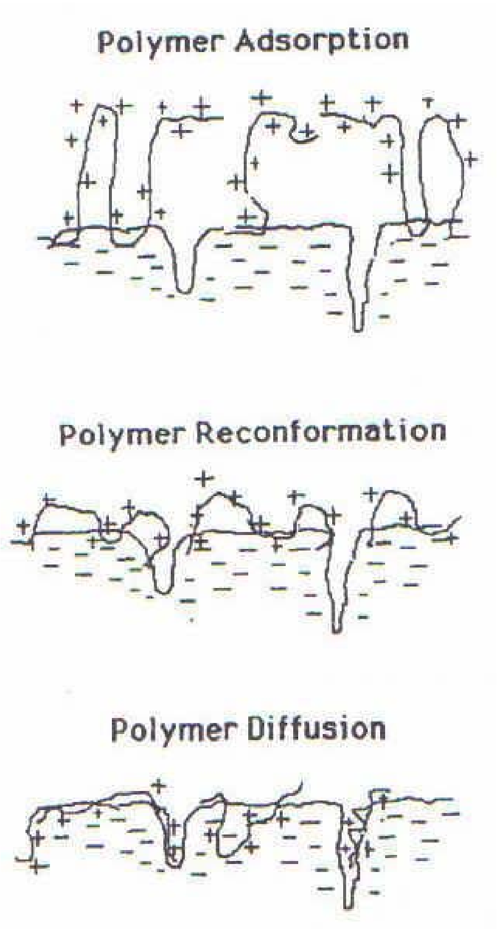

Figure 25 The interactions between polymer and fibres / 18, p. 118 /.

Polymer adsorption, reconformation, and diffusion occasions can be followed by measuring z-potential. Figure 26 shows, how the initial adsorption of the polymer make a sharp peak into the z-potential value, which is then rapidly declining during the reconformation process. The higher the molecular weight of the polymer, the higher the response. Also the initial slopes of charge decay curves are inversely related to the molecular weights. The surface charge of the fibres has also an impact on the curve: The the greater surface charge, the faster charge decay / 18, p. 118-119 /.

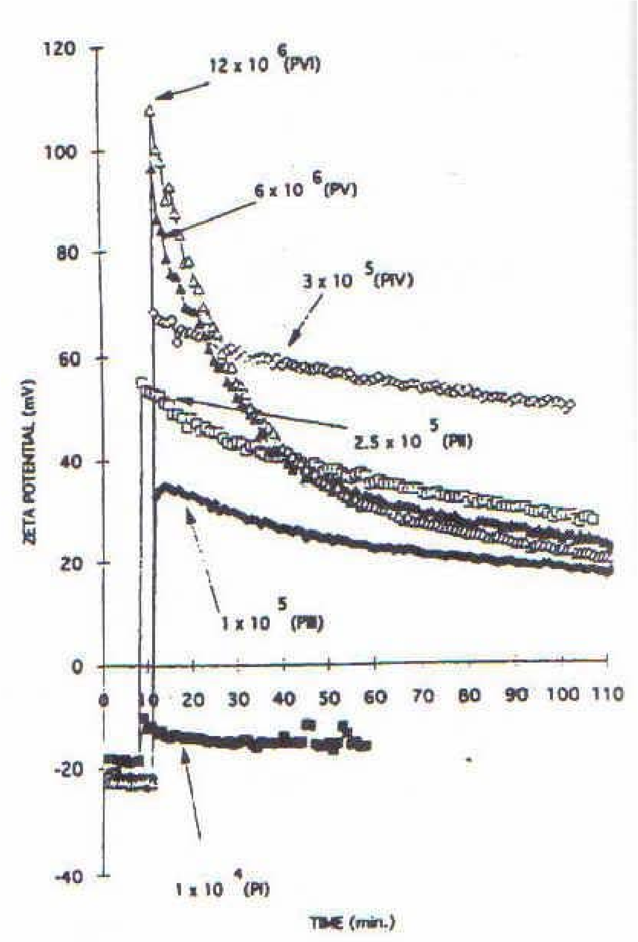

Figure 26 The charge decay phenomena of different polyelectrolytes / 18, p. 118 /.

5.6.6 The effect of shear forces

Like higher temperature, higher shear forces can be considered an energy input, which can help colloidal particles to flocculate / Winters, p. 33 /. High shear forces increase the amount of collisions between the fibres and polymer molecules and thus improve the flocculation result / 18, p. 229 /.

The term “shear” used in the context of papermaking means the same that the term “mixing time”. The greater the shear, the greater the mixing time. The effect of shear is dependent on the chemical used and the effect targeted. Agglomerants are used to control the anionicity of a given furnish, and they need more mixing to get the effect.

On the other hand, flocculants are added as close to the headbox to avoid the effects of shear and to get only the first reaction as well as possible. / 6, p. 25 /

Reflocculation phenomena

Shear forces can be so strong that they brake flocs. Flocs can be divided into soft flocs and hard flocs by their ability to resist the disruption of shear forces. Soft flocs are formed when low molecular weigth polyelectrolytes are used to produce aggregation in charge neutralizing or mosaic making systems. Under the influence of shear forces, the soft flocs break up and the polyelectrolyte sticks to the other surface. When the influence of shear forces decreases and particles are allowed to reflocculate, soft flocs reach the original level of retention. Soft flocs provide a good fines retention at a low level of turbulence and shear. / 17, p. 17 /

Hard flocs are formed when high molecular weight polyelectrolytes adsorb on the particle surfaces and form flocs through bridging mechanism (figure 27, a and b). Hard flocs provide a high level of first-pass retention and stability against shear forces for a short period of time. Extended exposure to shear forces breaks the bridges and a polyelectrolyte or part of it remains on the surface (c). When particles are allowed to reflocculate, they will act like particles covered with low molecular weight polyelectrolyte (mosaic model) and reflocculation happens via soft floc mechanism (d). As a conclusion, hard flocs tend to show good fines retention over a wide range of turbulence for a short periods of time, but longer exposure will cause decrease in retention. / 17, p. 17-18 /

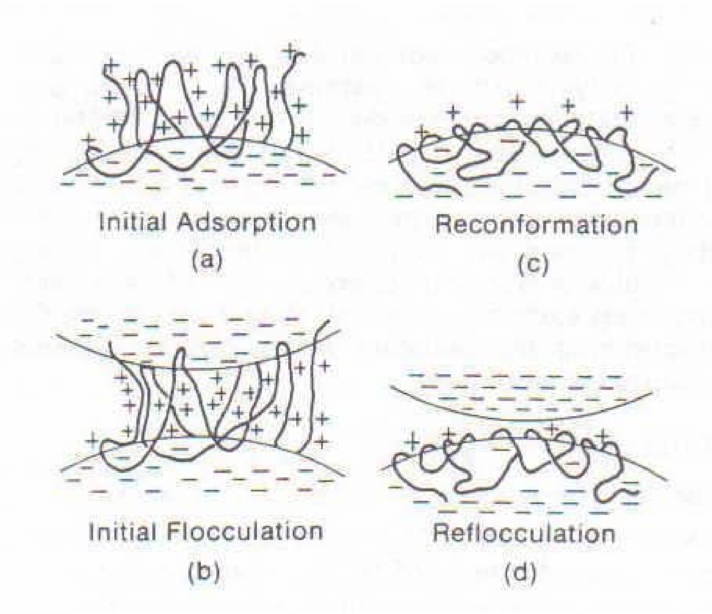

Figure 27 The reflocculation phenomenom / 17, p. 17 /.

As can be seen from the figure 28, reflocculation of hard-floccing system is also dependent on the dispersion-reflocculation times. Once the hard flocs have been broken, they will not reach their original strength. They will get weaker time after time and approach the behaviour of soft floc system. The solid curve in the picture represents the system without polyelectrolyte addition. / 17, p. 18 /

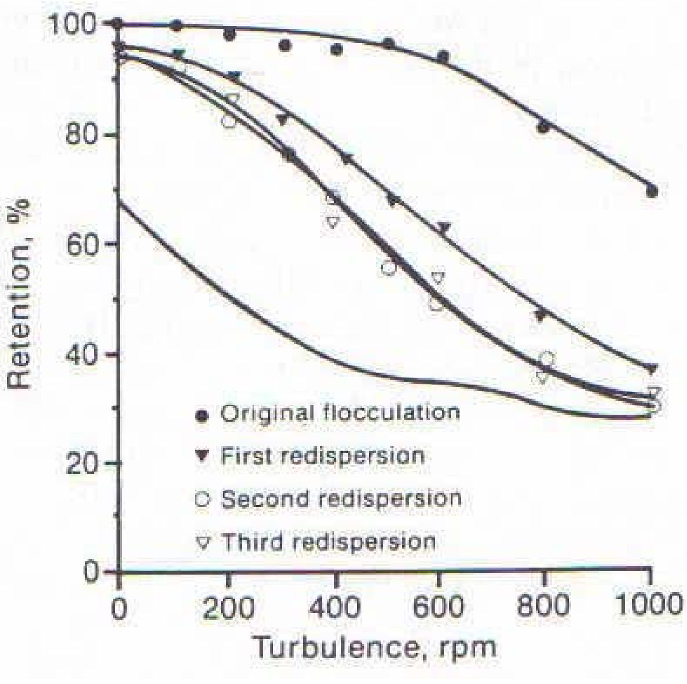

Figure 28 Flocculation- dispersion behaviour of hardfloccing polyelectrolyte system / 17, p. 18 /.

5.7 Operating principles of retention aid chemicals

5.7.1 Definition of coagulation

Figure 29 illustrates, how in coagulation or in other words agglomeration the small particles are first attached into the fibers, after which fibres are retained mechanically on the wire / 6, p. 14 /.

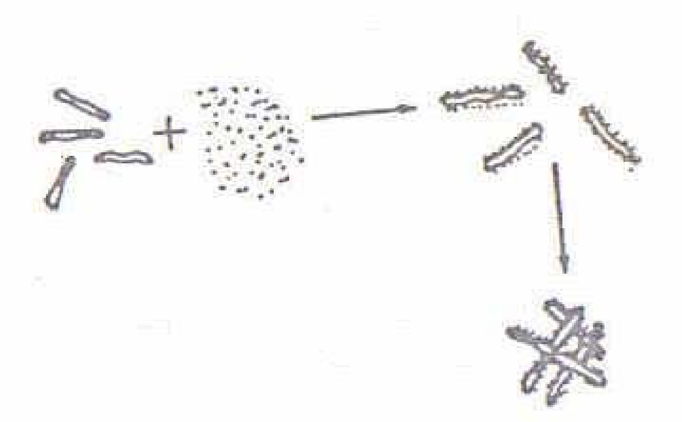

Figure 29 Illustration of retention of colloidal material by coagulation / 6, p. 14 /.

5.7.2 Coagulants

Besides the properties of fibers and fines, the properties of retention aid chemicals define strongly the quantity and quality of flocculation. Retention aids can be divided into coagulants and flocculants by their charge density. Coagulants are polymers, which have a very high cationic charge density, which is supposed to neutralize the charges of the particles. Common examples of coagulants are alum, polyamines, polyDACMACs, and polyethyleneimine (PEI) / 5, p. 161 /. Conventional coagulation phenomena are charge neutralizing, heterocoagulation, and mosaic making / 18, p. 119 /.

5.7.3 Definition of flocculation

It can be seen from figure 30 that flocculation is gathering the small particles first together into a macroparticle (1) with the help of retention aid chemical. Fibre mat (2) can then mechanically retain (3) the macromolecules / 6, p. 14 /.

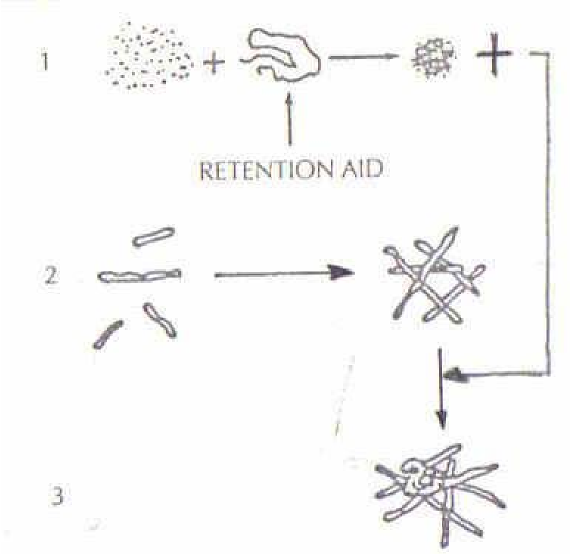

Figure 30 Illustration of retention of colloidal material by flocculation / 6, p. 14 /

5.7.4 Flocculants

Flocculants are polymers with certain charge, which can be cationic, anionic, or nonionic. In addition to that, they have a very high in molecular weight. Common examples are polyacrylamides (PAM) and polyethyleneoxide (PEO) / 5, p. 161 /. Conventional flocculation phenomena are flocculation by bridging and network flocculation / 18, p. 119 /.

5.7.5 Flocculation by bridging polymers

Flocculation by bridging is the most common macroflocculation method. In bridge formation (figure 31), the polymer adsorbs onto particle surface forming a series of extending loops and tails, which extends at least twice further than the electrical double layer (a). Flocculation (b) occurs when these loops and tails react with other negatively charged particles. / 18, p. 26 /

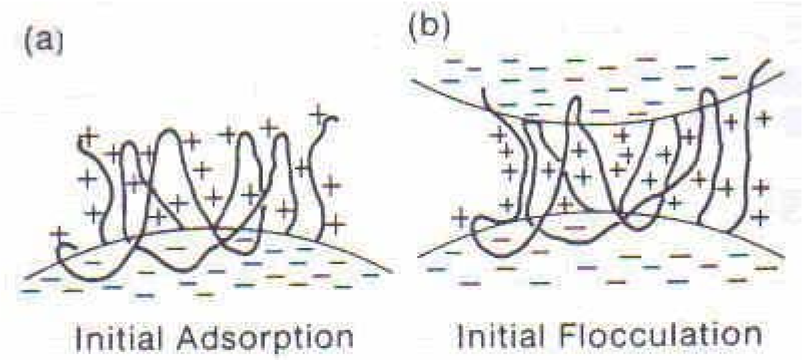

Figure 31 A schematic presentation of bridging flocculation / 17, p. 5 /.

The polymer must have a high molecular weight and a linear structure to allow bridging. These polymers are called macroflocculants and they can be divided into two different categories based on their molecular structure: polyacrylamides (PAM) and polyethylene oxides (PEO) / 5, p. 169 /.

Charge density and molecular weight are very important for bridging polymers. Higher molecular weight increases bridging because longer polymer chains can extend further from the surfaces. Polymer charge density affects the attraction between the polymer and the particle surfaces. The higher the polymer charge, the stronger the agglomerates. / 18, p. 26 /

5.7.6 Charge mosaic model

In mosaic making model (figure 32), or in other words patch model, short chain, cationic, high charge density polyelectrolytes are mixed into the water suspension including anionic particles. The polymer molecules forms a positively charged patches onto particles. After the adsorption, the collision between the positively charged patch and negatively charged particle surface leads to the coagulation. / 18, p. 25 /

Mosaic making is charge neutralizing phenomenom, which produces closely packed aggregates which provides good drainage and even sheet structure / 18, p. 26 /.

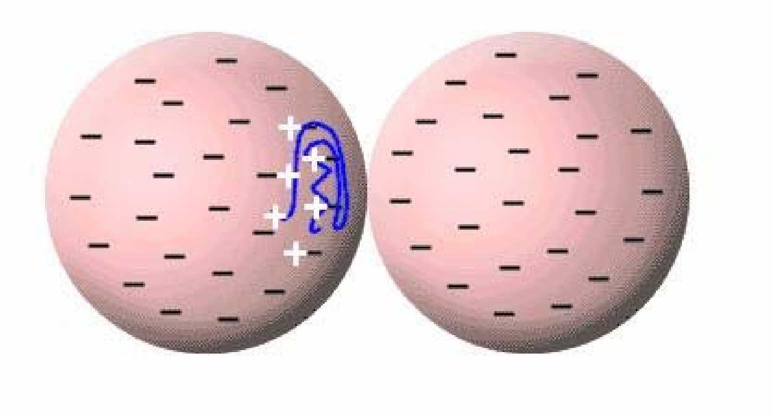

Figure 32 A schematic representation of mosaic making model / 23 /.

5.7.7 Coagulation by charge neutralization

Electrical double layer of the particles has a certain thickness depending on the chemical circumstances. The thickness of the double layer can be decreased by increasing the availability of counterions by adding electrolytes into the water suspension. Increased amount of counterions decreases the z-potential and the repulsive component of the total force, after which particles can more easily approach each other and make aggregates. Coagulation by this kind of mechanism is called charge neutralization, because it moves the net potential towards zero charge / 18, p. 25 /

There are two important points concerning charge neutralization method. Firstly, the critical concentration of salt, on which the double layer is suppressed enough for coagulation to progress.This concentration is normally called the *critical coagulation concentration*. Second issue is the relative effectiveness of different cations in decreasing the size of double layer for anionic particles. The higher the valence of neutralizing ion, the more effective the ion is in decreasing the surface charge. / 18, p. 25 /

Coagulation produces tight aggregates, in which particles are close to each other. Such aggregates drain well and forms even sheet structure / 18, p. 25 /.

5.7.8 Dual systems

It is often possible to get advantages by combining the effects of several retention agents, which interact electrostatically. Figure 33 presents an example about dual polymer system, in which a low molecular weight, high charge density cationic polyelectrolyte is added first forming cationic patches onto the particles. It is followed by a high molecular weight, low charge density anionic polyelectrolyte, which adsorbs onto the cationic patches. Negative charges on particle surfaces make anionic polymer to reach out from the particle surface. Then the extending anionic polymer chain reacts with a positive patch on another particle and form a strong link between the particles. Sequential addition of two polyelectrolytes with opposite charges has found in practice to make very tenacious flocculation. / 18, p. 122 /

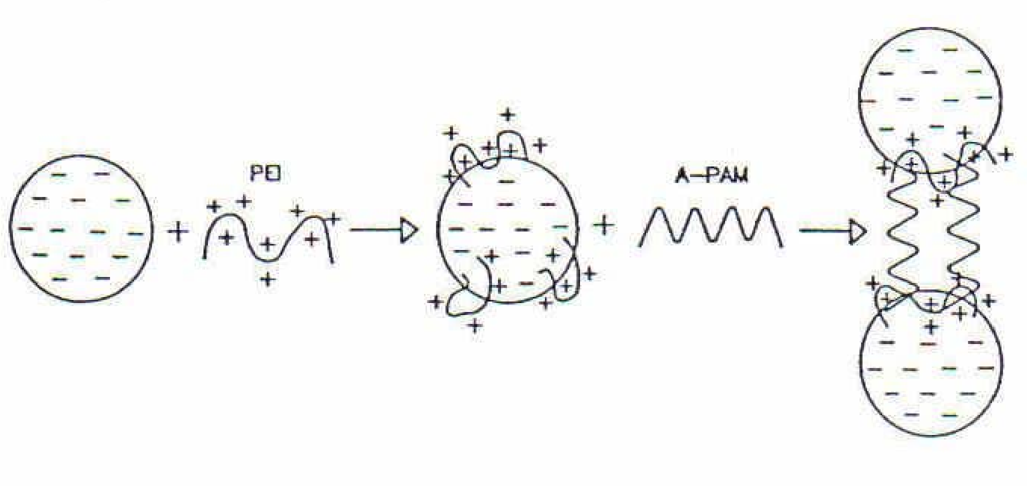

Figure 33 Flocculation with typical coagulant-PAM system / 18, p. 122 /.

5.7.9 Micro- and nanoparticle flocculation

Coagulation and flocculation have their own operating principles and their own disadvantages. Coagulation creates small reversible structures which can give good drainage and formation, but poor retention. Macroflocculation creates large agglomerates, which deteriorates the drainage and formation when targetted to high retention. The micro- and nanoparticle technique was developed to avoid the disadvantages of coagulation and macroflocculation. It allows a high first pass retention, an improved formation, and increased drainage, which gives an opportunity to save energy . In addition to that, method is not remarkable dependent on pH and the z-potential of the system. / 5, p. 175; 7, p. 33 /

Figure 34 demonstrates the chemical phenomenom in micro- and nanoparticle flocculation. Microflocculation utilizes two components. First component is cationic, which has coagulation or flocculation capabilities and gives cationic sites into the stock. This component makes flocs by bridging. Flocs are then broken with hyrodynamic shear forces and the molecule chain attaches more closely to the particle surfaces, after which bridge making is not possible anymore. / 6, p 175 and 7, p. 33 /

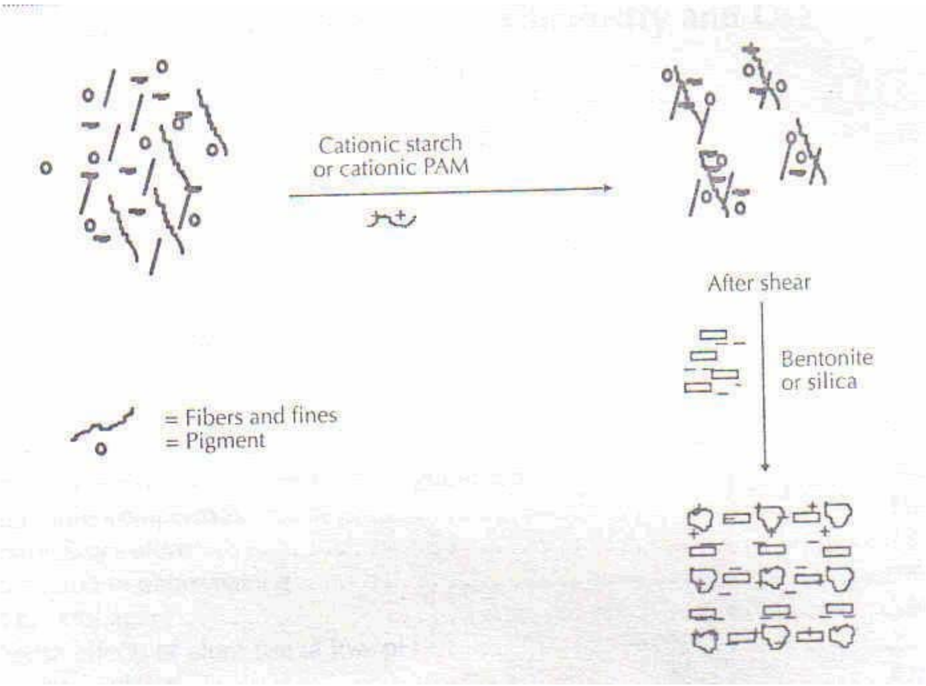

Figure 34 Demonstration of micro- or nanoparticle flocculation technique / 5, 175 /.

Second component is a very small microparticle, which is negatively charged and because of that, capable of attaching itself to the stock anionic sites. The two most widely used microparticle systems are:

-cationic starch and/ or cationic PAM with colloidal silica
-cationic coagulant and/or cationic PAM with hydrated bentonite. / 5, p. 175 /

5.8 Retention aid chemicals

5.8.1 Cationic starches

Starch is formed as a result of photosynthesis in green leaves and plants. First glucose and oxygen are formed from water and carbon dioxide. Then starch is formed in condenstation polymerization of glucose with the help of starch synthetizing enzymes as follows:

$$nC_6H_2O_6 \rightarrow (C_6H_{10}O_5)n + nH_2O \qquad (8)$$

The biopolymer starch is a polyglucoside like cellulose and it is build up from anhydro glucose units. As can be seen from the table 5, the starch content of all raw materials is about the same, while other components vary in some extent, which explaines the differences between the properties of starches / 4, p. 199-201 / When the starch is isolated from its source, modifications of native starches are carried out to provide starch products with the properties required for different end-uses. One of the modifications is cationization, in which either tertiary or quaternary amine groups are added to made it cationic / 18, p. 54 /. Despite the modifications, the distinctive composition and properties of raw material is clearly present also in the modified starches / 4, p. 213-214 /.

Table 5 The chemical composition of starch raw materials in weight percentages / 4, 201 /.

Source	**Starch**	**Moisture**	**Protein as Nx6.25***	**Lipids**	**Fiber**	**Starch on dry subst.**
Potato	17	78	2	0.1	1	77
Dent corn	60	16	9	4	2	71
Wheat	64	14	13	2	3	74
Tapioca	26	66	1	0.3	1	77
Waxy Maize	57	20	11	5	2	71
*N=Nitrogen content						

When searching for the differences between the commercial starches, the special attention must be paid into the starch granule properties, composition of starch granules, amylose and amylopectin content, and gelatinization characteristics. / 4, p. 199- 220 /.

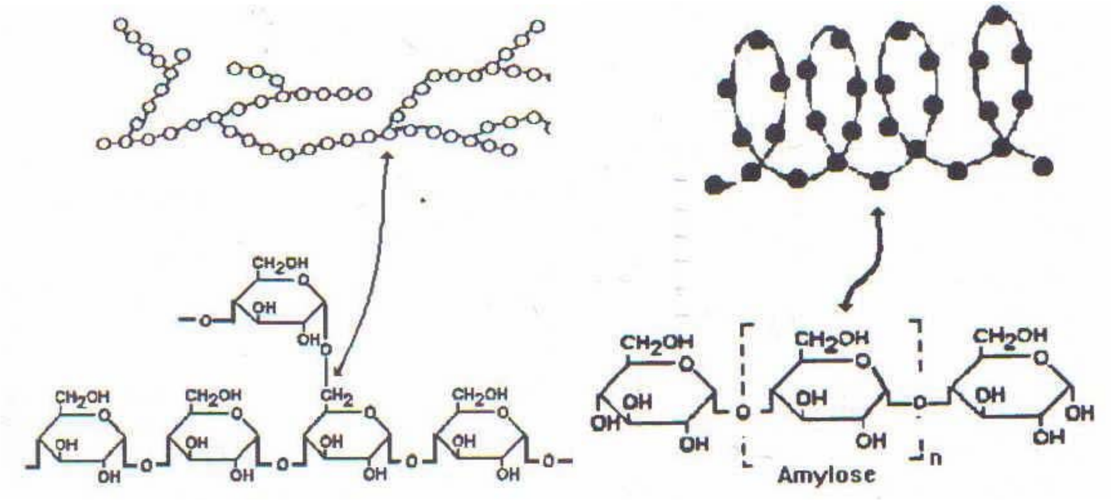

Figure 35 Starches include branched amylopectin (left) and linear amylose / 18, p. 52-53 /.

The majority of starches are mixtures of branched amylopectin and linear amylose (figure 35). These components are different in water dissolution and that is why high amylopectin starches are used more in wet end addition. / 18, p. 53 /

The main principle is that synthetic cationic starches affect the cationic demand of the system acting as coagulants by neutralizing the anionic groups in the solution. The ability of a starch to neutralize charges is dependent on the cationicity of the starch i.e. the amount of cationic groups included in the molecule and its molecular weight. When regarding starches, the typical term for cationicity is the degree of substitution. / 5, p. 164 /

The role of cationic starches in bentonite microparticle system

If strength requirements are low, bentonite microparticle system does not require cationic starch to work. Then no starch or a low dose of cationic cornstarch will provide sufficient strength. The combination of polycrylamide and bentonite can be used alone for fine particle retention. There are still conditions where cationic starch should be included into the system like high strength or retention requirements, systems which cannot tolerate high amounts of cationic polymer, or with such low shear forces, which cannot brake high molecular weight polymer / 6, p. 95 /.

The performance of organic polymeric microparticle system is dependent on the properties of starch including starch cationicity, starch type, and starch molecular weight / 1, p. 95 /.

5.8.2 Polyacrylamides (PAM)

Polyacrylamides can be cationic, anionic, or nonionic by charge and they have a high molecular weight. The simplest way to utilize poyacryamides in flocculation is to use cationic polyacrylamides to the negatively charged fibre fines. When cationic PAM approaches negatively charge particles, it is adsorbed by electrostatic forces. In addition to that, it can help in compressing the electrical double layer, but is is not the main role of cationic PAM. / 5, p. 171 /

Anionic and nonionic PAMs act as retention aids by more complex mechanisms. Nonionic PAMs have a slightly anionic charge in water suspension and therefore behave like anionic products. Before treating with anionic PAM, it is important that particles have some kind of charge neutralization with a coagulant, which can already be present in the solution or added specifically for this reason. When particles are treated with anionic PAMs, it adsorbs onto cationic sites of the particles and links the particles by bridging. Because the double layer is thicker than with cationic PAMs, a longer molecule i.e higher molecular weight is required. / 5, p. 172 /

The role of cationic PAMs in bentonite microparticle system

The cationic polyelectrolyte is added early into the thin stock normally at dilution or just after it. Cationic PAM first adsorbs onto the fibres and fines in a basic tail and loop configuration. To ensure that all small fines are totally covered with PAM, its addition level is quite high. Because the surfaces of fines is covered with cationic polymer, the agglomeration between the particles is minimized. / 1, p. 88 /

When the PAM covered particles are under high shear forces in pumps, cleaners, and screens, the shear forces deflocculate the aggregates that might have been formed in reactions between the loops and tails and fines. The shear forces also reduce the molecular weight of the adsorbed polymer and disperse the fine particle suspension. However, they cannot remove the particles from fibre surfaces. The dispersed fines coated with cationic polymer will be then retained by the addition of bentonite and the particles on fibre surfaces are retained with fibres. / 1, p. 88 /

5.8.3 Bentonite

Bentonites are aggregates of two or more minerals. The key mineral used for making bentonite microparticles is smectite, or montmorillonite, which has a di-octaedral structure. When montmorillonite crystal is placed in water suspension, it takes a strong negative charge, because its cationic metal ions diffuse away. This ability of cationic metal ions to diffuse away makes the electrical double layer and colloidal character of bentonite. Because bentonite clay has colloidal nature, high surface area and high charge density, it can be used to change significantly the charge density of wet end / 1, p. 85 /

In paper industry, bentonites are used as binding agents and rheology modifiers in paper coating applications, as a mineral filler in acid papermaking, in deinking and waste water treatment applications, an as drainage and retention aids in alkaline papermaking. However, the type of bentonite used in microparticle systems is quite different from the bentonites used in other papermaking areas / 6, p. 85 /.

Role of bentonite in microparticle system

If bentonite was not added into the microparticle system, the fine particle retention would be quite low, because dispersed fine particles are totally coated with cationic polymer and the whole system chemistry is on the cationic side. The high surface area and high anionic charge changes significantly the ionic character of the system and neutralizes the surface charges of fines-PAM agglomerates. The result is collapse of the electrical double layer of fines and formation of microfloc structure by coagulation / 1, p. 89 /

5.9 Chemical dosing points

Chemical dosing points in general

Dosing point of a chemical is dependent on the chemical used and the effect targetted. The critical factors with agglomerants, which are low molecular weight, high charge density polymers, are to get the chemical to the desired furnish component and to give the chemical sufficient time to react to get a stable product. If agglomerants are used to control anionic resins, they are added to the furnish going to the refiner. When agglomerants are used to control the anionicity of a furnish component, they are fed into the furnish component between the broke chest and machine chest. / 6, p. 25 /

Flocculants are added as close to headbox as possible to minimize the mixing and to get only the first interaction with the polymer and fines. With flocculants, the target is not to get a stable impact, but just the first interaction. / 6, p. 25 /

Chemical dosing points in microparticle system

Figure 36 illustrates the possible chemical dosing points in microparticle systems. As can be seen from the figure, there are several options for the points and the optimal dosing points are dependent on the individual machine dynamics and the microparticle system applied. There is not a common point where cationic starch is added, because it is dependent on the starch requirements, the microparticle system applied, and which variables are targetted. For example, the addition into the thick stock prior to other additives is possible, if corn starch is used for strength, but if the high molecular weight starch is used for drainage, retention, and strength, the addition point is more critical. Sometimes it is even necessary to have two dosing points for starch. / 1, p. 97

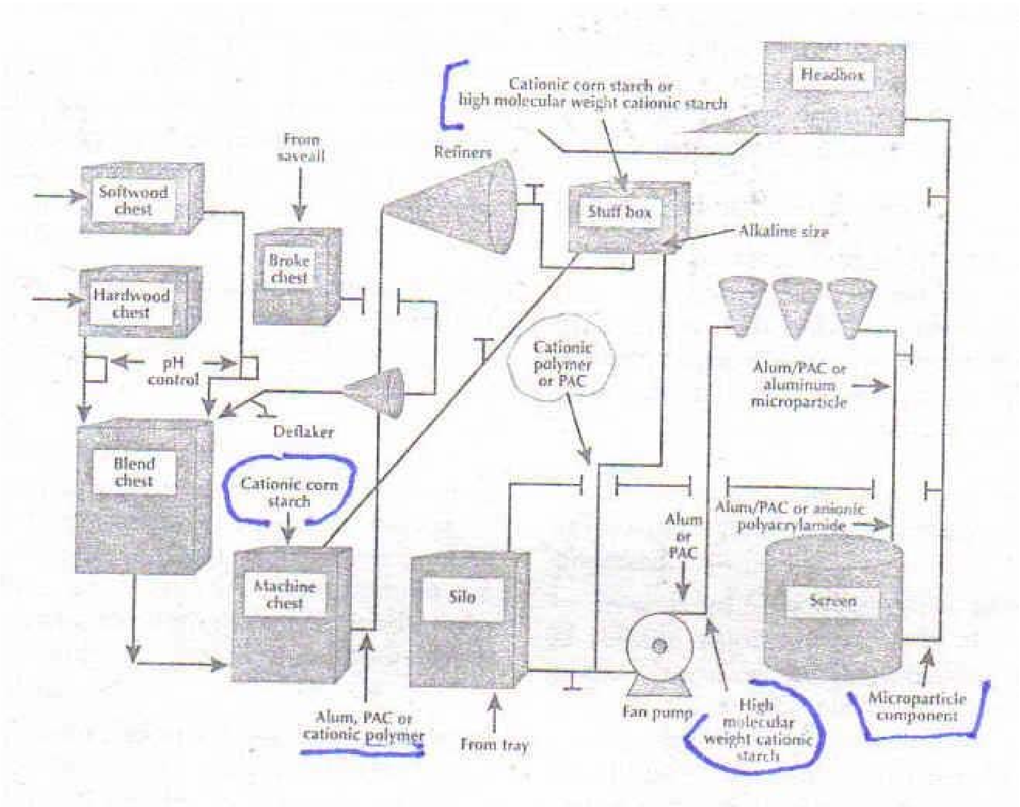

Figure 36 The chemical dosing points of microparticle system / 1, p. 97 /

The addition point of polyelectrolyte polymer retention aids is highly dependent on the system applied, but in the organic micropolymer or bentonite systems the polymer addition point is critical. The high molecular weight polymer must have time to be under shear forces, thus they are often added to the stuffbox or into the primary fan pump inlet. / 1, p. 97 /

The microparticle additive is almost always added last into the system. Bentonite, colloidal silica, and other microparticle additives are added directly after the screens. An exception about this is colloidal alminium hydroxide, which needs more dwell time. / 1, p. 97 /

Experimental part

6 COMPARISON OF FRESH PULP AND BROKE WITH HANDSHEETS

6.1 Target of the study

The study with the handsheets was accomplished to find out the effect of selective chemical pre-treatment of fibre fractions on paper structure and properties, and to compare the differences in paper structure with fresh pulp and slushed uncalendered broke.

6.2 Furnishes

The furnishes used in this study were:

1) pure mechanical furnish from a Finnish TMP plant
2) slushed uncalendered broke from a Finnish SC paper machine including:
    -90 % TMP
    -10 % kraft pulp
    -32 % filler i.e clay.

6.2.1 Preparation of the furnishes

Because the target was to compare the properties of the furnishes, they had to be prepared in a comparable way. To reach that kind of situation, the dry uncalendered broke was slushed and the TMP was prepared to include the same amount of chemical pulp and filler as broke. In addition to that, a part of the furnishes were fractionated to make possible the further selective chemical pre-treatments.

6.2.2 Slushing of broke

Slushing of broke was done with a minislusher (figure 38), which is a special equipment used for the slushing of small furnish amounts.

Figure 38 The structure of minislusher equipment.

After pre-tests, suitable parameters for the slushing circumstances were set to be:

- consistency ~5 %
- temperature ~ 40 °C
- time 30 minutes
- rotating speed 1000 rpm

The required amount of pulp was calculated to be about 600 g meaning that, with the slusher volume of about 5 liters, the whole amount was handled with 4 slushing times.

6.2.3 Mixing of fresh pulp

To reach the situation, where TMP and broke are comparable, they have to contain equal proportions of stock components. This means, that corresponding amount of kraft pulp and clay had to be added into TMP, which was included in dried uncalendered broke. The target was to make 1000 grams of stock with a following recipe:

-10 % of refined kraft pulp
-90 % TMP.
-32 % filler.

6.2.4 Fractionation

To find out the effect of the selective chemical pre-treatment, a part of the furnishes was fractionated and a part was reserved as a stock reference. These non-fractionated furnishes are later in this report referred as whole pulps. The fractionation was done with a special laboratory device, which was similar to conventional pressure screen (figure 39). The fractionation aimed at the fibre length ratio between short fraction and long fraction SF/LF = 0,5.

Figure 39 The structure of laboratory fractionation equipment.

6.3 Chemical additives

The chemical system utilised in this study was the microparticle system meaning that three kinds of chemicals were prepared and used for making the handsheets. The chemicals and their product names are presented in table 6.

Table 6 The chemicals used in the handsheets.

Chemical	Product name
Cationic starch	Raisamyl 30021: Low DS
Cationic polymer	Percol 47: M to HMW c-PAM
Bentonite	Hydrocol SH

6.4 Preparation of the handsheets

The handsheets were made at Metso Paper Anjalankoski Fiber Technology Center between February 11-22, 2008. The measurements from the handsheet were made at Metso Paper Rautpohja Paper Technology Center between February 25-26, 2008.

The handsheets were made according to ISO 5269-1:2005 standard, except the longer mixing time (70 s) and the higher consistency. Higher consistency was due to smaller volume of the mixing chamber in the sheet former. The surface area of the bottom of mixing chamber was the same as in standard equipment, but filling was done up to 223 mm (standard 350 mm). Thus, the volume was 6,1 liters compared to 9,5 liters, which increases the consistency from 0,019 to 0,03 %.

The target was to make 6 kinds of handsheets:

1. Fresh whole pulp (WP) without chemical pre-treatment.
2. Fresh whole pulp (WP) with conventional chemical pre-treatment.
3. Fresh pulp short fraction (SF) and long fraction (LF) with separate chemical pre-treatment.
4. Broke whole pulp (WP) without chemical pre-treatment.
5. Broke whole pulp (WP) with conventional chemical pre-treatment.
6. Broke short fraction (SF) and long fraction (LF) with separate chemical pre-treatment.

The grammage target for the dry sheets was set to 60 g/m² meaning that fibre dosage per sheet (165x165 mm) was 1,64 g. A couple of pre-test sheets were made before every sheet series to find out suitable stock dosages to reach the targetted grammage. Stock dosages for the sheets were around 1,80 g.

The chemical addition times and dosing points are presented in the following pictures. Figure 40 shows the sheet forming procedure for fresh and broke whole pulps without any chemical pre-treatment. After the addition of stock into the sheet former, it was mixed 70 seconds until opening the bottom valve.

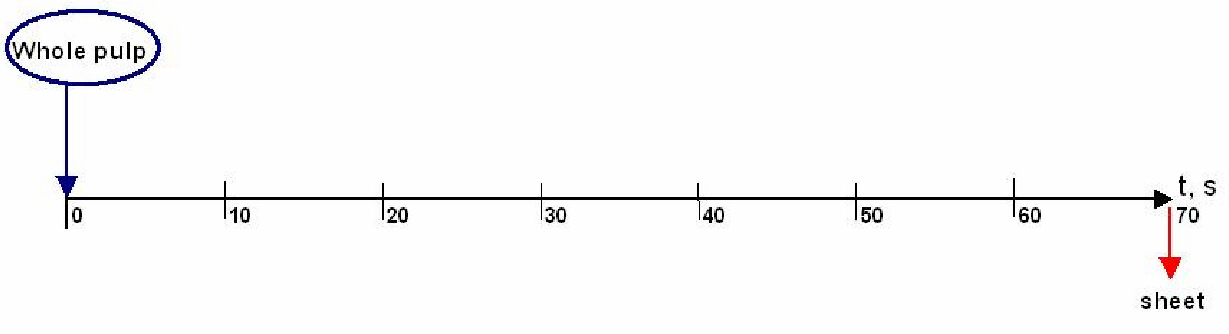

Figure 40 The sheet making procedure for whole pulps without chemical pre-treatment.

The timings for chemical dosing for the whole pulps with conventional chemical pre-treatment are presented in figure 41. Starch was added after 10 seconds of mixing, polymer after 40 seconds, and bentonite 10 seconds before opening the bottom valve.

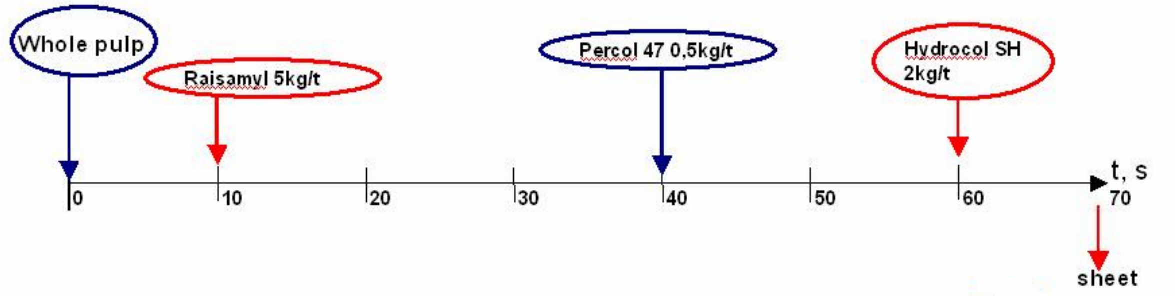

Figure 41 The sheet making procedure for conventionally chemically treatment.

As can be seen from figure 42, the procedure of chemical dosing points and timings is more complicated for selectively chemically treated fresh pulp and broke. The mixing was started simultaneously for both fractions, but only long fraction was in sheet former, while short fraction was mixed in a separate bucket. Starch was added into the long fraction after 10 seconds of mixing and polymer to the short fraction after 40 seconds. After 55 seconds of mixing, the fractions were combined. The bentonite was added 10 seconds before the opening of the bottom valve.

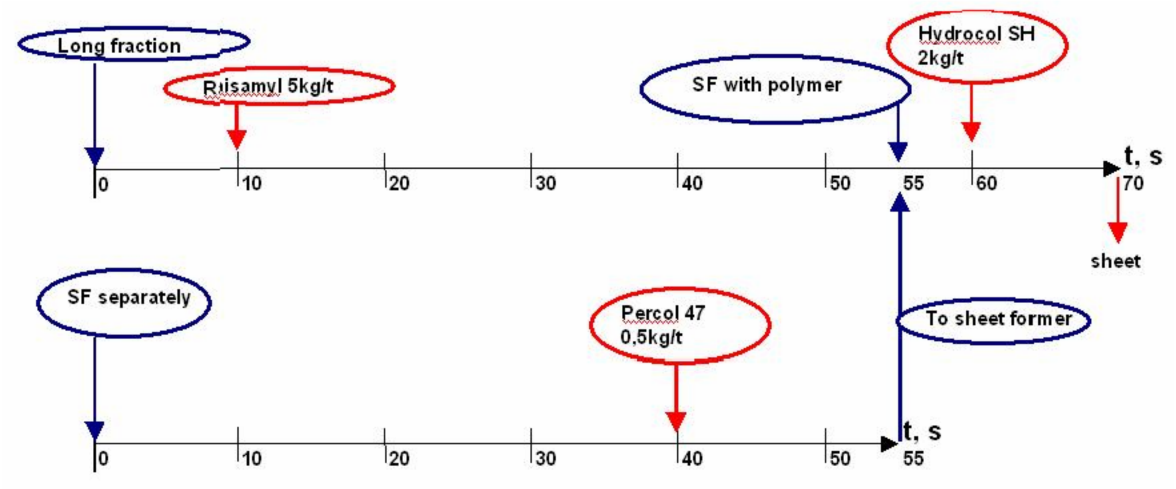

Figure 42 The sheet making procedure for selective chemical treatment.

6.5 Methods

Measurements from the sheets were done according to the following standards:

1. Air-conditioning: ISO EN 20187:1995.
2. Grammage: ISO 536:1996 Determination of grammage.
3. Caliper, density, and bulk: ISO 534:2005 Determination of thickness, density, and specific volume.
4. Ash content: ISO 1762:2001 Determination of residue ash on ignition at 525 °C. The ignition temperature used in the test was 540 °C, but it is inside the standard.
5. Formation: Values were measured with Ambertec β-formation tester and according to instructions given by the machine supplier.
6. Bendtsen air permeance: ISO 5636-3:1992.
7. Opacity: SFS-ISO 2471:2003 Determination of opacity.
8. Tensile strength: ISO 1924-3:2005 Determination of tensile properties.
9. Internal bonding strength: TAPPI T 569 pm-00 Huygen internal bonding strength.

6.6 Results

All results from the handsheet study are presented in appendix 2.

6.6.1 Basic properties

The grammage target for the dry sheets was 60 g/m², but figure 41 shows that after the air-conditioning the grammage values were around 65 g/m². The variation of the figures is so small that it was possible not to take grammage variations into account when comparing e.g formation or strength properties.

Even though, the target was to produce sheets with the same ash level from both furnishes, it can be seen from the figure that the ash content values of broke sheets ended up approximately 3% higher compared to fresh pulp. However, as a whole results seemed to be comparable.

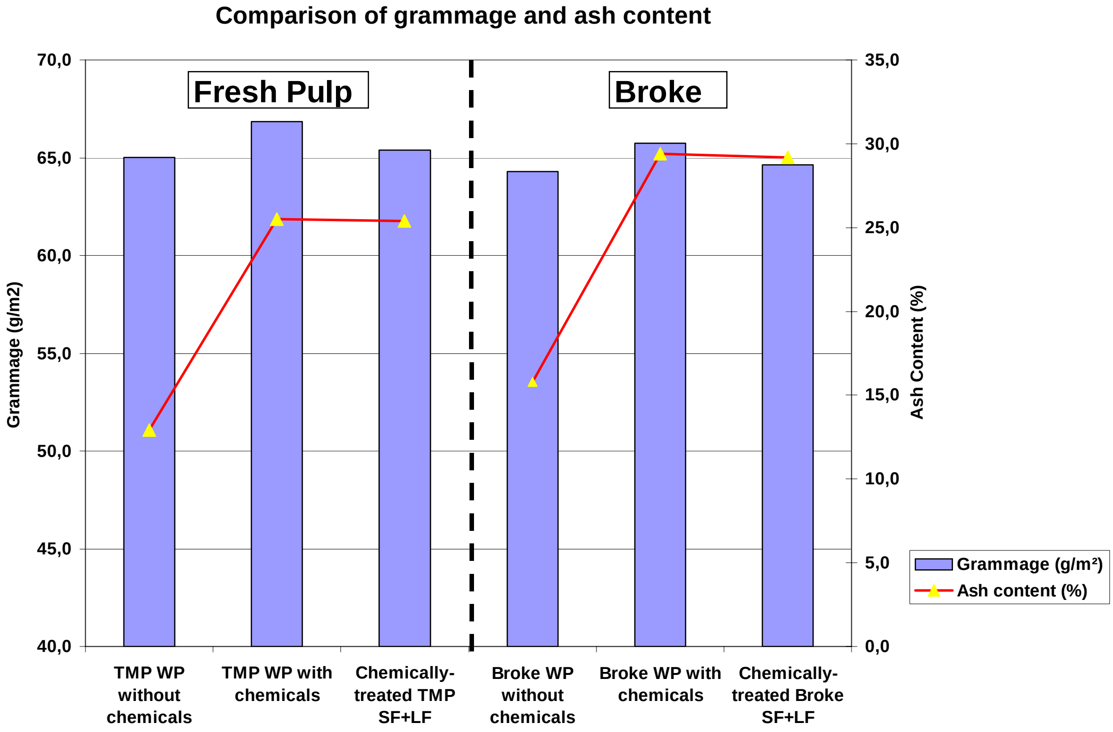

Figure 41 Comparison of grammage and ash content values from the handsheets made of fresh pulp and broke.

Figure 42 illustrates the difference of broke and fresh pulp thickness values. Broke sheets were significantly thinner compared to fresh pulp sheets, thus resulting in correspondingly lower bulk and higher density values. This can be explained by collapsing of fibres, because broke has gone already once through press nips and drying section.

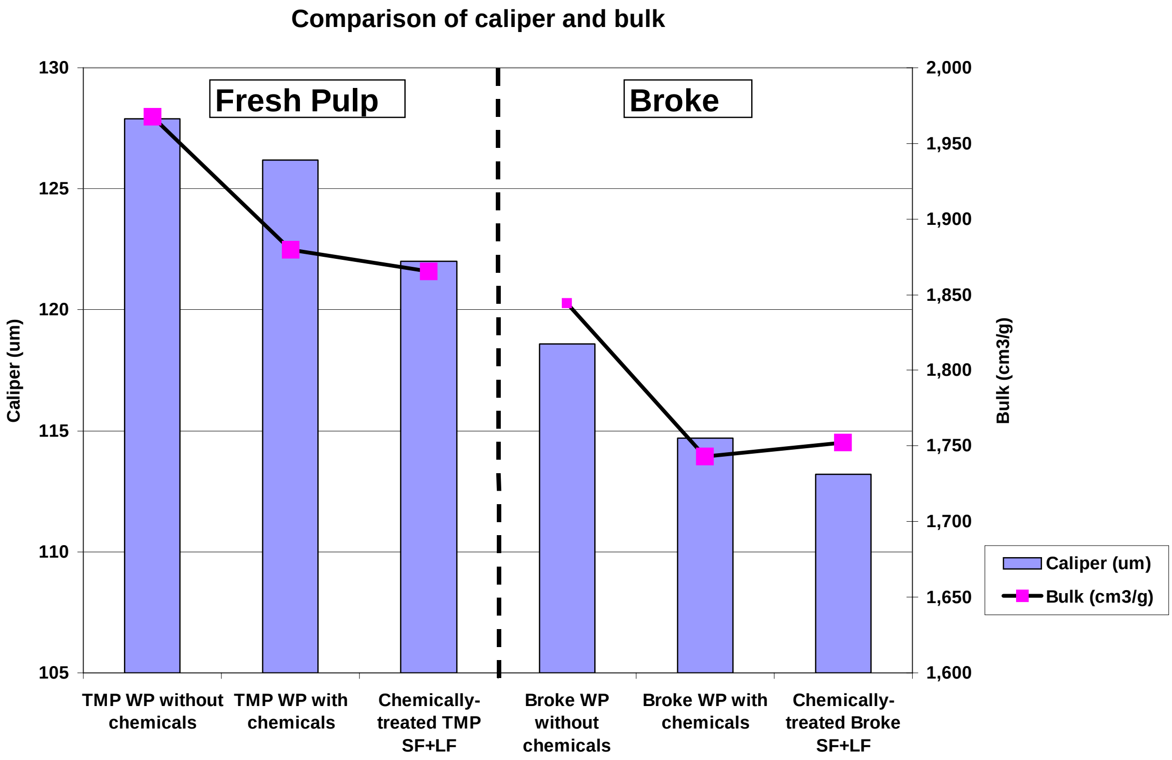

Figure 42 Comparison of caliper and bulk values from the handsheets made of fresh pulp and broke.

6.6.2 Structural properties

It can be seen from the figure 43 that chemically untreated furnishes provided the best formation values. On the other hand, it is natural that the formation values are worse with broke than with fresh pulp. It is interesting that when the fractions were treated separately, the formation values were better compared to unfractionated conventional solution. It was unexpected that fresh pulp produced worse formation values than broke, when they were conventionally chemically treated. Fractionally treated furnishes behaved normally and ended up in worse formation values with broke.

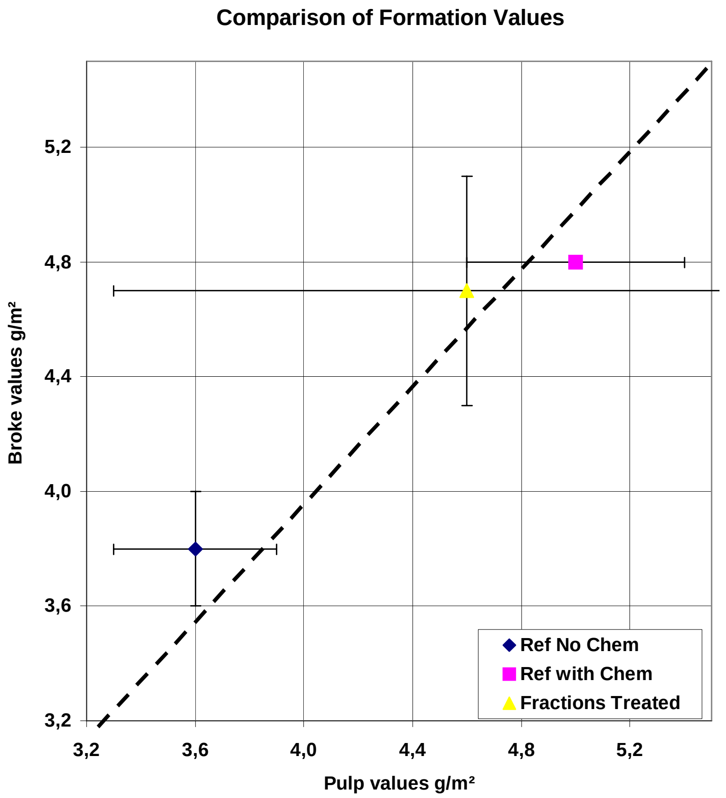

Figure 43 Comparison of formation values of handsheets made of fresh pulp and broke.

As can be seen from figure 44, the air permeance values of broke are significantly higher than the values of fresh pulp. The structure of the broke sheets is more uneven because broke fibres are never totally disintegrated in slushing. Fibre flocs create a lot of void spaces around them, which increases the air permeance values. When this kind of fibres are chemically treated, they collect more material themselves increasing their size and air permeance values. Figure 44 shows that chemical treatment and especially fractional chemical treatment, has an increasing effect on air permeance values.

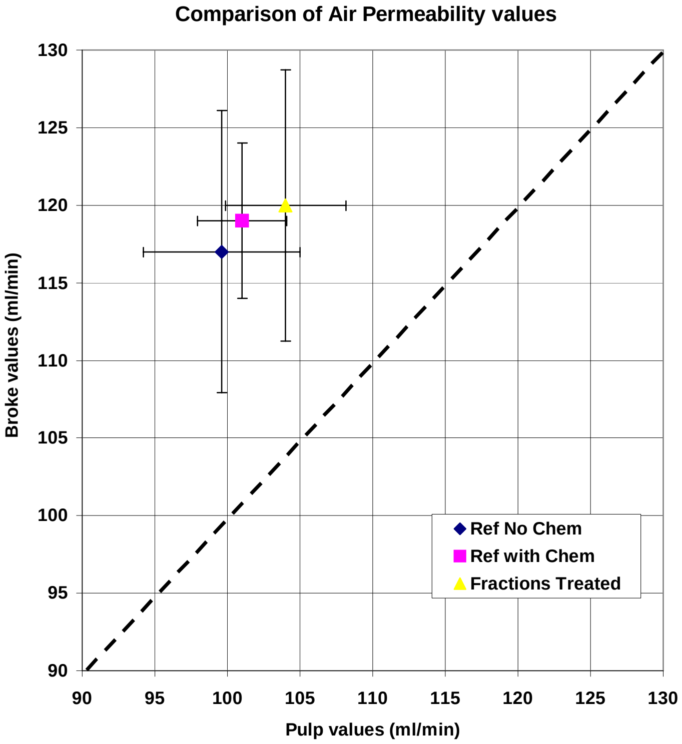

Figure 44 Comparison of air permeance values of handsheets made of fresh pulp and broke.

6.6.3 Optical properties

Figure 45 shows that the opacity values of broke sheets were significantly higher than the values of fresh pulp, which was mainly due to darker colour of the broke furnish and higher filler content of the broke sheets. There can be seen also that opacity values are better when furnishes were chemically treated. Chemical treatments (both standard and selective) increased the ash content in paper from 12-15 % to 25-29 % giving about 2 units higher opacity values. In the comparison of the treatments, conventional chemical treatment provided slightly better (ca. 0,5 units) opacity values.

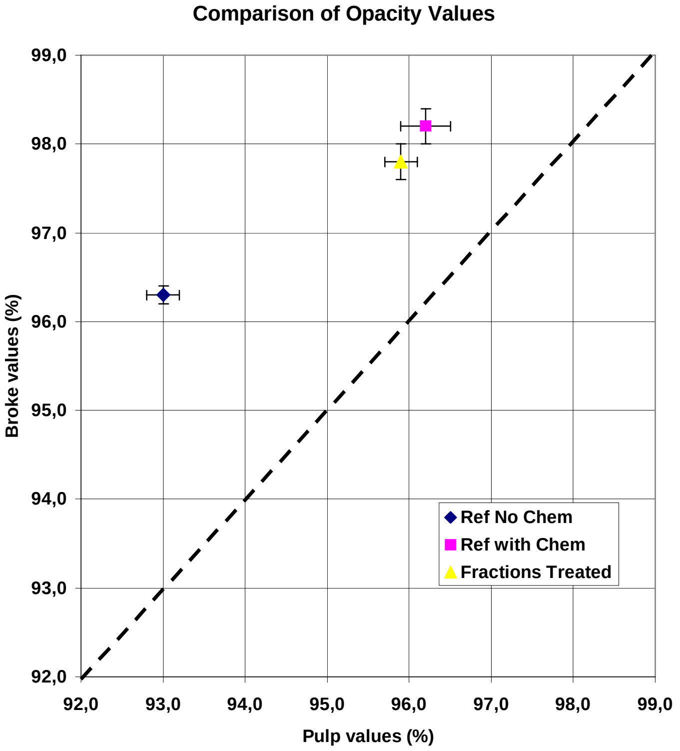

Figure 45 Comparison of opacity values of handsheets made of fresh pulp and broke.

6.6.4 Strength properties

Figure 46 shows that tensile strength values were highest with chemically untreated whole pulps, because both standard and selective chemical treatments increased filler content approximately 12-15 %. On the other hand, chemical treatments had a negative impact on formation values, which together with increased filler level may have contributed in worse tensile strength values.

Any improvement could not be seen in tensile levels between the chemical treatments, but there were some differences between the furnishes. Fresh pulp was stronger than broke with conventionally treated whole pulps. Fresh pulp and broke provided similar tensile strength properties with fractional treatment and with untreated furnishes,

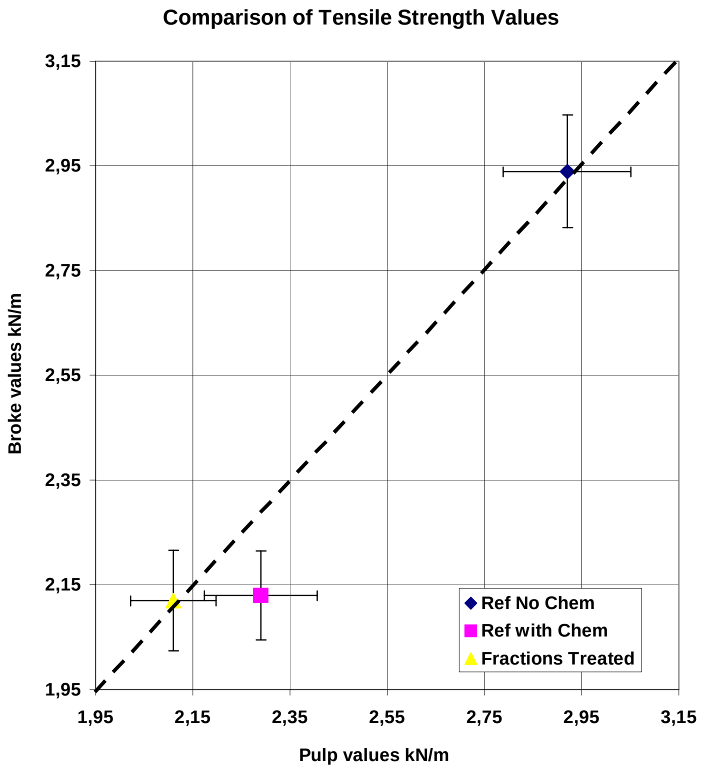

Figure 46 Comparison of tensile strength values of handsheets made of fresh pulp and broke.

Figure 47 shows that chemically untreated whole pulps provided also the best the internal bonding strength values, of which the values of broke were slightly higher. The filler content of the sheets made wit chemical treatments was significantly higher decreasing the internal bonding strength values.

When comparing the chemical treatments, any improvement could not be seen in internal bonding strength values between conventionally treated and fractionally treated furnishes. On the other hand, any significant differences could not be seen in the internal bonding strength values of broke and fresh pulp. However, fresh pulp gave clearly better results than broke with fractional treatment, but with conventional chemical treatment and untreated furnishes, the results were somewhat the same for both fresh pulp and broke.

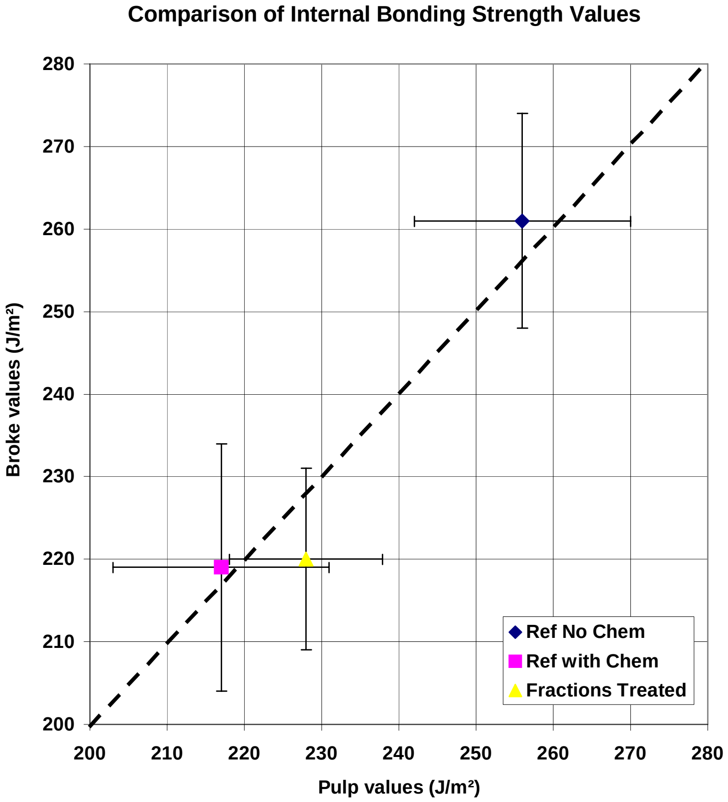

Figure 47 Comparison of internal bonding strength values of handsheets made of fresh pulp and broke.

6.7 Conclusions

Broke vs. fresh pulp

1. Broke provides significantly thinner sheets than fresh pulp resulting significantly higher density and lower bulk values.
2. Broke provides worse formation values than fresh pulp.
3. The air permeance values of broke are significantly higher than the values of fresh pulp.
4. Broke provides significantly higher opacity values than fresh pulp.
5. Broke and fresh pulp provides similar tensile and internal bonding strength values.

Standard vs. selective treatment

1. Selective treatment provides slightly better formation values than conventional treatment.
2. Selective chemical treatment increases the air permeance values of paper.
3. Through higher ash content and worse formation values, both chemical treatments had a negative impact on tensile and internal bonding strength.
4. Selective and conventional chemical treatments provide similar tensile and internal bonding strength to paper.

In the comparison of broke and fresh pulp, broke sheets were significantly thinner compared to fresh pulp sheets, thus resulting in correspondingly lower bulk and higher density values. This can be explained by collapsing of fibres, because broke has gone already once through press nips and drying section.

When comparing the furnishes from the formation point of view, broke naturally provided worse formation values than fresh pulp, and chemically untreated furnishes provided better formation values than chemically treated furnishes. It was interesting that in the comparison of chemical treatment, the formation values of fractionally treated furnishes were slightly better than the values of conventional treatment.

Results showed that the air permeance values of broke were significantly higher than the values of fresh pulp. This is due to the fact that all the flocs cannot be disintegrated, when broke is slushed. When broke is chemically treated, these disintegrated flocs collect the fines creating bigger flocs and more inhomogenous paper structure. This phenomenon is even stronger with fractional treatment, when the fines are processed separately. Floccy structure causes more void spaces in paper resulting in significantly higher air permeance values with broke.

The opacity values of the broke were significantly higher compared to fresh pulp. The reason behind this may lay in darker colour of broke sheets and their little bit higher filler content. These together contribute to higher opacity values.

Both conventional and selective chemical treatments increased the ash content approximately 12-15 %, which decreased their tensile and internal bonding strength values. Another issue, which decreased the strength values of chemically treated furnishes was their worse formation values.

There could not be seen any difference in tensile or internal bonding strength levels between conventional and fractional chemical treatments with these furnishes.
The low strength responses may be due to the low contact time of starch between the long fraction. On the other hand, furnishes were not refined before chemical treatments, which is not the case in normal mill-scale operation.

7 COMPARISON OF FRESH PULP AND BROKE WITH A MINIFORMER TRIAL

7.1 Target of the study

To see the effect of shear forces in the comparison of fresh pulp and broke, it was crucial to run the same kind of experiment as with the handsheets with a pilot paper machine. The target of the experiment was to find out the differences in paper properties between broke and fresh pulp with two filler levels, and to compare the impact of selective pre-treatment of fiber fractions on paper properties.

7.2 Furnishes

The furnishes used in this study were:

1) Slushed newsprint paper from a Finnish paper mill including:
    -55 % TMP
    -45 % DIP
    - 8 % filler, i.e clay
2) Machine chest stock from the same machine taken during the same run the paper above was produced.

7.2.1 Preparation of the furnishes

Because the target was to compare the properties of the furnishes, they were supposed to be in a comparable form. To reach that kind of situation, the dry uncalendered broke was slushed and a part of the furnishes was fractionated to make possible the further selective chemical pre-treatments. Adding the correct amount of filler and mixing of chemicals were done during the trials as it is presented in appendixes 5 and 6.

7.2.2 Slushing of broke

Slushing of broke was done at Metso Paper Technology Center in Anjalankoski during the trials with conventional slushing equipment.

7.2.3 Fractionation

Fractionation of the furnishes was done at Metso Fiber Technology Center in Anjalankoski. Only a part of the furnishes was fractionated and other part was saved for the whole pulp trials. Fractionation was done with following parameters:

$$-\,Fiber\ length\ ratio = \frac{Av.\ Fibre\ Length\ of\ Short\ Fraction}{Av.\ Fibre\ Length\ of\ Long\ Fraction} = 0{,}5 \qquad (14)$$

- $RR_m = 70\ \%$

Reject ratio was selected to lead into the fibre length ratio above. In selective chemical treatment trials, the dosing of fibre fractions was done according to the same reject ratio to reach the same kind of fibre length distribution.

7.3 Chemical additives

The miniformer trial utilised also microparticle system and the same chemical additives as the handsheet study meaning that three kinds of chemicals were prepared and used. The chemicals and their product names are presented in table 7.

Table 7 The chemicals used in the sheets.

Chemical	Product name
Cationic starch	Raisamyl 30021: Low DS
Cationic polymer	Percol 47: M to HMW c-PAM
Bentonite	Hydrocol SH

7.4 Description of the trials

The trials were carried out 13-14 March, 2008 at Metso Paper Technology Center in Anjalankoski, Finland, including separate test trials for both fresh pulp and broke and for unfractionated and fractionated furnishes.

7.4.1 Equipment

The trials were carried out with Miniformer, which is according to its name a former part (gapformer) of the paper machine. Machine width of Miniformer is 12 centimeters. The structure and layout of Miniformer can be reviewed closer in appendix 4.

7.4.2 Procedure

In the trials, the basis weight was fixed into 50 g/m2, headbox flow into 12 l/s, and machine speed into 800 m/min. The target was to produce the sheets with filler levels of 10 and 20 %. The chemical dosing points and the process layout can be seen separately for fractionated pulps and whole pulps in appendixes 5 and 6. Chemical dosages were performed as follows:

- starch: -into whole pulps for reference 4, 8, 12 kg/t
  -into long fractions in the selective treatment trial 4, 8, 12 kg/t
- polymer: -into whole pulps for reference as retention aid and as strength additive
  -into short fractions 0,5 to 2 kg/t

The schedule of the trials and closer information about the performing of the test points with chemical dosage information is presented in appendix 1.

7.5 Methods

Stock measurements were done during the trials by laboratory personnel of Anjalankoski Paper Technology Center. Stock measurement were carried out according to the following standards:

1. Fibre length: TAPPI T 271 om-02 Fibre length of pulp and paper by automated optical analyser using polarised light.
2. Consistency: SFS-EN ISO 4119:1996.
3. Canadian Standard Freeness: ISO 5267-2:2001.
4. pH: ISO 6588-1:2005 Determination of pH of aqeuos extracts. Part 1: -Cold exctraction.

Retention values were calculated based on the consistency measurements done during the trials, which can be seen in appendix 7.

Measurements from the dry sheets were carried out 17-19 March, 2008 in Metso Paper Technology Center in Jyväskylä, Finland. Measurements were done according to the following standards:

1. Air-conditioning: ISO EN 20187:1995.
2. Grammage: ISO 536:1996 Determination of grammage.
3. Caliper, density, and bulk: ISO 534:2005 Determination of thickness, density, and specific volume.
4. Ash content: ISO 1762:2001 Determination of residue ash on ignition at 525 °C. The ignition temperature used in the test was 540 °C, but it is inside the standard.
5. Formation: Values were measured with Ambertec β-formation tester according to instructions given by the machine supplier. Normalised formation values were calculated by using a following formula:

$$Normalised\ \ formation = \frac{Formation\ value}{\sqrt{Grammage}} \qquad (15)$$

6. Bendtsen air permeance: ISO 5636-3:1992.
7. Opacity: SFS-ISO 2471:2003 Determination of opacity.
8. Tensile strength: ISO 1924-3:2005 Determination of tensile properties. Tensile index values were calculated based on tensile strength as follows:

$$Tensile\ index = \frac{Tensile\ strength\ value}{Grammage} \qquad (16)$$

9. Internal bonding strength: TAPPI T 569 pm-00 Huygen internal bonding strength.

7.6 Results

All results from the miniformer trial can be found in appendix 3.

7.6.1 Basic properties

Figure 48 illustrates the grammage and the ash content values of broke and fresh pulp , which have been fractionally and conventionally treated. As can be seen from the figure, the grammage target of the trials was fixed into 50 g/m², and the results seem to be inside a reasonable area. On the other hand, the ash content values were also aimed to be as close to each other as possible, which was guaranteed by setting the ash level results of fresh pulp trial as a target in broke trial. From that point of view, it can be seen from figure 48 that ash content curves are similar for both furnishes, and it can be concluded that the results are comparable regarding ash content and grammage values.

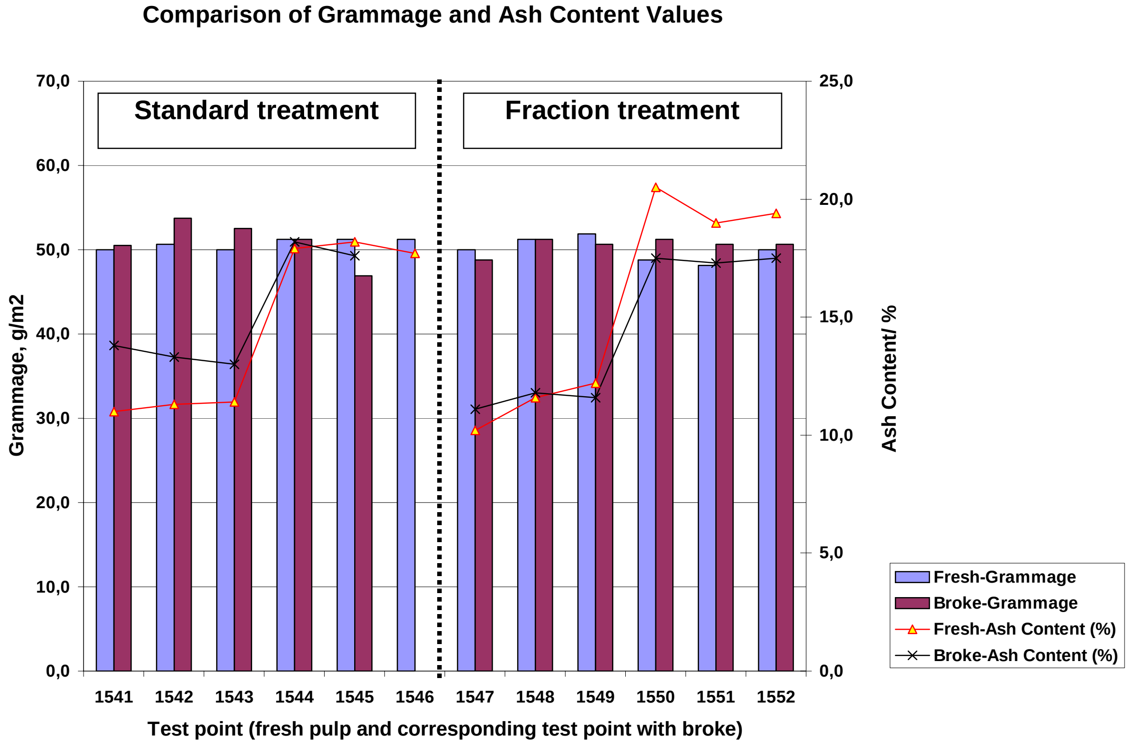

Figure 48 Comparison of grammage and ash content values of the sheets made of fresh pulp and broke and treated with three different polymer and starch addition rates.

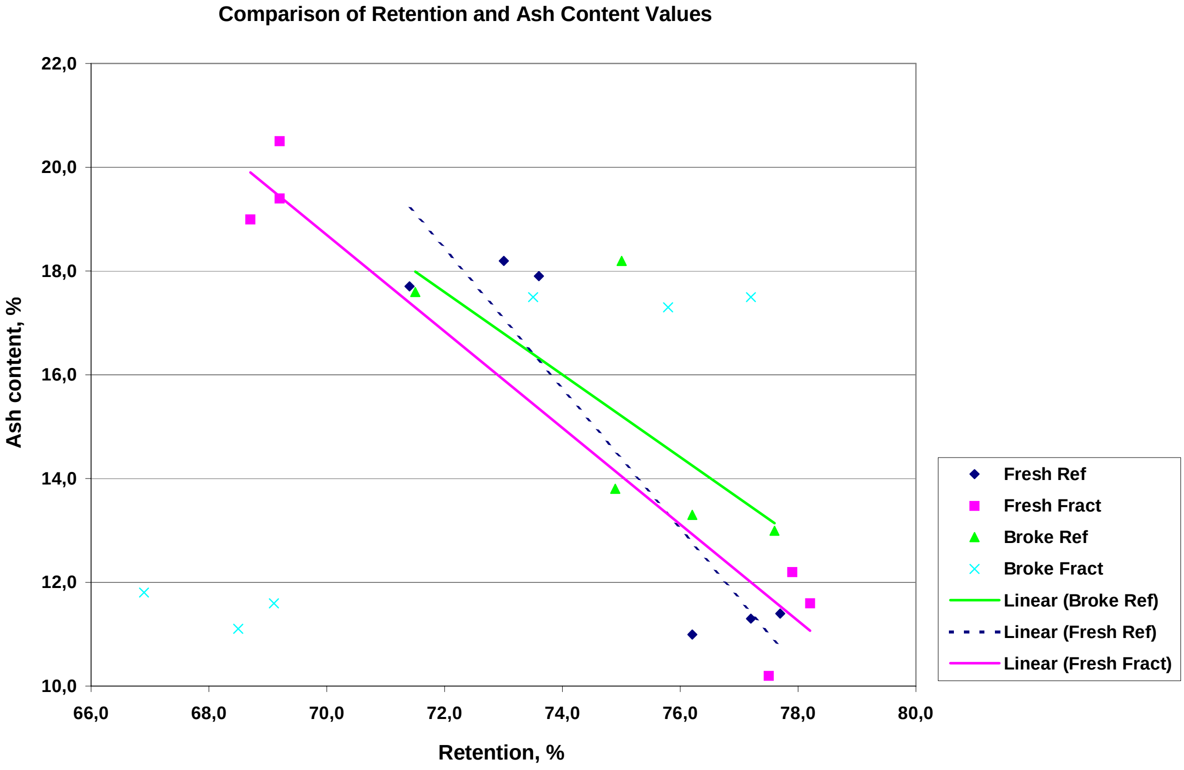

Figure 49 Comparison of retention and ash content values of the sheets made of broke and fresh pulp and treated with three different polymer and starch addition rates.

In figure 49 can be seen the negative interdependence of retention and ash content. In other words, when the retention decreases, the ash content increases. Figure 49 shows that there cannot be seen any significant differences in retention values between broke and fresh pulp, or between conventional and selective chemical treatments. It was surprising that for some unknown reason, fractionated broke did not obey the general rule giving increasing retention with increasing ash content values (no trendline).

7.6.2 Structural properties

In general, when retention is improving, formation is getting worse. This interaction can be seen also in the figure 50 with all the cases, except conventionally treated fresh pulp (no trendline). It can be seen from the figure that broke resulted in worse formation values than fresh pulp with both conventional and selective treatments.

On the other hand, selective chemical treatment seemed to have negative impact on formation. At least with broke, the negative impact of selective treatment has been strong. This is due to the fact that broke is not totally disintegrated before chemical treatment. It has some aggregation left from previous production times including fines-fines, fibre- fines, and fibre-fibre aggregates (i.e fibre flocs). These non-integrated fibre flocs are most harmful from formation point of view, because when they are chemically treated, they start to collect more material themselves and their size increases. Fractionation increases the amount of flocculation even more, which can be seen as worse formation values. To prevent this and to give even z-directional fines distribution, the target normally is to promote forming of fibre-fines aggregates.

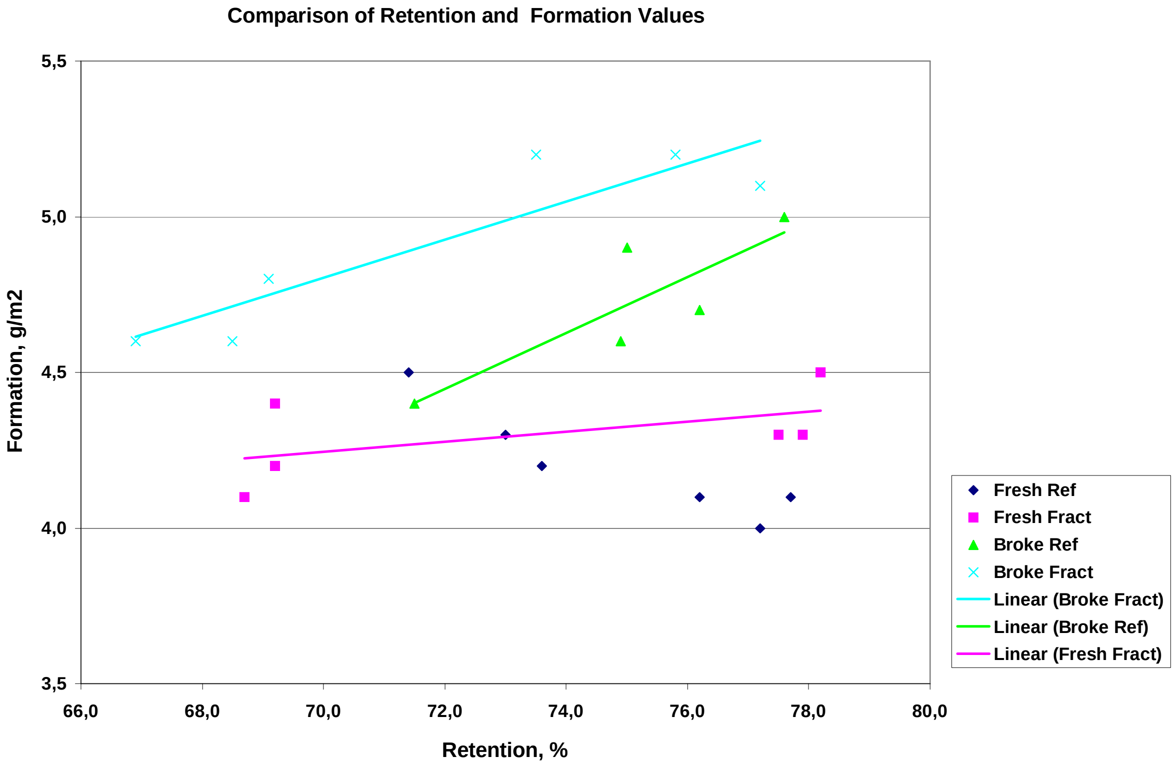

Figure 50 Comparison of retention and formation values of the sheets made of broke and fresh pulp and treated with three different polymer and starch addition rates.

In general, when the ash content is increasing, the air permeance values are also increasing. This phenomena can be seen in figure 51 with all the cases except conventionally treated fresh pulp. When comparing the furnishes, it can be seen from the figure that broke resulted in significantly higher air permeance values than fresh pulp. The reason behind this is again more uneven paper structure of broke sheets.

When comparing the chemical treatments, it can be seen from the results that the air permeance values of selectively treated furnishes are significantly higher than the values of conventionally treated furnishes especially with broke. Selective chemical treatment with microparticle system causes strong and tight flocculation, which together increases the size and amount void spaces in paper structure. Even though, the structure of paper is more inhomogenous with broke, also fresh pulp ended up in higher air permeance values with selective treatment.

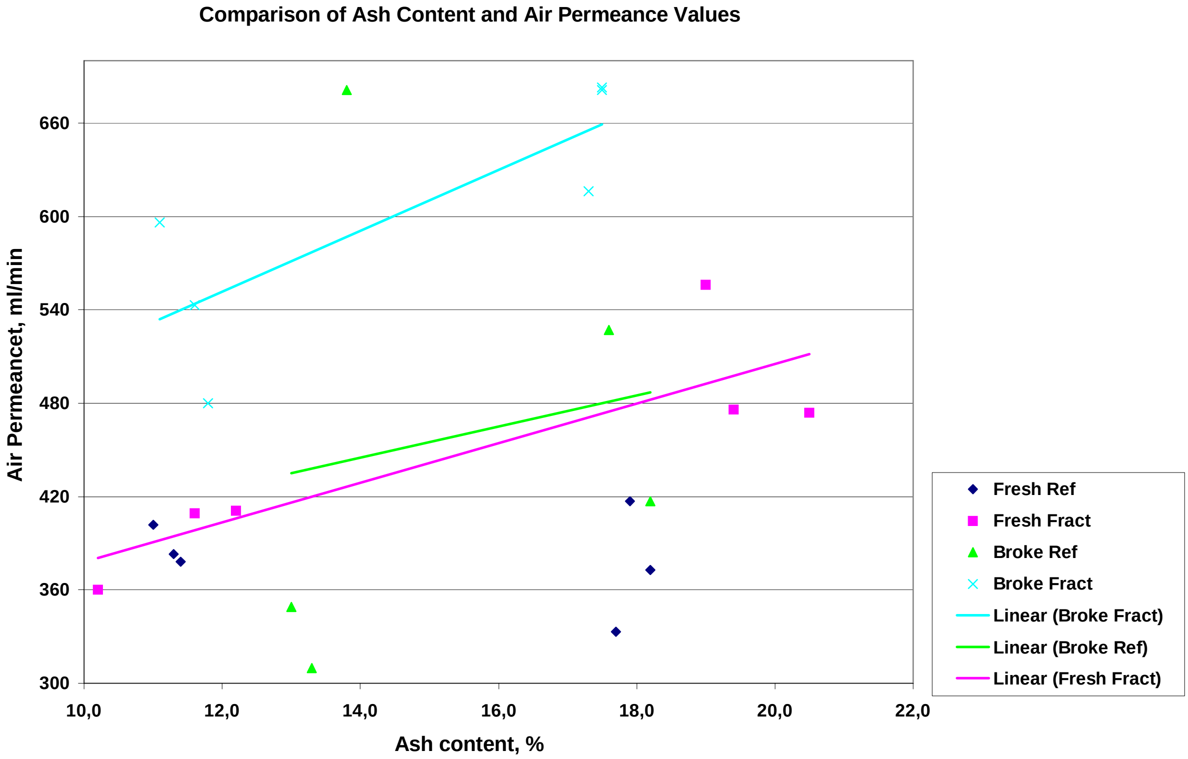

Figure 51 Comparison of ash content and air permeance values of the sheets made of broke and fresh pulp and treated with three different polymer and starch addition rates..

7.6.3 Optical properties

In general, opacity values are increasing simultaneously with increasing ash content values. Figure 52 shows this interaction with all the furnishes, except conventionally treated broke. With both furnishes, selective chemical treatment provided slightly worse opacity values than conventional treatment. This may be due to stronger flocculation caused by selective chemical treatment, which reduces the amount of free scattering particles in paper. On the other hand, the opacity values of broke are significantly higher than the opacity values of fresh pulp, which is mainly due to darker colour of broke.

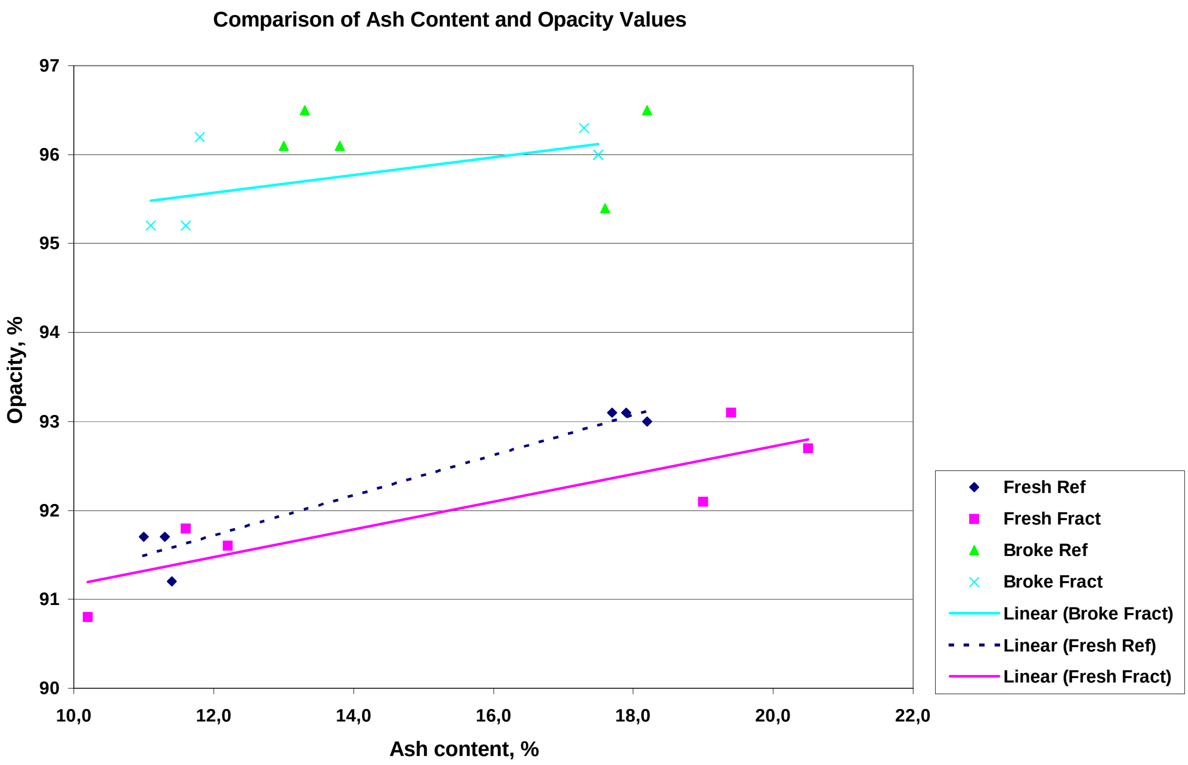

Figure 52 Comparison of ash content and opacity values of the sheets made of broke and fresh pulp and treated with three different polymer and starch addition rates.

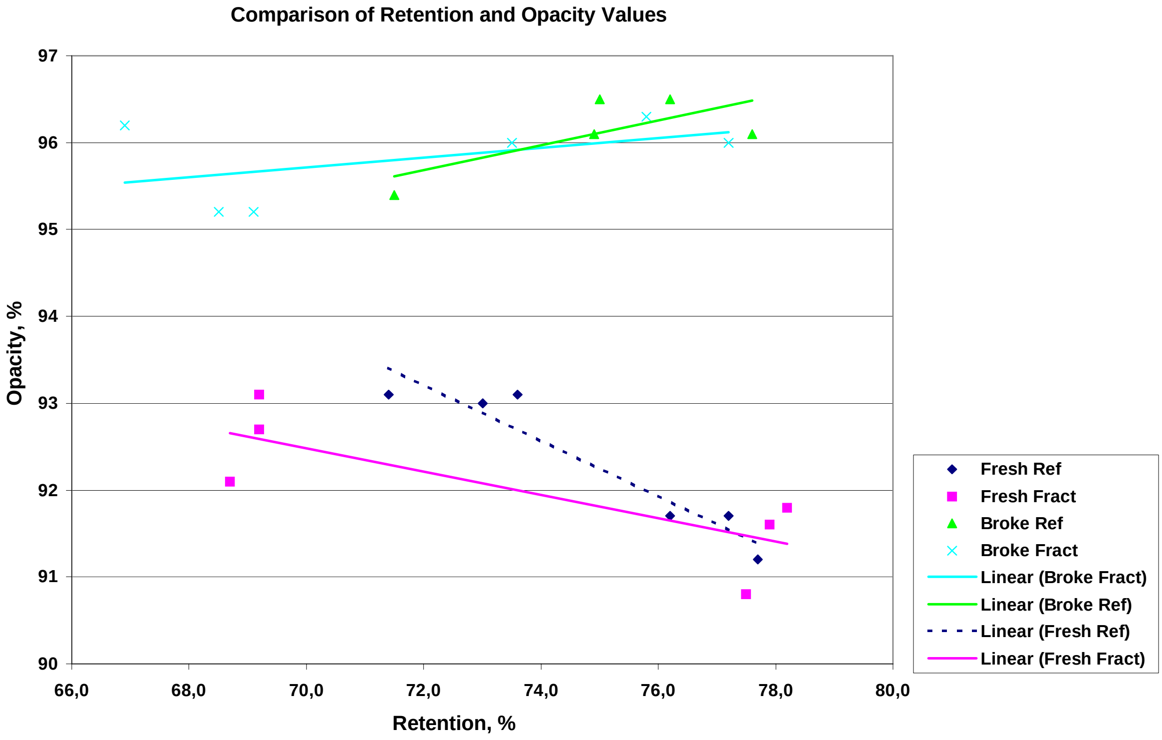

Figure 53 Comparison of retention and opacity values of the sheets made of broke and fresh pulp and treated with three different polymer and starch addition rates.

Because retention and ash content are negatively interdependent, it was somewhat expected that the relationship between retention and opacity is opposite. It can be seen again from figure 53 that the opacity values of broke with same retention levels are significantly higher than the opacity values of fresh pulp. In addition to that, there can be seen different kind of relationship between retention and opacity with fresh pulp and broke. Fresh pulp acted as expected giving decreasing opacity with increasing retention values, because simultaneously ash content was expected to decrease. For some reason, broke acted contrary to the fresh pulp giving increasing opacity results with increasing retention values.

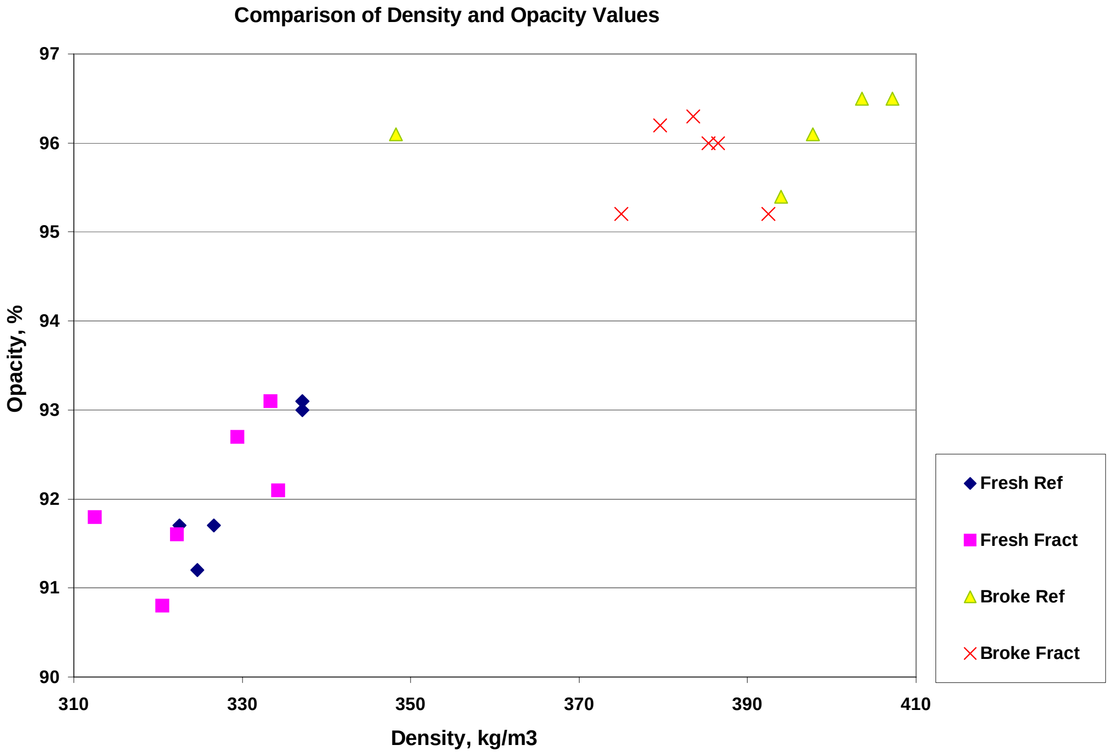

Figure 54 Comparison of density and opacity values of the sheets made of broke and fresh pulp and treated with three different polymer and starch addition rates.

Figure 54 shows the relationship between density and opacity values. Density and opacity values of broke are again significantly higher compared to fresh pulp. Higher density values are due to the fact that broke fibres have gone already once through pressing and drying phenomena and have been collapsed, thus forming thinner sheets with higher density values. Like said already, higher opacity is mainly due to darker colour of broke, because the ash level of the sheets were fixed into the same.

7.6.4 Strength properties

It is widely known that increasing ash content will have a negative effect on tensile strength of paper. This phenomenon can be seen with all the cases in figure 55. It is also known that broke has normally worse tensile values than fresh pulp, which can be seen from the figure, too.

When comparing chemical treatments, it can be seen from the figure that selective treatment of fibre fractions decreased at least the tensile strength values of fresh pulp. This can be explained with the stronger flocculation tendency of selective chemical treatment, which creates more uneven sheet structure. An uneven sheet includes more week points and as said, paper is as strong as its weakest point.

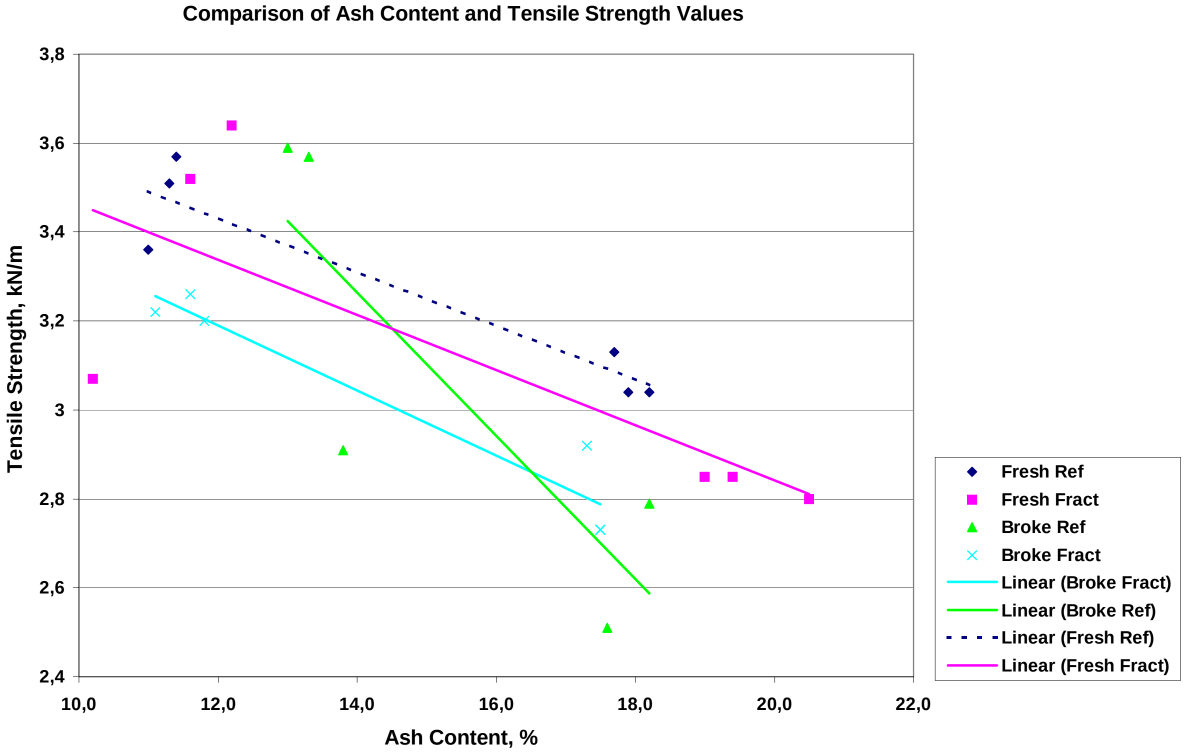

Figure 55 Comparison of tensile strength and ash content values of the sheets made of broke and fresh pulp and treated with three different polymer and starch addition rates.

Normally, when ash content is increasing, internal bonding strength values are getting worse. This relationship can be seen also from figure 56 with all the cases. However, clear differences could be found between broke and fresh pulp, and between selective and standard chemical pre-treatments. When comparing the furnishes, broke provided significantly higher internal bonding strength values than fresh pulp with both treatments. This is maybe due to the fact that broke fibres have been collapsed and are flat in shape. Flat broke fibres can provide greater relative bonded area than tubelike fresh pulp fibres.

When comparing the chemical treatments, standard chemical treatment led into better internal bonding strength values with both furnishes. The reason behind this is more likely the uneven sheet structure of selectively treated furnishes, because it means uneven sheet structure also in z-direction of paper. When fibres and fibre fines are unevenly distributed into the z-direction of the web, it reduces the required force to separate them i.e to split the paper web.

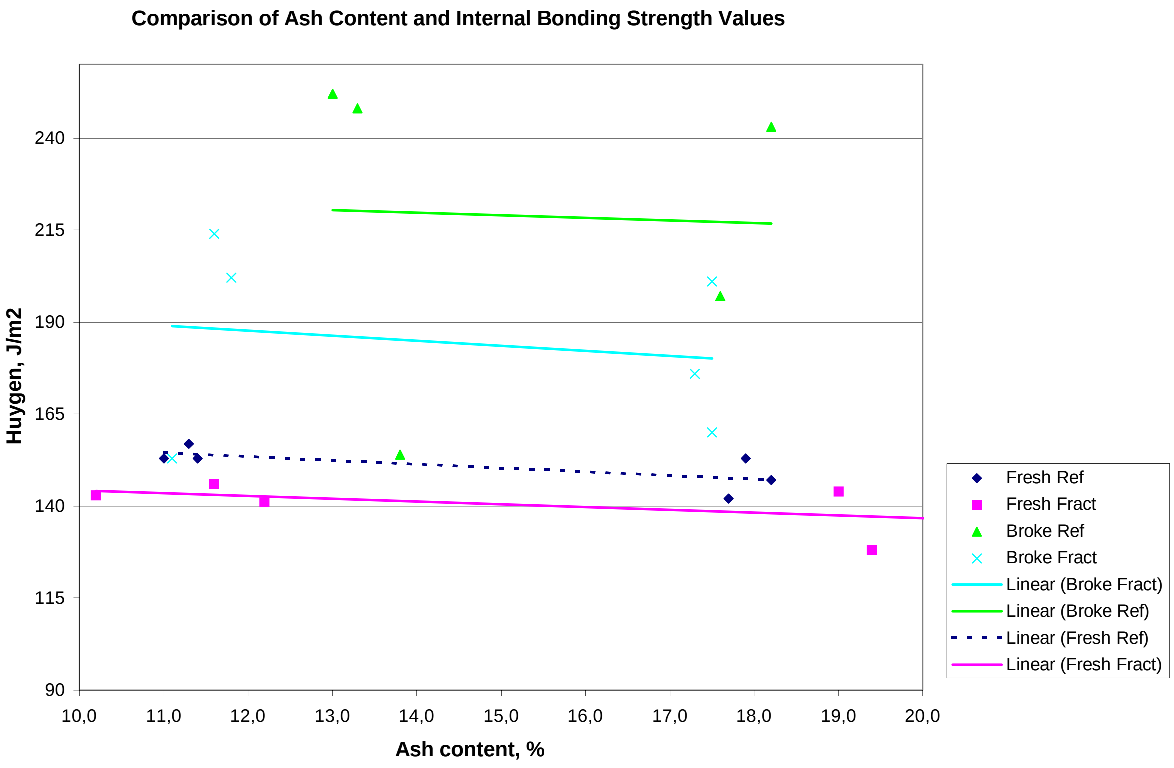

Figure 56 Comparison of ash content and internal bonding strength values of the sheets made of broke and fresh pulp and treated with three different polymer and starch addition rates.

In general, when density is increasing, internal bonding strength is getting better. Figure 57 illustrates once again the fact of higher density values of broke. In addition to that, it verifies the already discussed fact about weaker internal bonding strength results of selectively treated furnishes compared to conventionally treated furnishes.

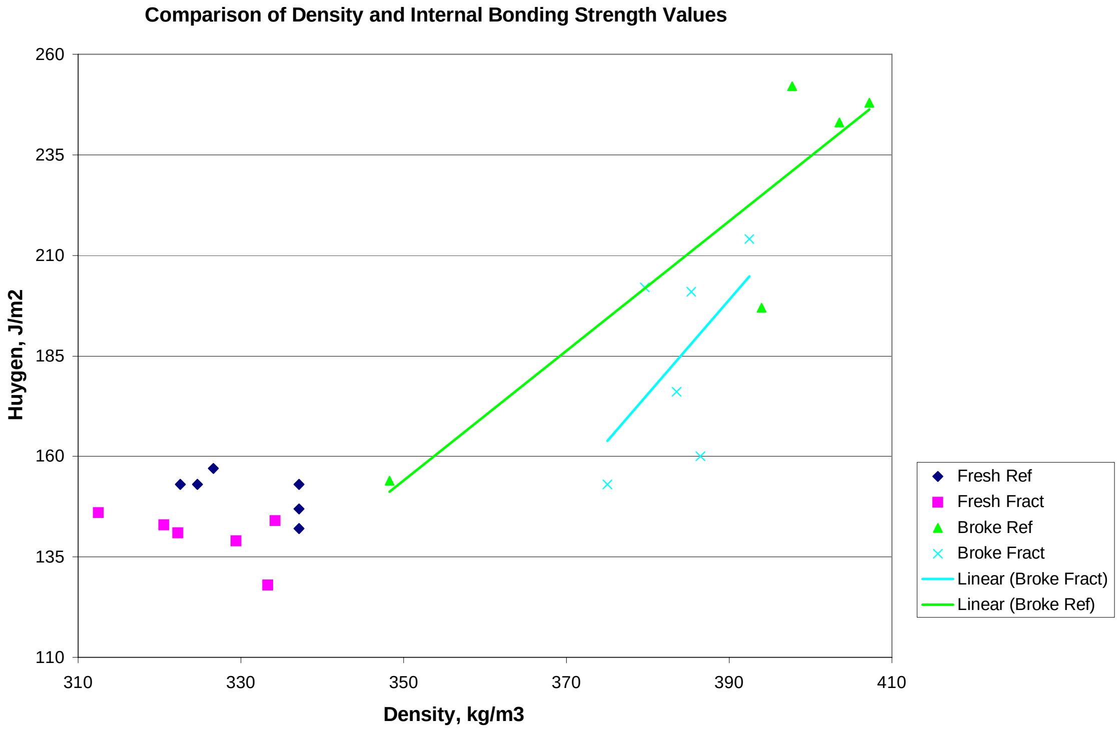

Figure 57 Comparison of density and internal bonding strength values of the sheets made of broke and fresh pulp and treated with three different polymer and starch addition rates.

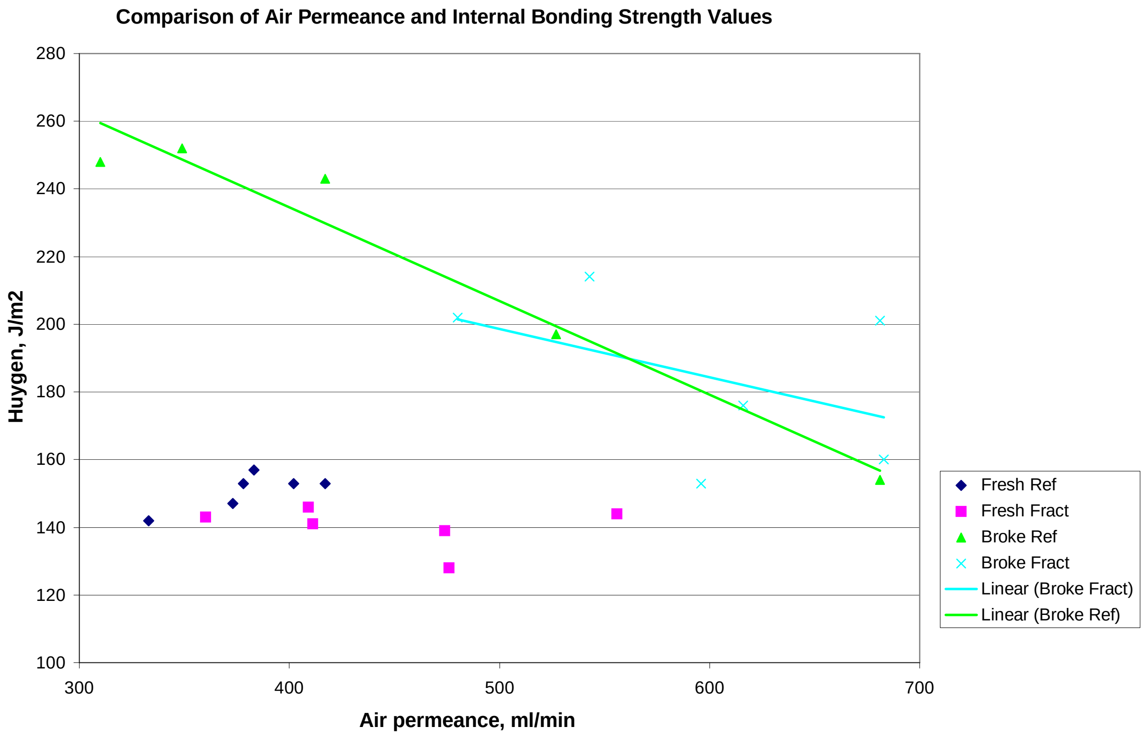

Figure 58 Comparison of air permeance and internal bonding strength values of the sheets made of broke and fresh pulp and treated with three different polymer and starch addition rates.

Increasing air permeance values normally have a negative impact on internal bonding strength. Air permeance describes, how evenly fibres and fines are distributed into the web. Fibre fines contribute strongly to the strength properties of paper and it is important that they are evenly distributed into the web, especially in z-direction when internal bonding strength is in question. Figure 58 shows that like in the handsheet study, the air permeance values of broke were clearly higher compared to fresh pulp, thus resulting in worse internal bonding strength values.

When comparing the chemical treatments, it can be seen from the figure that selective fractional treatment had an increasing effect on air permeability with both furnishes. As mentioned already, microparticle system causes strong flocculation, which increases the unevenness of paper structure and decreases the internal bonding strength values.

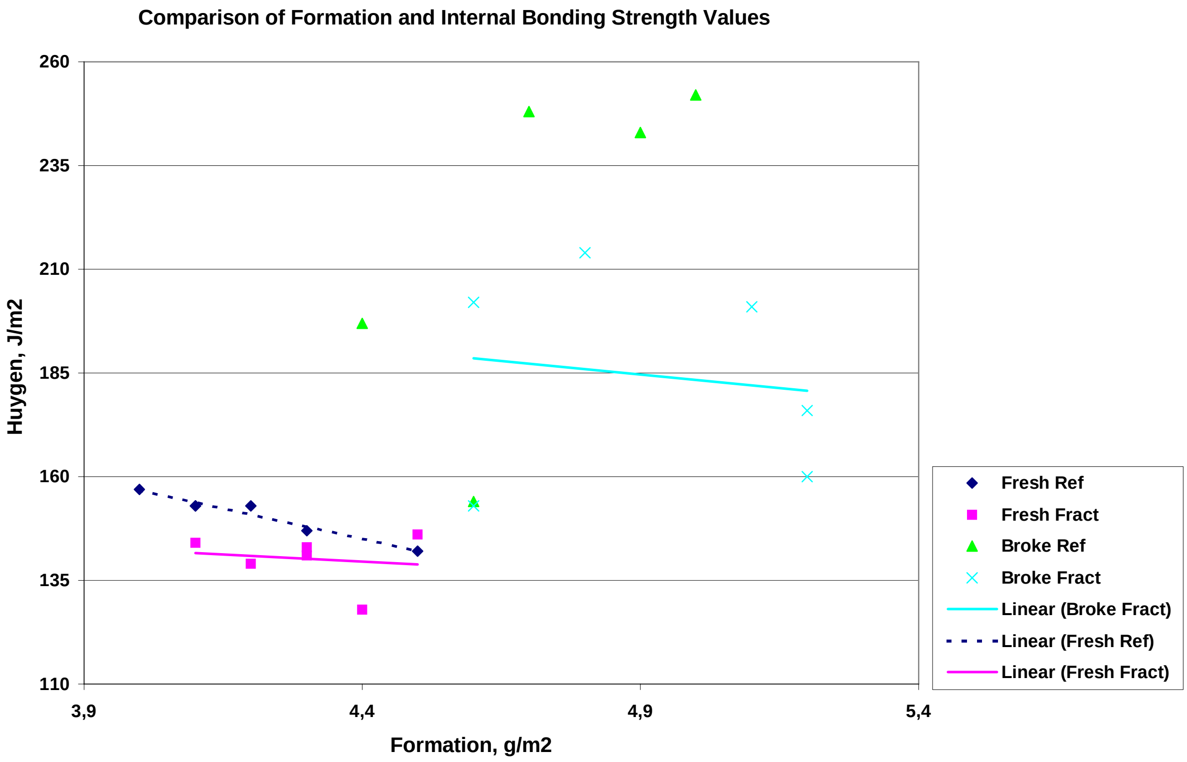

Figure 59 Comparison of formation and internal bonding strength values of the sheets made of broke and fresh pulp and treated with three different polymer and starch addition rates.

Figure 59 makes a comparison between formation and internal bonding strength values. When comparing the furnishes, fresh pulp provided clearly better formation values, but significantly lower internal bonding strength values than broke. Worse

formation values of broke are caused by the fact that its fibres are not totally disintegrated before chemical treatment, in which they collect more material themselves and increase their size. Better internal bonding strength values of broke may be due to flat collapsed fibres, which can offer greater relative bonded area than tubelike fresh pulp fibres.

When comparing the chemical treatment, it can be seen from the figure that this kind of selective chemical treatment provided worse internal bonding strength values than conventional chemical treatment.

7.7 Conclusions

Broke vs. fresh pulp

1. Broke provides worse formation values than fresh pulp.
2. Broke results in significantly higher air permeance values than fresh pulp.
3. Broke provides significantly higher opacity values than fresh pulp.
4. Increasing retention values decreases the opacity values of fresh pulp and increases the opacity values of broke.
5. Broke provides significantly higher density and lower bulk values than fresh pulp.
6. Broke provides worse tensile strength values than fresh pulp.
7. Broke provides significantly higher internal bonding strength values than fresh pulp.

Standard vs. selective treatment

1. Both treatments provide equal retention levels.
2. Selective chemical treatment has a negative impact on formation especially with broke.
3. Selective chemical pre-treatment provides significantly higher air permeance values than conventional chemical treatment.
4. Selective chemical treatment provides slightly worse opacity values than conventional chemical treatment.

5. Selective treatment decreases the tensile strength values of fresh pulp.
6. Selective chemical treatment leads into worse internal bonding strength values.

Retention and ash content are normally negatively interdependent meaning that retention decreases, when ash content increases. There could not be found any significant differences in retention values between broke and fresh pulp, or between conventional and selective chemical treatments.

In general, when retention is improving, formation values are getting worse. Even though broke is slushed and deflaked, there is always some aggregation left in broke from previous production times. When broke is chemically treated, the size of these flocs increases. Chemical treatments especially with fractionation changes also the nature of flocs by shrinking and increasing the size them and the size of void spaces around them. This can be seen as worse formation and higher air permeance values especially with broke. Also fresh pulp resulted in higher air permeance and worse formation values when it was fractionally treated.

Normally in papermaking, opacity values are increasing simultaneously with increasing ash content values. Because of darker colour of broke, it provided significantly higher opacity values than fresh pulp with both treatments.

Fractional treatment resulted in slightly worse opacity values with both furnishes than conventional treatment. This is maybe due to stronger flocculation caused by selective chemical treatment, which reduces the amount of free scattering particles in paper.

It was expected that the relationship between retention and opacity is opposite to the relationship ash content and opacity, because retention and ash content are negatively interdependent. Fresh pulp acted according to the rule, but for some reason, broke acted contrary to the fresh pulp giving increasing opacity results with increasing retention values.

Density values of broke were significantly higher compared to fresh pulp, because broke fibres have gone already once through pressing and drying phenomena and have been collapsed, thus forming thinner sheets with higher density values.

It is widely known that increasing ash content will have a negative effect on tensile strength of paper. It is also known that broke has normally worse tensile values than fresh pulp.

Selective treatment of fibre fractions decreased at least the tensile strength values of fresh pulp. This can be explained with the stronger flocculation tendency of selective chemical treatment, which creates more uneven sheet structure. An uneven sheet includes more week points and as said, paper is as strong as its weakest point.

Broke provided significantly higher internal bonding strength values than fresh pulp with both treatments. This is maybe due to the fact that broke fibres have been collapsed and are flat in shape. Flat broke fibres can provide greater relative bonded area than tubelike fresh pulp fibres.

When comparing the chemical treatments, standard chemical treatment led into better internal bonding strength values with both furnishes. The reason behind this is more likely the uneven sheet structure of selectively treated furnishes, because it means uneven sheet structure also in z-direction of paper. When fibres and fibre fines are unevenly distributed into the z-direction of the web, it reduces the required force to separate them i.e to split the paper web.

Selective fractional treatment seemed to have an increasing effect on air permeance values with both furnishes, because of higher amount of void spaces in paper structure caused by stronger flocculation and tighter flocs. However, the air permeance values of broke are still higher than the values of fresh pulp.

When comparing the furnishes, fresh pulp provided clearly better formation values, but significantly lower internal bonding strength values than broke. Worse formation values of broke are caused by the fact that its fibres are not totally disintegrated before

chemical treatment, in which they collect more material itselves and increase their size. Better internal bonding strength values of broke may be due to flat collapsed fibres, which can offer greater relative bonded area than tubelike fresh pulp fibres.

8 SUMMARY AND SUGGESTIONS FOR FURTHER STUDIES

It can be concluded based on the committed studies that compared to fresh pulp, broke provides:

-significantly thinner sheets resulting higher density values.
-worse formation values.

-significantly higher air permeance values.
-significantly higher opacity values than fresh pulp.
-worse tensile strength values.
-significantly higher internal bonding strength values.

Broke forms thin sheets with uneven paper structure, which leads into inferior tensile strength values. The colour of broke is darker than the colour of fresh pulp, which contribute its higher opacity values. Broke fibres have been collapsed into flat form, which makes on the other hand thin sheets but also may contribute to the relative bonded area of the fibres, thus resulting in superior internal bonding strength values.

As a conclusion can be mentioned that broke cannot deliver the same paper quality than fresh pulp. This has to be taken into account, if some trials are committed with slushed broke in the future.

Compared to standard chemical treatment, selective treatment of fibre fractions provides:

-worse formation values especially with broke.
-significantly higher air permeance values.
-slightly worse opacity values.
-worse tensile strength values.
-worse internal bonding strength values.

Selective treatment of fibre fractions causes a strong flocculation, which have a negative impact on paper structure. The unevenness of paper structure can be seen as worse formation and higher air permeance values, and it contributes to worse tensile strength and internal bonding strength as well. In addition to stronger flocculation, microparticle system causes a little bit tighter flocs than in conventional solution, which together contribute to slightly lower opacity values.

Based on low strength responses and an extremely uneven paper structure in both studies, one option for future studies in the field of selective treatments would be a use of refining of long fraction before chemical treatment. At least starch, which was used for strength additive, requires well-fibrillated fibres to operate. In addition to that, refining of long fraction before addition of strength chemicals would increase the natural bonding ability of fibres. For broke, refining would brake the remaining fibre flocs and open the hornified fibre surfaces. If the fibre flocs were open, chemical treatment would collect the material on separate fibre surfaces. This could distribute the chemicals and fines more evenly into the paper, which could improve the strength and structure properties of the sheet.

REFERENCE LIST

Printed sources:

1 Aloi, F., Retention in Neutral and Alkaline Papermaking. Retention of Fines and Fillers During Papermaking, Edit. Gess, J., TAPPI, Atlanta, USA, 1998, 357 p.

2 Beck, M., The Importance of Wet End Equipment and Its Influence on Retention, Retention of Fines and Fillers During Papermaking, Edit. Gess, J., TAPPI, Atlanta, USA, 1998, 357 p.

3 Bliss, T. Screening. Pulp and Paper Manufacture, 3rd Edition, Vol. 6, Stock Preparation, TAPPI, Atlanta, 1990, 311 p.

4 Brouwer, P., Johnson, M., & Olsen, R. Starch and Retention. Retention of Fines and Fillers During Papermaking, Edit. Gess, J., TAPPI, Atlanta, USA, 1998, 357 p.

5 Doiron, B., Retention Aid Systems. Retention of Fines and Fillers During Papermaking, Edit. Gess, J., TAPPI, Atlanta, USA, 1998, 357 p.

6 Gess, J. The Chemistry and Mechanics of Fine Particle Retention. Retention of Fines and Fillers During Papermaking, Edit. Gess, J., TAPPI, Atlanta, USA, 1998, 357 p.

7 Haapasalo, L., The effect of chemical pre-treatments of fibre fractions on the control of wet-end, MSc Thesis, TKK, Puunjalostustekniikka, Espoo 2006, 83 p.

8 Hautala, J., Hourula, I., Jussila, T., & Pitkänen, M., Screening and Cleaning. Mechanical Pulping, Edit. Sundholm, J., Fapet Oy, Jyväskylä, Finland 1999, 427 p.

9 Heikkurinen, A., & Leskelä, L., The Character and Properties of Mechanical Pulps. Mechanical Pulping, Edit. Sundholm, J., Fapet Oy, Jyväskylä, Finland 1999, 427 p.

10 Holmberg, M., Paper machine water chemistry. Papermaking Chemistry, Edit. Neimo, L., Fapet Oy, Jyväskylä, Finland 1999, 329 p.

11 Huusari, E., Refining of shives and coarse fibres. Mechanical Pulping, Edit. Sundholm, J., Fapet Oy, Jyväskylä, Finland 1999, 427 p.

12 Jokinen, H., Screening and Cleaning of Pulp – A Study to the Parameters Affecting Separation, Doctoral Thesis, University of Oulu, Dept. of Process and Environmental Engineering, Oulu 2007, 102 p.

13 Lancaster, P., Retention: Definitions, Methods, and Calculations. Retention of Fines and Fillers During Papermaking, Edit. Gess, J., TAPPI, Atlanta, USA, 1998, 357 p.

14 Norell, M., Johansson, K., & Persson, M. Retention and drainage. Papermaking Chemistry, Edit. Neimo, L., Fapet Oy, Jyväskylä, Finland 1999, 329 p.

15 Petander, L. Paperikoneen kemiallisen tilan seuranta, Paperinvalmistus 2, Jakso 1, Metsäteollisuuden koulutuskeskus, Jyväskylä.

16 Retulainen, E., Niskanen, K., & Nilsen, N., Fibers and Bonds. Paper Physics, Edit. Niskanen, K., Fapet Oy, Jyväskylä, Finland 1998, 324 p.

17 Scott, W. An Introduction to Wet End Chemistry, TAPPI, Atlanta, USA, 1992, 72 p.

18 Scott, W. Principles of Wet End Chemistry, TAPPI, Atlanta, USA, 1996, 185 p.

19 Stenius, P. Macromolecular, surface, and colloid chemistry. Forest Products Chemistry, Edit. Stenius, P., Fapet Oy, Jyväskylä, Finland 2000, 350 p.

20 Unbehend, J., Wet-end chemistry of retention, drainage and formation aids. Pulp and Paper Manufacture, 3rd Edition, Vol. 6, Stock Preparation, TAPPI, Atlanta, 1990, 311 p.

21 Winters, J. Introduction to the Electrokinetics of Papermaking. Retention of Fines and Fillers During Papermaking, Edit. Gess, J., TAPPI, Atlanta, USA, 1998, 357 p.

Electrical sources:

22 Poranen, P., A part of the training material ”Paperikoneen märkäosan kemiaa Metson sisäiseen käyttöön” based on the source: KCL, 2. Haavanlammi/Valmet.

23 VTT Tuotteet ja tuotanto. Knowpap [online]. Version 9.0, VTT Tuotteet ja tuotanto. 2007 [referred 1.2-30.3.2008]. Available: file://///book/knowpap/suomi/knowpap_system/user_interfaces/tuotantoprosessit/papvalm.htm

APPENDICES

APPENDIX I THE TRIAL SETTINGS FOR MINIFORMER TRIALS

Table 8 The trial settings for the fresh pulp trial.

TP	Measuring	Filler	Filler	Starch	Polymer	Ret. Aid	Bentonite	ash	Gram	Ret
	point	at SF	at Wirepit	at LF	at SF	at Hbx suction	at Hbx pipe	%	g/m2	%
		%	%	kg/t	kg/t	g/t	g/t			
1	**1541**		**10**	4	0	300	2000	7	49	76,2
2	**1542**		**10**	8	0	300	2000	8,3	51	77,2
3	**1543**		**10**	12	0	300	2000	7,1	50	77,7
4	**1544**		**20**	12	0	500	2000	14,9	52	73,6
5	**1545**		**20**	8	0	500	2000	14,6	52	73
6	**1546**		**20**	4	0	500	2000	15,2	51	71,4
7	**1547**	**10**		4	1	100	2000	6,2	50	77,5
8	**1548**	**10**		8	1	100	2000	7,6	49	78,2
9	**1549**	**10**		12	1	100	2000	8,2	52	77,9
10	**1550**	**20**		12	1	200	2000	17	48	69,2
11	**1551**	**20**		8	1	200	2000	15,4	49	68,7
12	**1552**	**20**		4	1,5	200	2000	16,9	49	69,2

Table 9 The trial settings for the broke trial.

TP	Measuring	Filler	Filler	Starch	Polymer	Ret. Aid	Bentonite	ash	Gram	Ret
	point	at SF	at Wirepit	at LF	at SF	at Hbx suction	at Hbx pipe	%	g/m2	%
		%	%	kg/t	kg/t	g/t	g/t			
1	**1555**		**10**	4	0	300	2000	6,9	47	74,9
2	**1556**		**10**	8	0	300	2000	8,9	53	76,2
3	**1557**		**10**	12	0	300	2000	9,10	52	77,6
4	**1558**		**20**	12	0	500	2000	14,3	50	75,0
5	**1559**		**20**	8	0	500	2000	13,9	49	71,5
6	**1560**		**20**	4	0	500	2000			
7	**1561**	**10**		4	1	100	2000	7	48	68,5
8	**1562**	**10**		8	1	100	2000	8,1	51	66,9
9	**1563**	**10**		12	1	100	2000	7,4	51	69,1
10	**1564**	**20**		12	1	250	2000	15,2	50	77,2
11	**1565**	**20**		8	1	250	2000	12,7	51	75,8
12	**1566**	**20**		4	1,5	250	2000	13,9	50	73,5

APPENDIX II STATISTICAL INFORMATION OF THE HANDSHEET STUDY

Table 10 Values of the basic properties from the handsheets.

	Grammage g/m²	Caliper/um	Density/kg/m3	Bulk m3/kg
TMP WP without chemicals	65,0	128	508	1,968
TMP WP with chemicals	66,9	126	532	1,880
Chemically-treated TMP SF+LF	65,4	122	536	1,865
Broke WP without chemicals	64,3	119	542	1,844
Broke WP with chemicals	65,8	115	574	1,743
Chemically-treated Broke SF+LF	64,6	113	571	1,752

Table 11 Ash content values from the handsheets.

	Ash content (%)
TMP WP without chemicals	12,9
TMP WP with chemicals	25,5
Chemically-treated TMP SF+LF	25,4
Broke WP without chemicals	15,8
Broke WP with chemicals	29,4
Chemically-treated Broke SF+LF	29,2

Table 12 Formation and normalised formation values from the handsheets.

	Formation(g/m²)	Std.(+/-)	c.v (%)	Norm.formation(sqrt(g)/m)
TMP WP without chemicals	3,6	0,3	8,3	0,4465
TMP WP with chemicals	5,0	0,4	8,0	0,6113
Chemically-treated TMP SF+LF	4,6	1,3	28,3	0,5688
Broke WP without chemicals	3,8	0,2	5,3	0,4739
Broke WP with chemicals	4,8	0,0	0,0	0,5917
Chemically-treated Broke SF+LF	4,7	0,4	8,5	0,5848

Table 13 Bendtsen air permeability values measured from the handsheets.

	Air Permeance (ml/min)	Std. (+/-)	c.v (%)
TMP WP without chemicals	100	5,4	5,4
TMP WP with chemicals	101	3,1	3,0
Chemically-treated TMP SF+LF	104	4,2	3,9
Broke WP without chemicals	117	9,1	7,7
Broke WP with chemicals	119	5,0	4,2
Chemically-treated Broke SF+LF	120	8,7	7,2

Table 14 Opacity values measured from the handsheets.

	Opacity (%)	Std. (+/-)	c.v (%)
TMP WP without chemicals	93,0	0,2	0,215
TMP WP with chemicals	96,2	0,3	0,312
Chemically-treated TMP SF+LF	95,9	0,2	0,209
Broke WP without chemicals	96,3	0,1	0,104
Broke WP with chemicals	98,2	0,2	0,204
Chemically-treated Broke SF+LF	97,8	0,2	0,204

Table 15 Tensile strenght and tensile index values from the handsheets.

	Tensile Strength(kN/m)	Std.(N/m)	cv (%)	Tensile index(Nm/g)
TMP WP without chemicals	2,92	131	4,5	44,9
TMP WP with chemicals	2,29	116	5,1	34,3
Chemically-treated TMP SF+ LF	2,11	88	4,2	32,3
Broke WP without chemicals	2,94	108	3,7	45,7
Broke WP with chemicals	2,13	85	4,0	32,4
Chemically-treated Broke SF+ LF	2,12	96	4,5	32,8

Table 16 Huygen internal bonding strength values from the handsheets.

	Internal bonding strength (J/m²)	Std.(J/m²)	cv (%)
TMP WP without chemicals	256	14	5,5
TMP WP with chemicals	217	14	6,5
Chemically-treated TMP SF+ LF	228	9,9	4,3
Broke WP without chemicals	261	13	5,0
Broke WP with chemicals	219	15	6,9
Chemically-treated Broke SF+ LF	220	11	5,0

APPENDIX III STATISTICAL INFORMATION OF THE MINIFORMER TRIALS

Table 17 Grammage, ash content, and retention values from the fresh pulp sheets.

	Treatment	Grammage(g/m²)	Ash content (%)	Retention(%)
1541	**Standard**	50,0	11,0	76,2
1542	**Standard**	50,6	11,3	77,2
1543	**Standard**	50,0	11,4	77,7
1544	**Standard**	51,3	17,9	73,6
1545	**Standard**	51,3	18,2	73,0
1546	**Standard**	51,3	17,7	71,4
1547	**Fract.&chem.**	50,0	10,2	77,5
1548	**Fract.&chem.**	51,3	11,6	78,2
1549	**Fract.&chem.**	51,9	12,2	77,9
1550	**Fract.&chem.**	48,8	20,5	69,2
1551	**Fract.&chem.**	48,1	19,0	68,7
1552	**Fract.&chem.**	50,0	19,4	69,2

Table 18 Grammage, ash content, and retention values from the broke miniformer sheets.

	Treatment	Grammage(g/m²)	Ash content (%)	Retention(%)
1555	**Standard**	50,5	13,8	74,9
1556	**Standard**	53,8	13,3	76,2
1557	**Standard**	52,5	13,0	77,6
1558	**Standard**	51,3	18,2	75,0
1559	**Standard**	46,9	17,6	71,5
1560	**Standard**			
1561	**Fract.&chem.**	48,8	11,1	68,5
1562	**Fract.&chem.**	51,3	11,8	66,9
1563	**Fract.&chem.**	50,6	11,6	69,1
1564	**Fract.&chem.**	51,3	17,5	77,2
1565	**Fract.&chem.**	50,6	17,3	75,8
1566	**Fract.&chem.**	50,6	17,5	73,5

Table 19 Caliper, density and bulk values from the fresh pulp miniformer sheets.

	Treatment	Caliper(um)	Std. (+/-)	Density(kg/m3)	Bulk (cm3/g)
1541	**Standard**	155	6	323	3,10
1542	**Standard**	155	4	327	3,06
1543	**Standard**	154	5	325	3,08
1544	**Standard**	152	3	337	2,97
1545	**Standard**	152	7	337	2,97
1546	**Standard**	152	1	337	2,97
1547	**Fract.&chem.**	156	8	321	3,12
1548	**Fract.&chem.**	164	5	313	3,20
1549	**Fract.&chem.**	161	3	322	3,10
1550	**Fract.&chem.**	148	3	329	3,04
1551	**Fract.&chem.**	144	7	334	2,99
1552	**Fract.&chem.**	150	5	333	3,00

Table 20 Caliper, density, and bulk values from the miniformer sheets made of broke.

	Treatment	Caliper(um)	Std. (+/-)	Density(kg/m3)	Bulk (cm3/g)
1541	**Standard**	155	6	323	3,10
1542	**Standard**	155	4	327	3,06
1543	**Standard**	154	5	325	3,08
1544	**Standard**	152	3	337	2,97
1545	**Standard**	152	7	337	2,97
1546	**Standard**	152	1	337	2,97
1547	**Fract.&chem.**	156	8	321	3,12
1548	**Fract.&chem.**	164	5	313	3,20
1549	**Fract.&chem.**	161	3	322	3,10
1550	**Fract.&chem.**	148	3	329	3,04
1551	**Fract.&chem.**	144	7	334	2,99
1552	**Fract.&chem.**	150	5	333	3,00

Table 21 Formation and normalised formation values from the fresh pulp sheets.

	Treatment	Formation(g/m²)	Std.(+/-)	c.v (%)	Norm.formation(sqrt(g)/m)
1541	**Standard**	4,1	0,8	19,5	0,580
1542	**Standard**	4,0	0,5	12,5	0,562
1543	**Standard**	4,1	0,7	17,1	0,580
1544	**Standard**	4,2	1	23,8	0,587
1545	**Standard**	4,3	0,5	11,6	0,601
1546	**Standard**	4,5	0,5	11,1	0,629
1547	**Fract.&chem.**	4,3	1,1	25,6	0,608
1548	**Fract.&chem.**	4,5	0,1	2,2	0,629
1549	**Fract.&chem.**	4,3	0,2	4,7	0,597
1550	**Fract.&chem.**	4,2	0,4	9,5	0,602
1551	**Fract.&chem.**	4,1	0,7	17,1	0,591
1552	**Fract.&chem.**	4,4	0,3	6,8	0,622

Table 22 Formation and normalised formation values from the broke sheets.

	Treatment	Formation(g/m²)	Std.(+/-)	c.v (%)	Norm.formation(sqrt(g)/m)
1555	**Standard**	4,6	0,4	8,7	0,647
1556	**Standard**	4,7	0,2	4,3	0,641
1557	**Standard**	5,0	1	20,0	0,690
1558	**Standard**	4,9	0,4	8,2	0,684
1559	**Standard**	4,4	0,7	15,9	0,643
1560	**Standard**				
1561	**Fract.&chem.**	4,6	0,8	17,4	0,659
1562	**Fract.&chem.**	4,6	0,3	6,5	0,643
1563	**Fract.&chem.**	4,8	1,4	29,2	0,675
1564	**Fract.&chem.**	5,1	0,8	15,7	0,712
1565	**Fract.&chem.**	5,2	0,5	9,6	0,731
1566	**Fract.&chem.**	5,2	0,6	11,5	0,731

Table 23 Air permeance values from the fresh pulp sheets.

	Treatment	Air Permeance (ml/min)	Std.(+/-)	c.v (%)
1541	**Standard**	402	104	25,87
1542	**Standard**	383	80	20,89
1543	**Standard**	378	42	11,11
1544	**Standard**	417	46	11,03
1545	**Standard**	373	33	8,85
1546	**Standard**	333	24	7,21
1547	**Fract.&chem.**	360	14	3,89
1548	**Fract.&chem.**	409	42	10,27
1549	**Fract.&chem.**	411	74	18,00
1550	**Fract.&chem.**	474	55	11,60
1551	**Fract.&chem.**	556	73	13,13
1552	**Fract.&chem.**	476	56	11,76

Table 24 Air permeance values from the broke sheets.

	Treatment	Air Permeance (ml/min)	Std.(+/-)	c.v (%)
1555	**Standard**	681	75	11,01
1556	**Standard**	310	13	4,19
1557	**Standard**	349	32	9,17
1558	**Standard**	417	51	12,23
1559	**Standard**	527	10	1,90
1560	**Standard**			
1561	**Fract.&chem.**	596	88	14,77
1562	**Fract.&chem.**	480	59	12,29
1563	**Fract.&chem.**	543	43	7,92
1564	**Fract.&chem.**	681	93	13,66
1565	**Fract.&chem.**	616	62	10,06
1566	**Fract.&chem.**	683	96	14,06

Table 25 The opacity values from the fresh pulp sheets.

	Treatment	Opacity(%)	Std.(+/-)	c.v (%)
1541	**Standard**	91,7	0,6	0,654
1542	**Standard**	91,7	0,4	0,436
1543	**Standard**	91,2	0,5	0,548
1544	**Standard**	93,1	0,6	0,644
1545	**Standard**	93	0,3	0,323
1546	**Standard**	93,1	0,4	0,430
1547	**Fract.&chem.**	90,8	0,6	0,661
1548	**Fract.&chem.**	91,8	0,7	0,763
1549	**Fract.&chem.**	91,6	0,4	0,437
1550	**Fract.&chem.**	92,7	0,7	0,755
1551	**Fract.&chem.**	92,1	0,8	0,869
1552	**Fract.&chem.**	93,1	0,1	0,107

Table 26 The opacity values from the sheets made of broke.

	Treatment	Opacity(%)	Std.(+/-)	c.v (%)
1555	**Standard**	96,1	0,4	0,416
1556	**Standard**	96,5	0,7	0,725
1557	**Standard**	96,1	0,4	0,416
1558	**Standard**	96,5	0,3	0,311
1559	**Standard**	95,4	0,8	0,839
1560	**Standard**			
1561	**Fract.&chem.**	95,2	0,8	0,840
1562	**Fract.&chem.**	96,2	0,3	0,312
1563	**Fract.&chem.**	95,2	0,3	0,315
1564	**Fract.&chem.**	96	0,7	0,729
1565	**Fract.&chem.**	96,3	0,4	0,415
1566	**Fract.&chem.**	96	0,8	0,833

Table 27 Tensile strength and tensile index values from the fresh pulp miniformer sheets.

	Treatment	Tensile Strength (kN/m)	Std (N/m)	cv (%)	Tensile index (Nm/g)
1541	**Standard**	3,36	359	10,67	67,20
1542	**Standard**	3,51	226	6,45	69,33
1543	**Standard**	3,57	227	6,36	71,40
1544	**Standard**	3,04	258	8,5	59,32
1545	**Standard**	3,04	158	5,18	59,32
1546	**Standard**	3,13	214	6,83	61,07
1547	**Fract.&chem.**	3,07	373	12,14	61,40
1548	**Fract.&chem.**	3,52	384	10,9	68,68
1549	**Fract.&chem.**	3,64	333	9,14	70,16
1550	**Fract.&chem.**	2,8	364	12,98	57,44
1551	**Fract.&chem.**	2,85	352	12,36	59,21
1552	**Fract.&chem.**	2,85	238	8,34	57,00

Table 28 Tensile strength and tensile index values from the miniformer sheets made of broke.

	Treatment	Tensile Strength (kN/m)	Std (N/m)	cv (%)	Tensile index (Nm/g)
1555	**Standard**	2,91	151	5,2	57,62
1556	**Standard**	3,57	307	8,58	66,42
1557	**Standard**	3,59	269	7,49	68,38
1558	**Standard**	2,79	150	5,38	54,44
1559	**Standard**	2,51	93	3,71	53,54
1560	**Standard**				
1561	**Fract.&chem.**	3,22	232	7,21	66,05
1562	**Fract.&chem.**	3,2	208	6,5	62,44
1563	**Fract.&chem.**	3,26	309	9,49	64,39
1564	**Fract.&chem.**	2,73	266	9,72	53,27
1565	**Fract.&chem.**	2,92	248	8,51	57,67
1566	**Fract.&chem.**	2,73	255	9,34	53,92

Table 29 Internal bonding strength values from the fresh pulp miniformer sheets.

	Treatment	Internal bonding strength (J/m²)	Std (J/m²)	cv (%)
1541	**Standard**	153	9,0	5,9
1542	**Standard**	157	12,0	7,6
1543	**Standard**	153	8,3	5,4
1544	**Standard**	153	13,0	8,5
1545	**Standard**	147	12,0	8,2
1546	**Standard**	142	8,9	6,3
1547	**Fract.&chem.**	143	12,8	9,0
1548	**Fract.&chem.**	146	11,0	7,5
1549	**Fract.&chem.**	141	9,1	6,5
1550	**Fract.&chem.**	139	9,0	6,5
1551	**Fract.&chem.**	144	12,0	8,3
1552	**Fract.&chem.**	128	8,3	6,5

Table 30 Internal bonding strength values from the fresh pulp miniformer sheets.

	Treatment	Internal bonding strength (J/m²)	Std (J/m²)	cv (%)
1555	**Standard**	154	9,4	6,1
1556	**Standard**	248	19,0	6,1
1557	**Standard**	252	20,0	7,9
1558	**Standard**	243	24,0	9,9
1559	**Standard**	197	16,0	8,1
1560	**Standard**			
1561	**Fract.&chem.**	153	8,6	5,6
1562	**Fract.&chem.**	202	13,0	6,4
1563	**Fract.&chem.**	214	19,0	8,9
1564	**Fract.&chem.**	201	14,0	7,0
1565	**Fract.&chem.**	176	9,6	5,5
1566	**Fract.&chem.**	160	10,0	6,3

APPENDIX IV

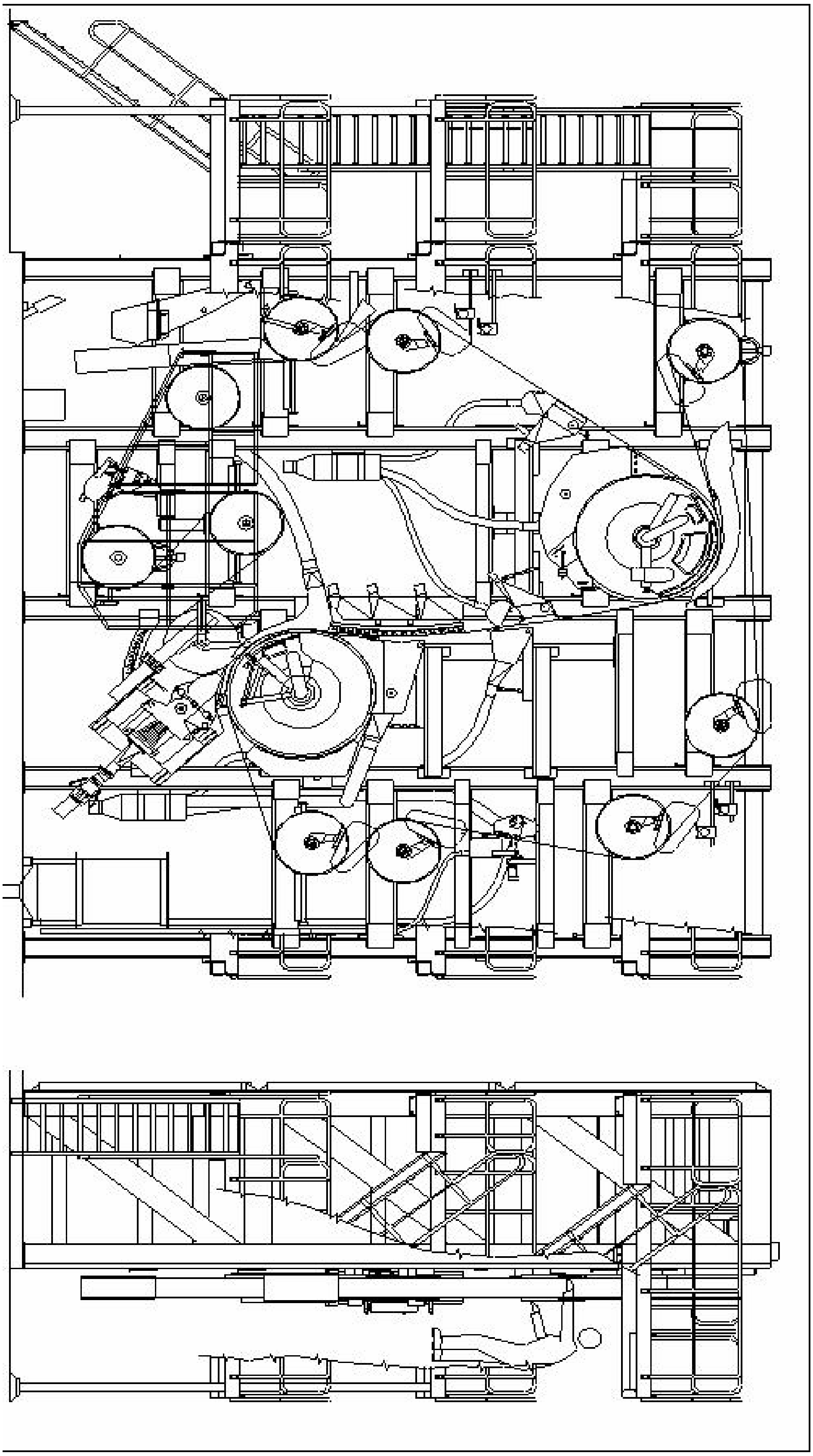

Figure 60 Machine layout of Miniformer.

APPENDIX V

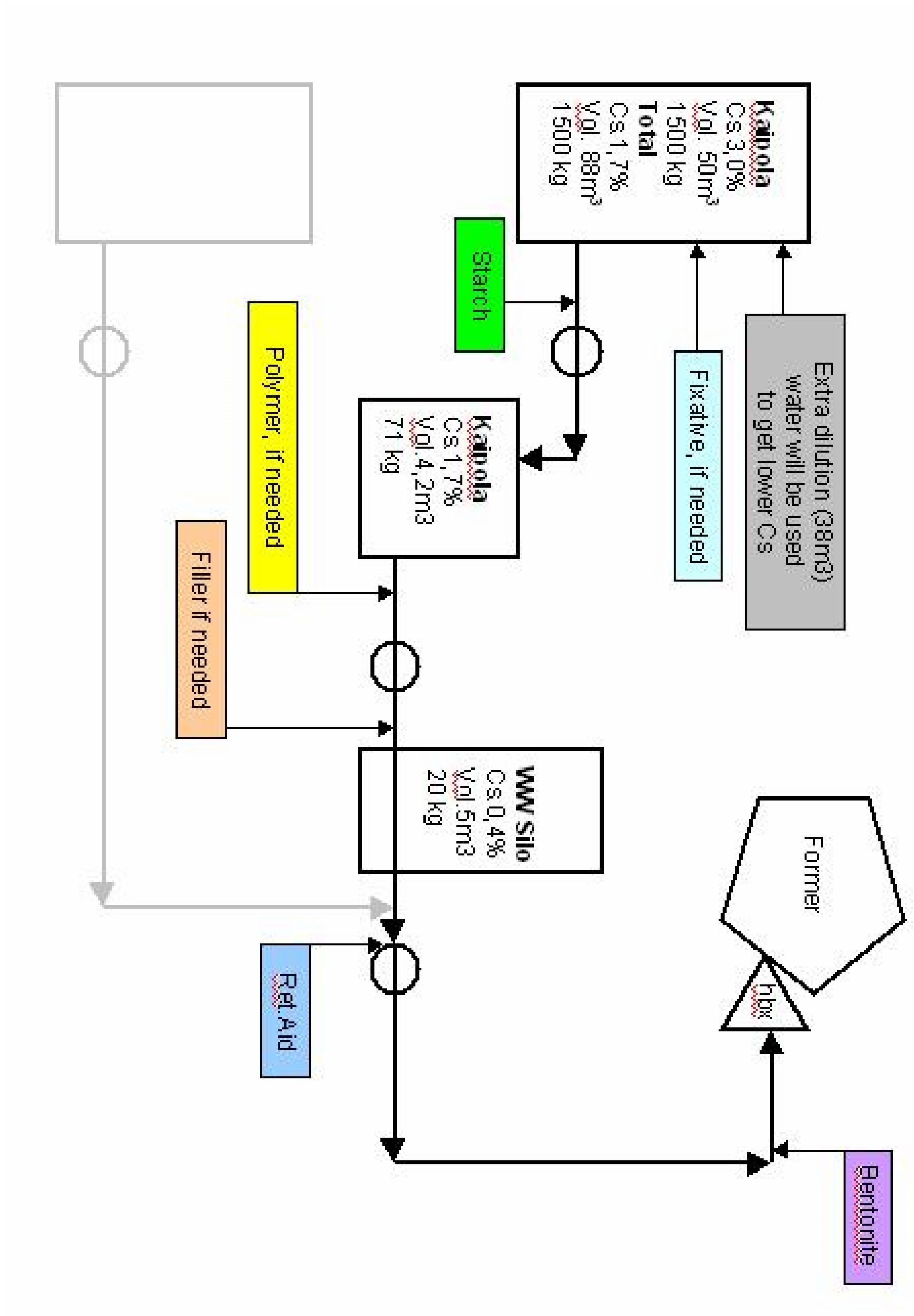
Kaipola
Cs 3,0%
Vol. 50m³
1500 kg
Total
Cs 1,7%
Vol. 88m³
1500 kg
Starch
Extra dilution (38m3) water will be used to get lower Cs
Fixative, if needed
Kaipola
Cs 1,7%
Vol 4,2m3
71 kg
Polymer, if needed
Filler if needed
WW Silo
Cs 0,4%
Vol 5m3
20 kg
Former
hbx
Ret.Aid
Bentonite

Figure 61 The chemical dosing points and the process parameters of the miniformer trial for the unfractionated fresh pulp and broke.

APPENDIX VI

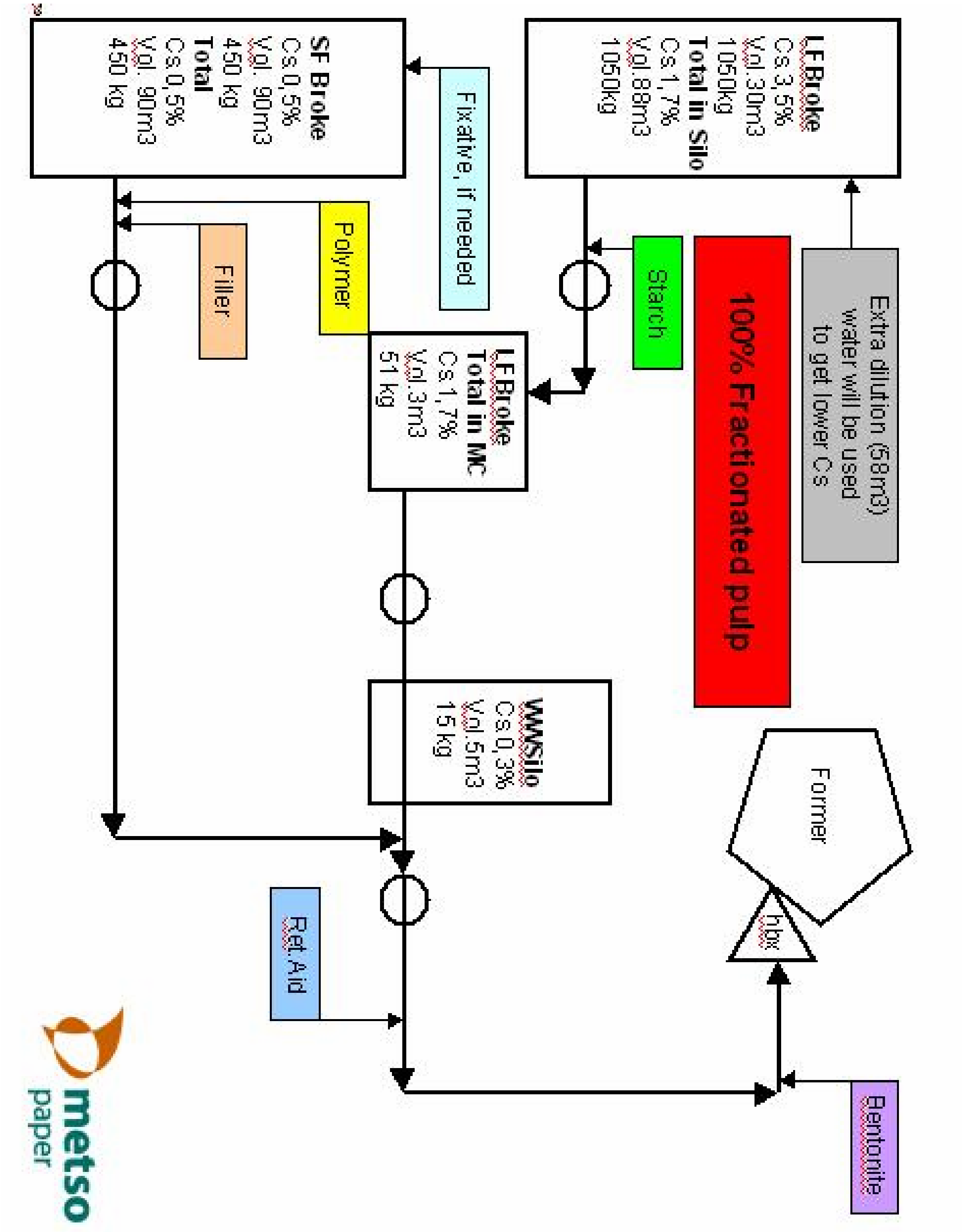

Figure 62 The chemical dosing points and the process parameters of the miniformer trial for fractionated fresh pulp and broke.

APPENDIX VII STOCK MEASUREMENTS FROM THE MINIFORMER TRIAL

Table 31 Stock measurements from the miniformer trial.

Day	Trial Point	Tank 527, long fiber					Headbox				White water		Headbox / White water	Tank 526, short fiber					Broken		Macine-chest				
		Consis-tence %	CSF ml	Ash %	pH	Fiber length mm	Consis-tence %	CSF ml	Ash %	Fiber length mm	Consis-tence %	Ash %	Retention %	Consis-tence %	CSF ml	Ash %	pH	Fiber length mm	Consis-tence %	Ash %	Consis-tence %	CSF ml	Ash %	pH	Fiber length mm
13.3.2008	1541						0,88				0,21		76,2												
	1542	2,46	158		6,1	1,88	0,88	59		1,66	0,20		77,2	0,46	13		5,9	0,89			1,22	52		6,1	1,72
	1543						0,88				0,20		77,7												
	1544						0,96				0,25		73,6												
	1545	2,36	149		6,1	1,84	0,97	67		1,65	0,26		73,0	0,46	12		5,9	0,87			1,2	51		6,0	1,69
	1546						0,96				0,28		71,4												
	1547						0,87				0,20		77,5												
	1548	1,18	150		6,3	1,86	0,91	74		1,67	0,20		78,2	0,49	17		6,1	0,89							
	1549						0,93				0,21		77,9												
	1550						0,98				0,30		69,2												
	1551	1,07	134		6,5	1,88	0,96	78		1,63	0,30		68,7	0,96	67		6,8	0,82							
	1552						0,98				0,30		69,2												
	1553						0,99				0,30		69,5												
	1554						1,12	82		1,62	0,32		71,4	1,16	80		7,2	0,78	2,74		1,92	129		6,8	1,77
14.3.2008	1555						0,90				0,23		74,9												
	1556	2,46	262		7,7	1,68	0,91	100		1,48	0,22		76,2	0,59	23		7,8	0,77			1,33	105		7,8	1,51
	1557						0,90				0,20		77,6												
	1558						0,92				0,23		75,0												
	1559	2,45	264		7,6	1,69	0,87	103		1,39	0,25		71,5	0,59	23		7,8	0,80			1,24	93		7,7	1,47
	1561						0,87				0,27		68,5												
	1562	1,18	249		8,0	1,68	0,89	109		1,43	0,29		66,9	0,60	24		7,8	0,74							
	1563						0,90				0,28		69,1												
	1564						0,93				0,21		77,2												
	1565	1,19	254		8,1	1,64	0,93	131		1,38	0,22		75,8	0,62	27		7,8	0,77							
	1566						0,94				0,25		73,5												
	1567						0,97				0,24		75,7												
	1568	1,18	252		8,0	1,67	0,98	126		1,38	0,25		74,7	0,66	29		7,8	0,77	2,40		1,37	242		8,0	1,63
	1569						1,02				0,27		73,9												