

SOME ASPECTS ON THE SPECIFIC ENERGY REDUCTION IN REFINING CAUSED BY CHEMICAL TREATMENT

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Summary

Mechanical pulping is a process for production of wood pulp in papermaking.

Thermomechanical Pulp (TMP) and Groundwood (GW) are historically the two production methods used for mechanical pulping. Because of high electrical prices and increasing requirements in pulp quality it is of interest to improve the mechanical pulping process. The Advanced Thermomechanical Pulp (ATMP) process is a development of the TMP process developed to reduce the electrical energy consumption in production of mechanical pulp. ATMP also has better strength properties and optical properties compared to TMP. Andritz, Paper and Fibre Research Institute (PFI) and Norske Skog together have developed this production method throughout several pilot plant trials with excellent results.

Mechanical pre-treatment of wood chips with a screw press and chemical addition in a high intensity primary refining stage are the features of the ATMP process. This process has recently been described (Hill et al. 2009, Hill et al. 2010, Gorski et al. 2011 and Johansson et al. 2011). Improvements in the electrical energy efficiency in refining of up to 0,65 MWh/odt or 34 % as well as higher brightness and lower shive contents compared to reference TMP pulp were shown for spruce raw material (Gorski et al. 2011)

To further understand what happens with the pulp in ATMP process compared to the TMP process different investigations were carried out. Methylene blue sorption were evaluated and used to measure the total amount of anionic groups on both ATMP and TMP produced pulps. ATMP produced pulps achieved a higher number of acidic groups compared to pulps without addition of chemicals for not only the whole pulp but also for three different fractions of each pulp. Additional tests are now carried out with conductometric titration to further verify the results from these tests.

Laboratory sheets were produced from different fibre fractions of these pulps. Optical properties, strength properties, Ambertec formation and charge decay properties were measured on these sheets. The brightness and light absorption were significantly better for all fractions of ATMP pulps compared to pulps without addition of chemicals. Pulps added bisulphite achieved the highest light absorption and lowest light scattering in these trials. The results from light scattering showed that pulps produced without addition of chemicals achieved significantly poorer result for the long fraction compared to the other pulps.

However, for the middle and fines fraction the ATMP produced pulps achieved high light scattering but not necessary the highest light scattering. TMP achieved high light scattering for both the middle and fines fraction. It is however difficult to compare the different ATMP pulps without an optimization of the addition of chemicals.

Both strain and tensile index were measured to calculate the Tensile Energy Absorption (TEA). These results showed that to produce pulp with high intensity in the primary refining stage it is preferable to have a mechanical pre-treatment prior to this refining stage. TMP was produced with low intensity in the primary refining stage resulting in poor tensile index and TEA for the long fraction. The measurements of tensile strength in the z-direction showed that ATMP (Bisulphite) gave significantly higher z-strength compared to the other pulps for all fractions.

Measurements of Ambertec formation were also carried out. The long fraction of TMP had significantly poorer ambertec formation compared to the long fraction of the other pulps. For the middle and fines fraction there were difficult to conclude with anything, the reason is probably because of the lack of agitation prior to the production of sheets from these fractions.

Evaluation of charge decay properties were difficult to perform since the results varied from day to day. The variation in these results was probably due to differences in relative humidity. The humidity differences could be described by a hysteresis curve that describes differences in humidity from absorption and desorption of water going from one air humidity to another.

Sammendrag

Mekanisk massefremstilling er en prosess for fremstilling av tremasse til produksjon av papir. Termomekanisk masse (TMP) og slipmasse (GW) er historisk sett de to produksjonsmetodene brukt for fremstilling av mekanisk masse. På grunn av høye priser på elektrisitet og et høyere krav til kvalitet i papirproduksjon er det av interesse å forbedre den mekaniske massefremstillingen. Avansert termomekanisk masse (ATMP) er en videreutvikling av TMP prosessen. Denne metoden er utviklet for å redusere det elektriske forbruket i produksjonen av mekanisk masse. ATMP har samtidig bedre styrke- og optiske egenskaper sammenlignet med TMP. Andritz, Papir- og fiberinstituttet (PFI) og Norske Skog har i samarbeid utviklet denne produksjonsmetoden gjennom flere pilot forsøk med lovende resultater.

Mekanisk forbehandling av treflis ved hjelp av en skruepresse og tilsats av kjemikalier i et første raffineringsteg med høy intensitet er karakteristisk for ATMP prosessen. Denne prosessen har nylig blitt beskrevet (Hill et al. 2009, Hill et al. 2010, Gorski et al. 2011, Johansson et al. 2011). Forbedringer i energi reduksjon opp til 0,65 MWh/odt eller 34 % samt høyere lyshet og lavere innhold av flis sammenlignet med TMP masse har blitt bevist (Gorski et al 2011).

For å oppnå en bedre forståelse av hva som skjer med tremassen i ATMP prosessen sammenlignet med TMP prosessen har flere undersøkelser blitt utført. Metylen blå sorpsjon ble evaluert og brukt til å måle den totale mengden med anioniske grupper på både ATMP og TMP produsert masse. ATMP produsert masse oppnådde et høyere antall anioniske grupper sammenlignet med masse uten tilsats av kjemikalier for hele massen, dette resultatet gjaldt også for tre forskjellige fraksjoner av hver masse. Ytterligere tester blir nå utført ved hjelp av konduktometrisk titrering for å verifisere resultatene fra disse undersøkelsene.

Laboratorie ark ble produsert fra forskjellige fiberfraksjoner av disse massene. Optiske egenskaper, styrke egenskaper, Ambertec formasjon og charge decay målinger ble målt på disse arkene. Lyshet og lys absorpsjon var signifikant bedre for alle fraksjoner av ATMP masse sammenlignet med masse uten tilsats av kjemikalier. Masse tilsatt bisulfitt oppnådde den høyeste lysheten og den laveste lys absorpsjon i disse undersøkelsene. Resultatene fra lyssprednings målinger viste at masser uten tilsats av kjemikalier oppnådde signifikant lavere lysspredning for langfraksjonen sammenlignet med de andre massene. For mellom og

langfraksjon oppnådde derimot ATMP produsert masse høy lysspredning, men ikke nødvendigvis den høyeste lysspredningen. TMP oppnådde den høyeste lysspredningen for mellom og finfraksjon. Det er imidlertid vanskelig å sammenligne de forskjellige ATMP massene siden tilsatsen av kjemikalier ikke har blitt optimalisert.

Både tøyning og slitindeks ble målt for å regne ut tensile energy absorption (TEA). Disse resultatene viste at det er å foretrekke at masse som skal gjennom en høy intensitets raffinering har en mekanisk forbehandling. TMP ble produsert med lav intensitet i det første raffineringsteget, noe som resulterte i lav slit indeks og lav TEA for langfraksjonen. Målinger av slit styrke i z-retning viste at ATMP (Bisulphite) hadde signifikant høyere z-styrke sammenlignet med alle fraksjoner av de andre massene.

Målinger av Ambertec formasjon ble også utført. Langfraksjonen av TMP hadde signifikant dårligere ambertec formasjon sammenlignet med langfraksjonen de andre massene. De var vanskelig å konkludere med noe som helst for mellom og finfraksjon, grunnen til dette er sannsynligvis på grunn av manglende omrøring før produksjon av ark på disse fraksjonene.

Evaluerings av charge decay egenskaper viste seg å være vanskelig på grunn av variasjoner fra dag til dag. Variasjonene i disse resultatene skyldes sannsynligvis fuktighetsvariasjoner. Disse fuktighetsvariasjonene kan bli beskrevet gjennom en hysteresis kurve som beskriver forskjellen i fuktighet fra absorpsjon og desorpsjon av vann når man går fra en luftfuktighet til en annen.

Abbreviations

A

ATMP Advanced Thermomechanical Pulp

B

BDDJ Britt Dynamic Drainage Jar

C

CTMP Chemithermomechanical Pulp

D

DD Double Disc refiner

G

GW (SGW) Stone Groundwood

H

HC High Consistency

L

LC Low Consistency

LWC Lightweight Coated Paper (coated magazine paper)

M

ML Middle Lamellae

P

P Primary cell wall

PGW Pressure Groundwood

R

RMP Refiner Mechanical Pulp

S

S1 First outer layer of the secondary cell wall

S2 The dominating middle layer of the secondary cell wall

S3 Inner layer of the secondary cell wall

SD Single Disc Refiner

SEC Specific Energy Consumption

T

TEA Tensile Energy Absorption

TMP Termomechanical Pulp

TGW Thermo Groundwood

Content

1	Introduction	7
2	Theoretical background	8
2.1	Wood as a material for mechanical pulping processes	9
2.1.1	Different types of wood used for pulping	9
2.1.2	Wood chemistry	10
2.1.3	Wood structure	12
2.2	Mechanical pulping processes	13
2.2.1	Groundwood	14
2.2.2	TMP	17
2.2.3	CTMP	20
2.2.4	Fines	21
2.3	Chip pre-treatment	22
2.3.1	Mechanical pre-treatment	22
2.3.2	Chemical pre-treatment	24
2.4	ATMP process	25
2.5	Comparison of different pulp fibres and properties	27
3	Materials and Methods	30
3.1	Materials	30
3.2	Methods	33
3.2.1	Total charge measurements done by methylene blue sorption	33
3.2.2	Britt Dynamic Drainage Jar	35
3.2.3	Bauer McNett	36
3.2.4	Sheet making	38
3.2.5	Charge decay measurements	40
3.2.6	Sheet analyses	40
4	Results and Discussion	41
4.1	Methylene blue sorption as a method for measuring total charge	41
4.2	Total charge measured on different pulps made from Norway spruce	43
4.2.1	Total charge measured on whole pulps	43
4.2.2	Total charge measured on different fractions	45
4.3	Optical properties	47
4.3.1	Light absorption and brightness	47
4.3.2	Light scattering vs. SEC	50
4.4	Strength properties	53
4.4.1	Stress-strain curve	53
4.4.2	Internal bond strength of paperboard (z-strength)	57
4.4.3	Comparisation of strength properties for all pulps	61
4.5	Ambertec formation	64
4.6	Charge Decay	66
4.6.1	Relative humidity 50 %	69
4.6.2	Relative humidity 35 %	73
5	Conclusions and recommendations	75
6	Acknowledgements	78
7	References	79
8	Appendix	84

1 Introduction

The demand for a reduction in electrical energy consumption in refining is acute in mechanical pulping. Paper producers are working in a tough economic situation with low paper prices and decreasing demand for paper. Mechanical pulping is a production method to produce wood pulp used in the production of paper. This is a very energy demanding process and is one of the main cost drivers in the production of newsprint and magazine paper. An improvement in this area is critical to make papermaking from mechanical pulping sustainable.

For decades TMP and groundwood have been the two methods to produce mechanical pulp. Norske Skog in cooperation with Andritz and PFI has carried out extensive process development in this area during the last 10 years. One of the developments has been the ATMP process, which is based on the TMP process. ATMP was shown to reduce the energy demand in refining by up to 42 % with better optical properties and higher strength properties compared to TMP (Hill et al 2009, Hill et al 2010, Gorski et al 2011 and Johansson et al 2011).

The ATMP process combines mechanical pre-treatment of wood chips with addition of chemicals in a high intensity primary refining stage. Produced pulp has higher strength properties and light scattering compared to TMP. This is beneficial when producing low grammage paper like super calandered paper (SC), light weight coated paper (LWC) and newsprint.

The two main objectives in this thesis have been to:

- Evaluate methylene blue sorption as a method to measure total number of acidic groups in a pulp and use this method to measure the total number of anionic groups in different fibre fractions of TMP and ATMP produced in pilot scale.
- Produce laboratory paper sheets from different fibre fractions of these pulps and measure their optical properties, strength properties, Ambertec formation and charge decay properties.

2 Theoretical background

Pulping is a process for making wood pulp from logs. During pulping, fibres are separated from the wood and prepared for papermaking. Wood is a natural material that mainly consists of cellulose, hemicelluloses and lignin. There are two different ways for separating fibres from wood, chemical and mechanical pulping.

In chemical pulping wood fibres are separated by treating chips with cooking liquor containing for example sulphite or hydrogen sulphide and alkali in a digester. The heat and the chemicals dissolve the lignin and hemicelluloses, and fibres consisting mainly of cellulose are separated from the wood.

Mechanical pulping is divided into two areas, groundwood and refiner mechanical pulping. In the SGW or PGW process (Stone Groundwood or Pressure Groundwood) pulp is produced by pressing logs against a revolving pulpstone. In the TMP process, wood chips are disintegrated to fibres in a disc refiner. Chemicals can also be used to impregnate chips prior to TMP refining and the process is then referred to as CTMP (Chemo Thermo Mechanical Pulping). Grinding (groundwood) tends to produce a pulp with excellent optical properties, but not so good strength properties. Refining generally produces pulps with good strength properties but poorer optical properties (Sundholm 1999).

For more in-depth reading about mechanical pulping, wood raw material and papermaking processes can be found elsewhere (Panshin and de Zeeuw 1980, Fellers and Norman 1992, Sundholm 1999, Fengel and Wegener 2003).

2.1 Wood as a material for mechanical pulping processes

Wood is used in different forms in mechanical pulping, either as chips or as logs depending on the pulping process. Storage of the wood prior to pulping is however important for both logs and chips. Logs are sprayed with water to prevent the bark to dry out which would make these more difficult to debark in the debarking drum. Another important element is that the brightness of the pulp is influenced by the age of the logs. Pulp made from logs harvested during the summer usually has lower brightness compared to the rest of the year (Kellomäki 1998).

2.1.1 Different types of wood used for pulping

Different types of wood are used for pulping depending of where the mill is located and what the supply situation is. The different types of trees used for pulping are divided into two groups; softwood and hardwood. Softwood is the predominant type used for mechanical pulping (Kure 1999).

Softwood is mainly evergreen which means that the tree does not loose its needles or leaves depending on the time of the year. Softwood resources are mainly situated in the Baltic region, Russia, North America and in Scandinavia. Examples of softwood trees are spruce, fir, pine and hemlock (Sundholm 1999). In Norway and the other Scandinavian countries Norway spruce is commonly used as raw material for paper production. Softwood consists of two different kinds of cells: fibres (tracheids) and parenchyma cells. The fibres are the main component of the wood and are long, narrow cells with tapered ends. The parenchyma cells form epitel layer around resin vessels and also exist as ray cells (Kure 1999). The Spruce family is especially favourable for mechanical pulping since it has low extractives content, high initial wood brightness, and pulp produced from spruce has good strength, optical and surface properties (Liimatainen, H. et al. 1993).

Most of the hardwood trees are deciduous; this means that the trees loose their needles or leaves for a shorter period of the year. Poplars are the main family of hardwood. Poplar wood is normally chemical pre-treated if it is used for refiner pulping. This is because the hardwood has more complex fibre morphology and a different chemical composition compared to softwood. The strength properties of hardwood are poorer than of softwood, but hardwood yields pulp with good light scattering and sheet surface properties (Sundholm 1999).

2.1.2 Wood chemistry

Wood consists mainly of cellulose, hemicelluloses, lignin and some extractives. Cellulose contributes with the largest content, approximately 40-50 %, lignin with approximately 15-30 % and hemicelluloses with approximately 15-25 % and extractives 1-5 %. Lignin is the “glue” of the wood, gluing the fibres together in the middle lamella while the cellulose provides the mechanical strength properties of the tree.

Cellulose

Cellulose is the building block of the tree. It is a linear polymer, long molecular chain existing of thousands of glucose units. Glucose is the most common organic compound on earth. Because of its rigidity and fibrillar structure provides strength to the wood fibre (Fellers and Norman 1998).

The hydroxyl groups in cellulose make it hydrophilic and able to react with water which leads to fiber swelling. Fibre swelling contributes to flexibility and more intermolecular hydrogen bonds can be formed in the wet state. This leads to a more compact and stronger paper sheet (Niskanen 1998).

Hemicellulose

Hemicellulose is a carbohydrate which consists of short branched molecular chains. These are hydrophilic like cellulose because of the large amount of hydroxyl groups. The open structure of hemicellulose allows liquid transport and makes it soluble in alkali or water. It gives some flexibility to the material and acts as a binding material between cellulose and lignin (Fellers and Norman 1998).

Lignin

Lignin is the material that binds the fibres together in the middle lamellae. It is built up by aromatic hydrocarbons to form a very complex three-dimensional structure. Lignin contains small amounts of hydroxyl groups and therefore absorbs less water compared to cellulose and hemicellulose. When introducing alkali to lignin, it becomes more hydrophilic and swells (Fellers and Norman 1998). Since lignin contains chromophores it turns the paper yellow when exposed to air and light.

Extractives

In addition to cellulose, hemicellulose and lignin, wood pulp consists of many other components that are soluble in neutral organic solvents such as acetone, dichloromethane, petroleum ether or water. These components are called wood extractives and consist of among others terpenes, fatty acids, resin acids, waxes, alcohols and sterols. The extractives are divided into polar and non-polar. It is desirable to remove the extractives from wood prior to papermaking since these affect the pulp and paper strength (Levlin and Söderhjelm 1999, Fardim et al. 2005a, Opedal Tanase 2011). Chemical treatment of wood reduces the amount of extractives in the pulps and therefore contributes to higher strength in the paper (Sundholm 1999)

Fibre charge

The fibre charge is dependent on the number of anionic groups present in the fibre. These groups can originate from the wood raw material or be generated during pulping, bleaching and papermaking. Carboxyl, phenolic and sulfonic acid groups are the anionic groups present in pulps (Fardim et al 2005a). There are different titration and sorption methods to determine the total number of anionic groups like conductometric titration, potentiometric titration and methylene blue sorption. The acidic groups can interact with retention aid polymers in papermaking, contributing to formation and stability. These groups also affect the fibre swelling and could also serve as binding sites for paper additives (Fardim and Holmbom 2003).

Fibre swelling

Cellulose and hemicellulose contains OH-groups which makes the fibre hygroscopic. This results in adsorption of water molecules on the surface of the fibre. Together with the number of charged groups in the fibre this affects the swelling of fibres (Fellers and Norman 1998). Increased swelling reduces the beating energy needed to reach a given beating degree, it also increases the tensile strength of a paper due to a more flexible fibre (Neimo 1999). Water Retention Value (WRV) is a method to measure fibre swelling (Fellers and Norman 1998, Sundholm 1999).

2.1.3 Wood structure

The wood cells are held together by the middle lamella (ML), *Figure 2-1*. ML consists mainly of lignin and is in principle free of cellulose. Each wood cell is built up of two cell walls, the primary cell wall (P) and the secondary cell wall (S). The secondary cell wall is divided into three different layers: S1, S2 and S3. S3 is located around the lumen (L).

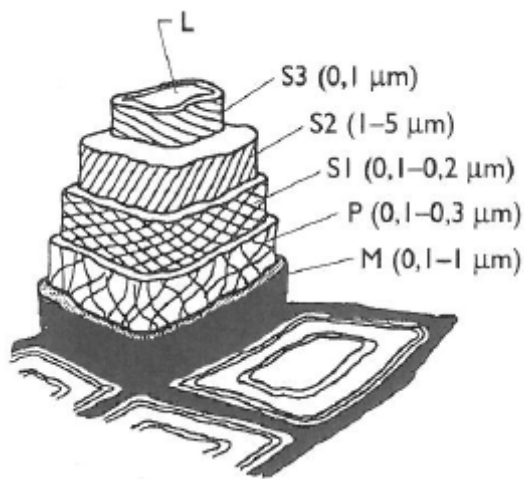


Figure 2-1 Illustration of wood cells (Fellers and Norman 1998).

The primary cell wall consists of cellulose fibrils and is the first layer deposited during the development of the cell. This system allows for an expansion of young cells (Fengel and Wegener 2003).

Secondary cell wall is divided in three different layers. The S2 layer is the thickest layer, it contains up to 90 % of the fibre mass (Kure 1999). Together with lignin and hemicelluloses, cellulose is embedded to form the cell walls. The secondary layer is wound together around the lumen where the S3 layer is closest to the lumen. The lumen acts like a pipe transporting liquid inside the tree.

2.2 Mechanical pulping processes

Mechanical pulp is produced mainly by using mechanical means, such as in the refiners or grinders. This process can be divided into two groups, groundwood (grinding) pulp (SGW and PGW) and refiner mechanical pulp (RMP). The main difference between these two methods is that for groundwood the pulp is made by pressing logs against a stone, while the chips are processed between two steel discs in the RMP method. The first grinding method was the Stone Groundwood, SGW, which was invented in 1843-1844 and the first known process for mechanical pulping. Developing this method has also led to other ways to grind pulp like PGW, pressure groundwood, and TGW, thermo groundwood (Sundholm 1999). The drawback of mechanical pulping is the high electrical energy demand.

The other method of mechanical pulp production is the RMP, refiner mechanical pulp. RMP, was invented already in 1881-1883, but the first commercial mill installation was not until Crown Zellerbach (United States) installed the process in 1960. RMP has later on developed to termomechanical pulp, TMP, and chemithermomechanical pulp, CTMP (Sundholm 1999). The advantage in using TMP is that the pulp has much higher strength properties compared to pulps made in grinders.

Mechanical pulps have some advantages compared to chemical pulps: low cost due to the high yield, fairly high brightness, high light scattering properties, high smoothness, good formation and high bulk. Yield in chemical pulping compared to mechanical pulping is much lower. The yield for mechanical pulping is approximately 95-98 % compared to chemical pulping where the yield is approximately 50 % since most of the lignin and hemicellulose are dissolved during cooking (Sundholm 1999) Even though the chemical pulp has better strength properties, it is not suitable for making low grammage paper with high strength and good opacity properties.

2.2.1 Groundwood

Grinding is a method to produce wood pulp by pressing logs against a rotating stone. This is the oldest method of pulp production in the industry. The first commercial stone grinders were installed in Germany as early as 1852. Since then the method has been developed several times, but the main principle is today still very much the same (Sundholm 1999). The first steps in grinding have always been to cut the tree into logs before it is debarked, *Figure 2-2*.

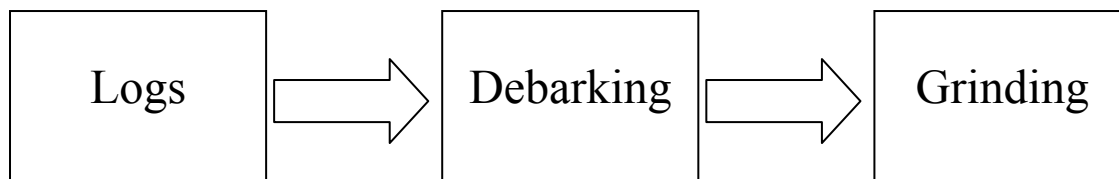


Figure 2-2 Overview over the first steps in SGW production.

There are three different methods for grinding logs; GW (groundwood), PGW (pressure groundwood) and TGW (thermo groundwood), *Figure 2-3*. Several investigations have proven that if the temperature in the grinder is increased, pulp strength will increase as well. The atmospheric grinder however had limitations regarding elevated temperature. Since the grinding is conducted under atmospheric conditions it could never be possible to raise the temperature to more than 100 °C. The energy in the form of steam that was produced in the grinder would be released since it was open. To improve this type of grinding the PGW were invented. Using grinding under pressurized conditions it was possible to elevate the temperature to over 100 °C which made it possible to make pulp with higher strength properties. As an alternative to PGW the TGW was invented. TGW has a 20-50 cm high water column over the grinding zone; the idea was to set the temperature at the beginning of the grinding zone to such a level that the target pulp temperature of 100 °C was reached. The idea was also that the water column would condense the vapour developed in the grinding zone to prevent energy loss (Sundholm 1999)

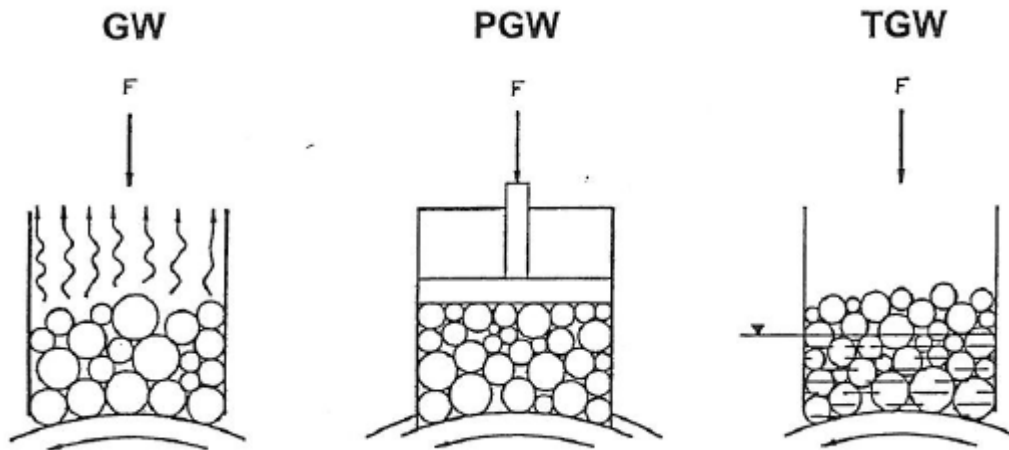


Figure 2-3 Principles of atmospheric grinding, pressure grinding and thermo grinding (Sundholm 1999).

The first grinders were so called Stone Grinders, open atmospheric grinders were the logs were pushed against the stone to produce wood pulp. Modern atmospheric stone grinders (GW), *Figure 2-4*, have two pockets for the logs on each side of the stone and shower heads that clean and cool down the stone. The logs used to these kind of grinders can be approximately 1,2 – 1,6 meters in length depending on the size of the grinder. They can produce from 80-100 tons/day of groundwood pulp with freeness 80-120 ml suitable for SC and LWC paper (Sundholm 1999).

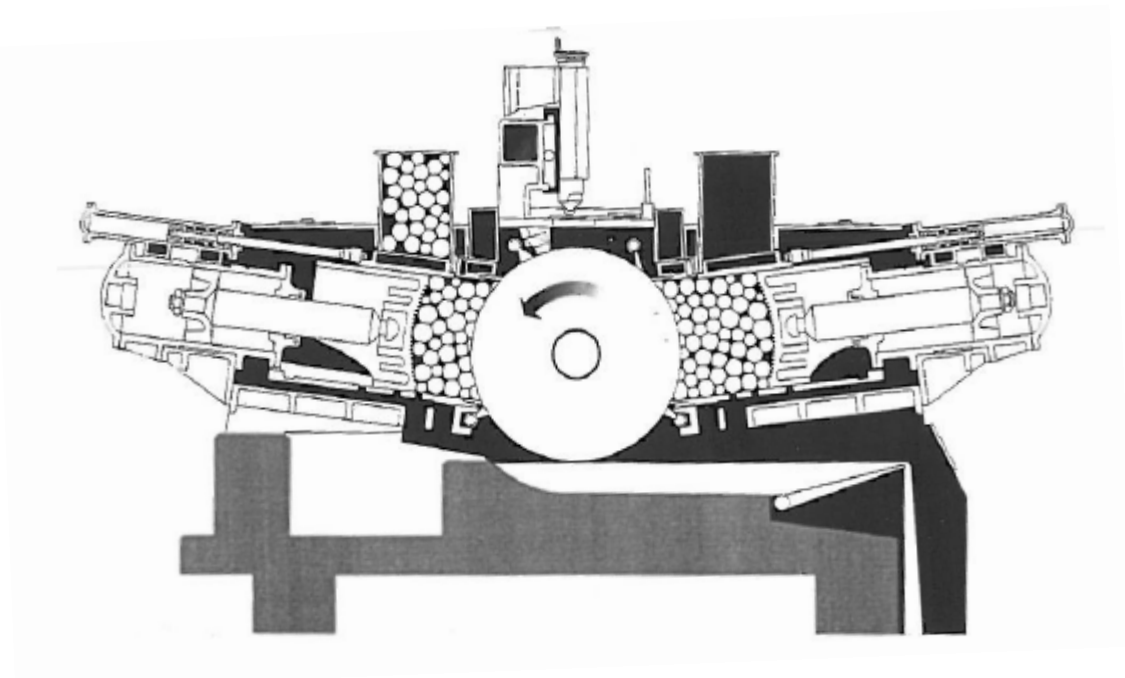


Figure 2-4 Modern atmospheric Valmet grinder (Sundholm 1999).

In the 1970's there was some development of the old GW resulting in a new method for grinding. PGW, pressure groundwood, upgraded the original GW to operate under pressurized conditions and elevated temperatures. With this upgrade it was possible to produce wood pulp with higher average fibre length and pulp strength properties. The main difference from GW to PGW was that the wood batches are fed into a pressure equalization chamber before grinding, *Figure 2-5*, which makes it possible to raise the pressure in the grinding zone. In the PGW grinders it is possible to operate with a pressure up to 3 bars. To improve the fibre length and pulp strength further the PGW-S grinder, super pressure groundwood, was introduced. PGW-S makes it possible to produce pulp with a pressure up to 5 bars (Sundholm 1999).

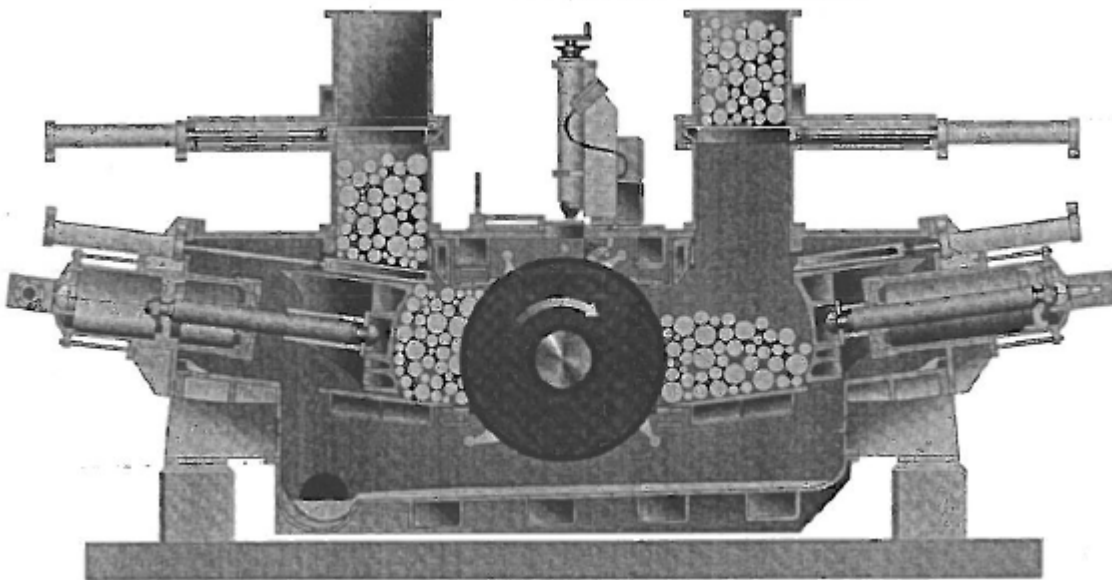


Figure 2-5 The Valmet PGW grinder (Sundholm 1999).

2.2.2 TMP

Thermomechanical pulps are made from chips which are refined between two steel discs. This process was developed from the early RMP, refiner mechanical pulp, and is the dominating process for mechanical pulp production today. The origin of RMP is simple groundwood reject refiners designed by J.M Voith in 1859, *Figure 2-6* (Reme 2000)

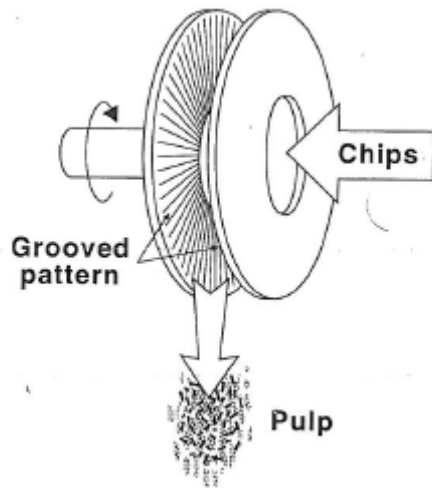


Figure 2-6 Principle of refiner mechanical pulping (Sundholm 1999).

TMP is made from logs that are debarked and cut into smaller chips. The chips are then washed and preheated before refining. The actual refining is done between two steel discs where at least one of the discs rotates. Chips are preheated to become softer and more easily refined. This makes it possible to produce pulp with higher strength properties.

A typical line for TMP production consists of two or three refiners in series. The chips are steamed atmospherically at approximately 100 °C to soften the wood structure and remove the air from the chips. Then the chips are washed with hot water to remove unwanted particles such as sand etc. After the washing the chips are sent to a pre-heater under elevated pressure conditions prior to refining in the primary refiner. From the primary refiner the pulp is sent to a steam separator before it is refined once more and then sent to latency chest through another steam separator. The latency chest lets the fibres release tensions and straighten up. Screening after the latency treatment separates the fibres into two fractions. One is ready for papermaking and the other one need more refining in a reject refiner (Reme 2000). *Figure 2-7* gives an overview of a typical TMP production plant.

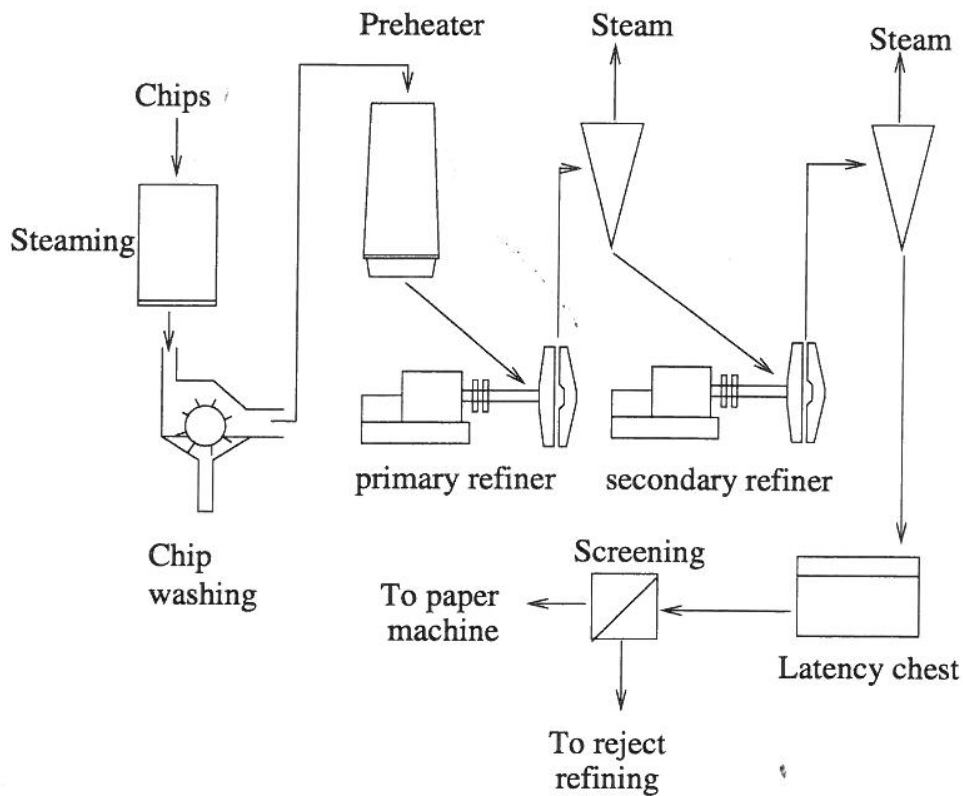


Figure 2-7 Overview of a typical TMP production plant (Reme 2000).

There are two main types of disc-refiners: single-disc (SD) and double-disc (DD). In SD refiners only one of the discs rotates while in a DD refiner both discs rotate. Single-disc (SD) refiners, *Figure 2-8*, consist of a rotating disc and a stationary disc. The pulp is fed between the two discs and then processed. How hard you process the pulp depends on how much motor load and hydraulic force is conveyed to the rotating disc while pressing it against the stationary disc.

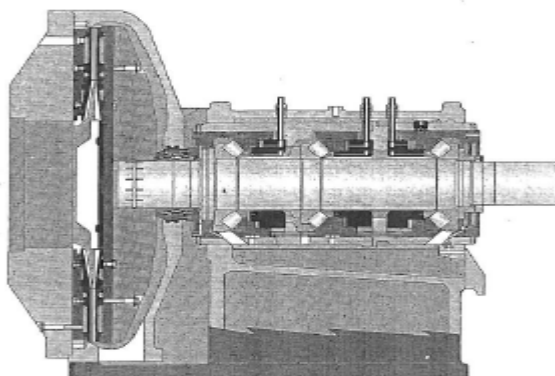


Figure 2-8 The RGP 268 refiner from Sunds Defibrator (Sundholm 1999).

Double-disc (DD) refiners, *Figure 2-9*, consist of two counter rotating discs, each disc driven by a separate motor. Chips are fed into the gap between the discs through openings in one of the rotating discs. A DD refiner uses approximately 300 kWh/t less energy than a SD refiner, and the produced pulp has somewhat shorter fibre length, higher light scattering and similar bonding properties (Sundholm 1999). Refining intensity may be defined as specific energy per bar impact (Miles and May 1990, Miles 1991). With a DD refiner it is easier to refine using higher intensity. The intensity depends on the speed of the discs, segment pattern, concentration of the pulp and production rate as well as the type and size of refiner used.

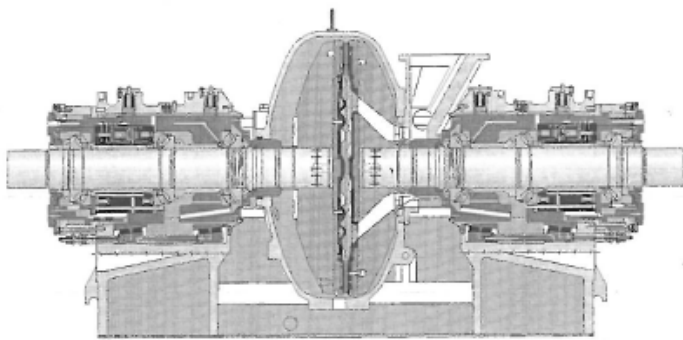


Figure 2-9 The RGP 68 DD refiner from Sunds Defibrator (Sundholm 1999).

2.2.3 CTMP

In CTMP (Chemithermomechanical Pulp) process, chemicals are added to the wood chips prior to refining. Chemicals used could be for instance sodium sulphite or alkali or both. These soften the wood prior to the refining stage. CTMP production has lower yields compared to TMP but drastically higher yields compared to chemical pulping.

The chemical pre-treatment in the CTMP process happens in the impregnation stage. The CTMP process was developed to make it possible to produce very high yield hardwood pulps and improve such softwood pulp properties as cleanliness, absorbency and strength properties (Sundholm 1999).

Figure 2-10 gives an overview of a typical chemimechanical pulping process. After the chips have been washed these are impregnated with chemicals. For CTMP production it is important to have an efficient impregnation stage. Preheating of the pulp is important to make the added chemicals to react with the chips. The equipment used in the refining stage in CTMP process is no different from the TMP process, the difference is what happens before the refining. Differences in pulp properties are described in chapter 2.5.

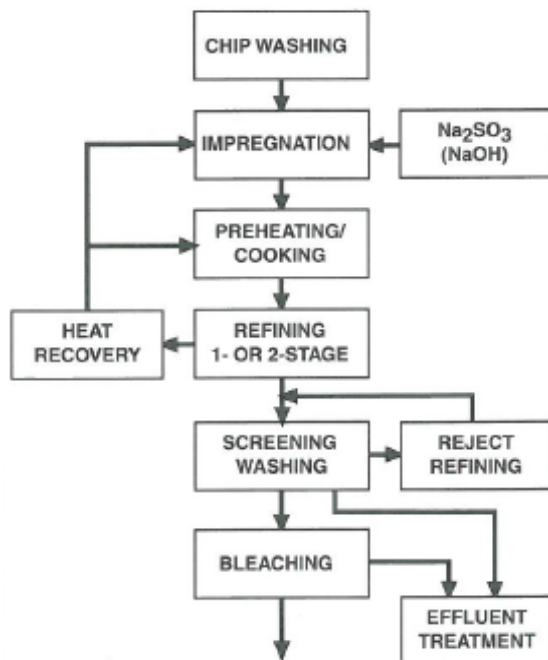


Figure 2-10 General block diagram for chemimechanical pulping.

2.2.4 Fines

Fines are the smallest fraction of the wood pulp. These are formed in the pulping process and are shards of fibre. It is often defined as the fraction passing through a screen plate with a screen opening of 76 μm (200 mesh). It is referred to as the “P200” fraction, which stands for “Pass 200 mesh”. Most of the fines in TMP pulping are created by a peeling action on the wood fibre, *Figure 2-11*. This implies that the fines originate from the outer parts of wood fibres, these are called flake-like fines (Heikkurinen, A. and Hattula, T. 1993). With an increase in specific energy consumption in refining more particles are peeled off from the secondary wall, these are called fibrillar-like fines (Luukko, K. 1999).

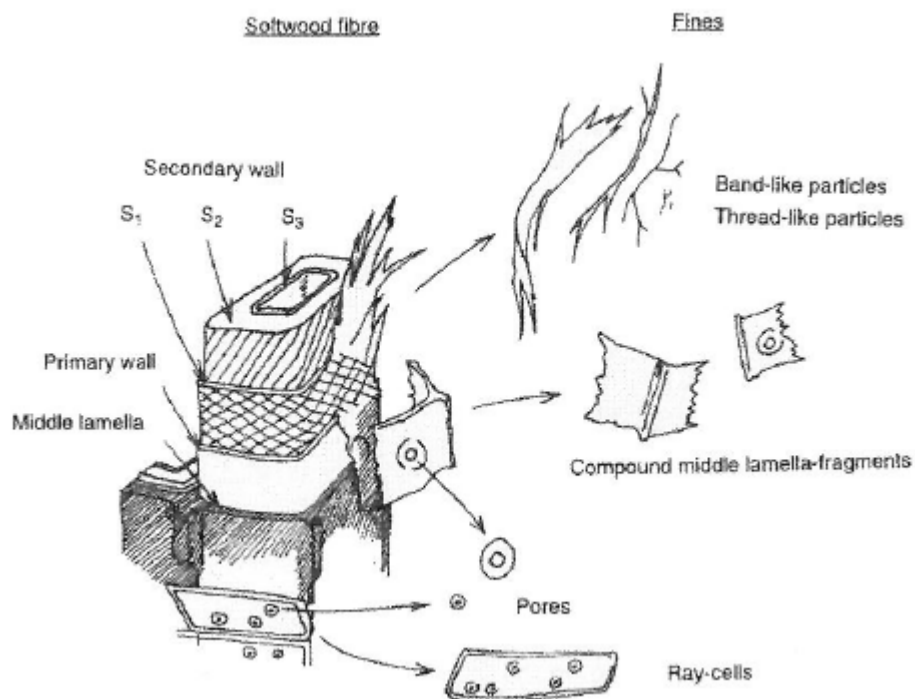


Figure 2-11 Illustration of the appearance and origin of TMP-fines (Rundlöf 2002).

2.3 Chip pre-treatment

Chip pre-treatment is a way to improve the refining by either reducing the specific energy demand or by improving the pulp quality. Chemical and mechanical pre-treatment are the two possible ways to treat the pulp before refining. Chemical treatment, utilized in the CTMP process, changes the chemical properties inside the wood by softening lignin etc. Breaking down the chips by mechanical treatment is done by compressing and/or shearing the chips.

2.3.1 Mechanical pre-treatment

There are several devices designed for mechanical pre-treatment of wood chips. Some of them were designed long ago, but have not really been a success. Some of these are used in production all over the world without being used as a pre-treatment tool, for example the screw feeders. Mechanical pre-treatment in the ATMP process consists of Impressafiner and Fiberizer.

Several other devices for mechanical pre-treatment have existed or exist on the market (Gorski et al 2010a):

- Frotapulper machine
- Plug screw feeder
- BiVis extruder
- PREX impregnator
- Roller nip compression devices
- Chips shear cutting equipment

Impressafiner

The Impressafiner is a compression screw where the compression happens under elevated temperature and high pressure (Sabourin et al. 2003).

The chips are fed into the screw with a typical inlet pressure of 1,5 bars, 10 seconds retention time. These pre-heated chips are fed into an Impressafiner, *Figure 2-12*, a specially designed plug screw with a 5:1 volumetric compression ratio (Gorski et al 2010a). After the chips have been compressed in the Impressafiner these will expand at the outlet and an efficient addition of water or chemicals is possible.

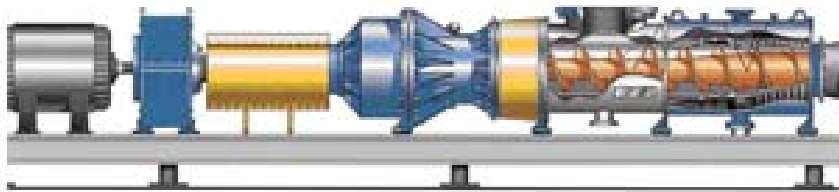


Figure 2-12 MSD 500 Impressafiner
(<http://www.andritz.com/ANONID1D5428AD4E91CE1/reactorfeedequipment-msdimpressafiner>).

Fiberizer

Fiberizer is a mildly pressurized single disc refiner, refining with an operating pressure of approximately 1,5 bars (Sabourin 2003). The purpose of Fiberizer is to defibrate wood chips to individual fibres and fibre bundles. This makes the wood and fibre structure more accessible for chemicals added later.

2.3.2 Chemical pre-treatment

Chemical pre-treatment of chips is used in CTMP and chemical pulping.

Sodium sulphite (Na_2SO_3) is normally used for softwood CTMP. Sodium sulphite (Na_2SO_3) and sodium hydroxide (NaOH) are used for hardwood CTMP. There are also processes that utilize hydrogen peroxide on hardwoods. Lignin is sulfonated or carboxylated upon the addition of chemicals and therefore becomes more hydrophilic. This makes the chips softer. Hardwood contains less lignin than softwood and besides sulphonation and carboxylation of lignin it is also important to modify the carbohydrates present. The chemical pre-treatment for hardwood stabilizes the hemicelluloses against degradation, partly because the acetyl groups are split off (Sundholm 1999).

The chemical pre-treatment can be carried out in different ways (Sundholm 1999):

- Spraying of chemicals onto the chips.
- Steaming the chips and then soaking them in a cold sulphite solution.
- Compressing the chips mechanically, followed by expansion in a sulphite solution.
- Addition of chemicals to the refiner.

2.4 ATMP process

At the International Mechanical Pulping Conference in 2003, Andritz introduced a new method of producing TMP pulp which included the RTF pre-treatment (Sabourin 2003). The pre-treatment was carried out in the Impressafiner and the Fiberizer.

Andritz and Norske Skog have later developed this process further on by adding chemicals in a high intensity primary refining stage (Hill et al. 2009, Johansson et al. 2011, Gorski et al. 2011). By adding different chemicals in the ATMP process it is possible to increase the brightness of the pulp and reduce the specific energy demand in refining as well as the shive content. This is achieved while light scattering and strength properties of ATMP are retained at the same level compared with TMP reference (Gorski 2011).

The ATMP process, *Figure 2-13*, consists of an Impressafiner, Fiberizer and high intensity refiner with addition of chemicals. By pre-compressing the chips it is possible to macerate the chips and remove extractives. The destructured chips are then impregnated with water at the Impressafiner outlet, which helps to reduce the variations in the moisture content.

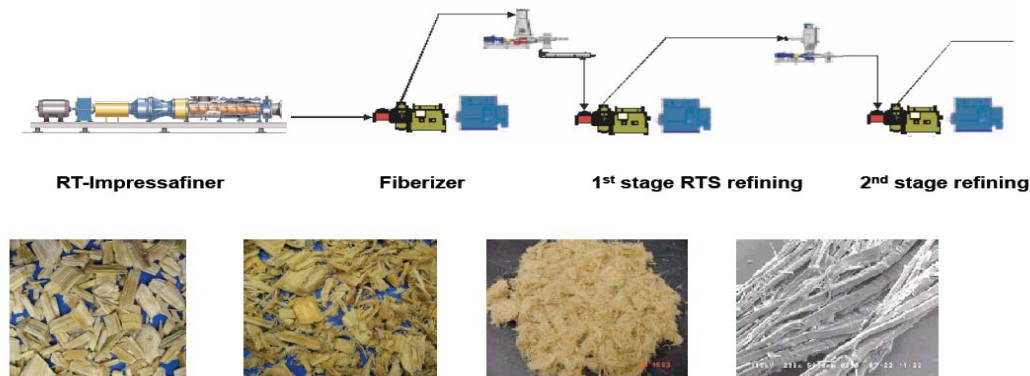


Figure 2-13 Picture describing the ATMP process with pictures of the pulp after each stage (Hill et al. 2009).

After the Impressafiner wood chips are fed into a Fiberizer. The Fiberizer is a single-disc refiner which fiberizes the chips before the 1st stage high intensity refining. By compressing and refining in moderately pressurized environment it is possible to separate the chips into fibres and fibre bundles. By refining the chips in a Fiberizer at low specific energy (100-200 kWh/odt) application it is also possible to produce fiberized pulp without an appreciable level of fibre development. Pre-treatment with an Impressafiner and a Fiberizer yields energy reduction in excess of 500 kWh/t subsequent refining (Hill et al. 2009).

Addition of chemicals to the high intensity primary refining stage is another part of the ATMP process. Different chemicals have been used, both reductive and oxidative. All yielded positive effect, lowering the energy demand in refining. The unique aspect of ATMP process is its ability to obtain preferential separation in the fibre wall areas similar to TMP pulping, despite the use of chemicals like bisulphite which typically demonstrate a high degree of separation in the middle lamellae when utilized in traditional CTMP process (Hill et al. 2009). The TMP-like fibre separation results in significantly improved optical properties such as high light scattering and opacity, which are key characteristics of pulps used for printing papers.

Investigations show that energy reduction due to the addition of chemicals is possible for most wood species (Hill et al. 2009, 2010, Johansson et al 2011, Gorski et al. 2011). It was also concluded that bisulphite was an effective chemical which resulted in lower energy demand, higher bonding strength, lower shive content, lower extractives content and higher bleached brightness (Hill et al 2009). Further investigations showed that treatment with hydrogen peroxide is more energy efficient and gives higher brightness (Hill et al. 2009). Treatment with hydrogen peroxide and magnesium hydroxide gave an improved energy efficiency by approximately 1,1 MWh/ODT or 42 % calculated at equal tensile index (25 Nm/g) compared to TMP when applied to Loblolly pine. In addition the shives content in ATMP was significantly lower and the brightness was higher (14 ISO %) compared to TMP (Gorski et al 2011).

2.5 Comparison of different pulp fibres and properties

Chemicals added in the CTMP process yield fibre separation inside the middle lamella due to its softening by chemicals. This gives a larger amount of undamaged fibres compared to the TMP process, *Figure 2-14*.

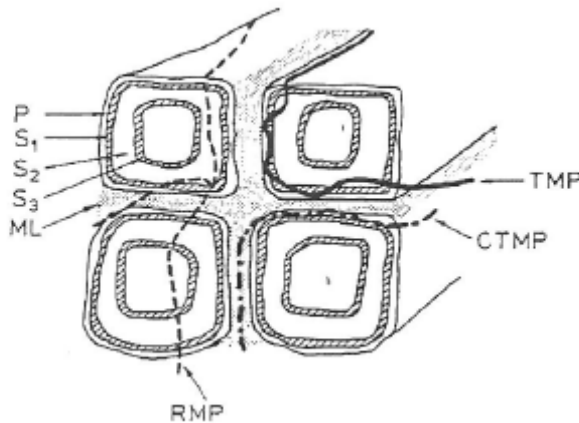


Figure 2-14 Illustration of fracture zones in softwood by different mechanical processes (Sundholm 1999).

CTMP fibres are longer than TMP fibres. Because the CTMP has longer fibres compared to TMP it would also have a higher tear strength which is very dependent on the length of fibres. Chemical treatment of CTMP pulp results in improved bonding capability due to an increase in the contact surface between fibres. This also improves the tensile strength; *Figure 2-15* (Fellers and Norman 1998).

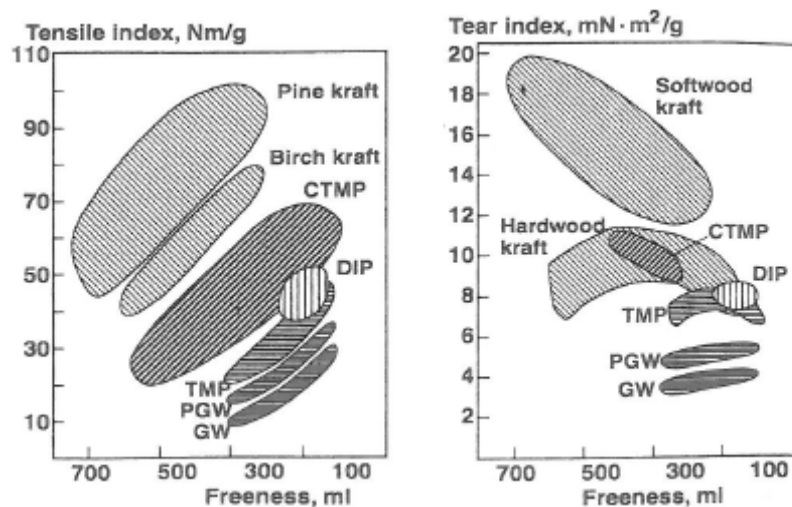


Figure 2-15 Differences in strength properties for various pulps (Sundholm 1999).

Since chips are separated to fibres in the middle lamellae and not inside the secondary fibre wall, like in the TMP process, decreased number of fibrils on the fibre surface and fines is produced. This gives a lower light scattering coefficient compared to TMP. Since the light scattering coefficient of CTMP is lower compared to TMP pulp, the CTMP is unsuitable for the making of magazine or newsprint, *Figure 2-16*. To compensate for the lower average fibre length in TMP, resulting in lowering the tear strength, sulphate pulp is added in magazine grades.

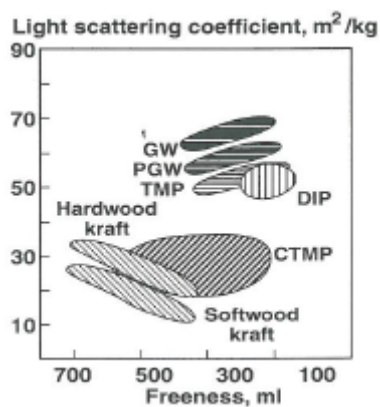


Figure 2-16 Differences in light scattering ability for various pulps (Sundholm 1999).

The ATMP with its mechanical pre-treatment and enhancement of fibre development with chemicals separates the fibre in the same way as in the TMP pulp. The chemicals added after the defibration can freely access the exposed fibre walls instead of the middle lamellae. After the defibration the surface is much larger and more accessible for chemicals. When adding chemicals to the CTMP pulp, the chemicals diffuse through the lumen of the fibres, leading to the impregnation of all fibre material while most of the softening happens in the reactive middle lamellae region.

With high intensity refining in the primary refining stage the ATMP pulp is produced with a much higher strength properties compared to TMP pulp at the same energy input, *Figure 2-17*. The brightness is higher and the amount of shives is lower which is important for the surface properties of the paper, *Figure 2-17* and *Figure 2-18*. This makes it ideal for papermaking.

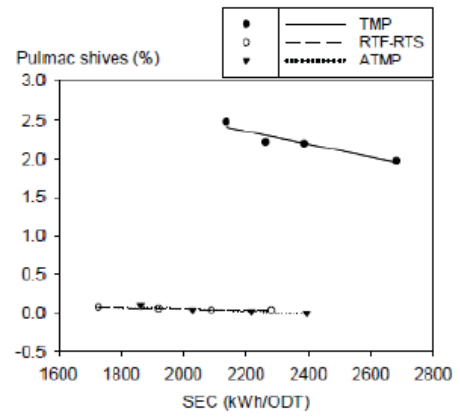
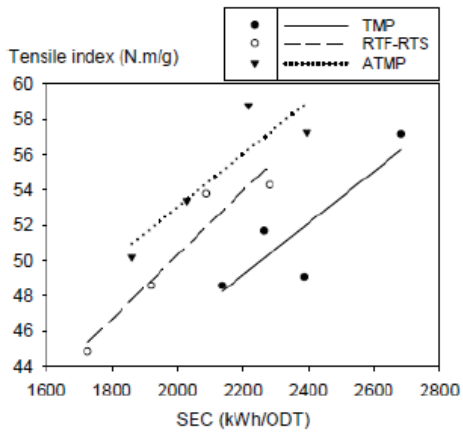


Figure 2-17 Differences in tensile index and amount of shives for various pulps (Gorski et al 2010b).

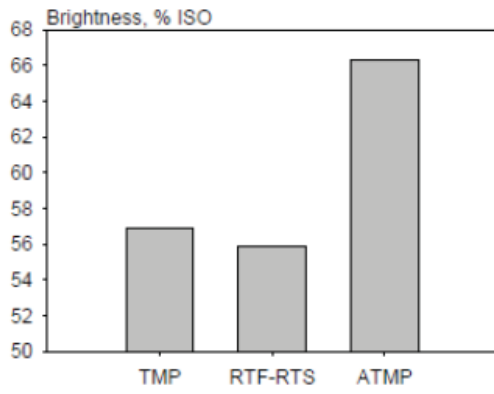


Figure 2-18 Differences in brightness for various pulps (Gorski et al 2010b).

3 Materials and Methods

Norway spruce (*Picea abies*) sawmill chips from Norske Skog Walsum, Germany, was used as raw material in this study and the chips were processed at Andritz pilot plant in Springfield, Ohio, USA. First stage pulps were used in this study. Measurements of total charge, sheet making, fractionation, optical properties and Ambertec formation were done at nsifOCUS in Halden, Norway. Strength properties were tested and evaluated at PFI in Trondheim, Norway.

An objective of this thesis was to implement methylene blue sorption as a method to measure total amount of acidic groups. To verify these results measurements were done on TMP pulp made from White spruce (*Picea glauca*) from Wisconsin, USA. White spruce is quite similar compared to Norway spruce.

3.1 Materials

The trial consisted of seven different process concepts, *Table 3-1*. Refining was conducted in only one stage. TMP and RTS refining were conducted without any mechanical pre-treatment. Mechanical pre-treatment was used for the rest of the pulps, consisting of Impressafiner and Fiberizer units. Chemical recipes for ATMP pulps are given in *Table 3-1*.

Table 3-1 Pulps and chemicals added in the pilot trial.

Pulp	Chemical recipe
TMP	None
RTS	None
ATMP (aq.)	None
ATMP (Bisulphite)	2.8% NaHSO ₃
ATMP (Bisulphite + Wash + Peroxide)	0.21% DTPA + 0.78% NaHSO ₃ + 3.8% H ₂ O ₂ + 1.9% Mg(OH) ₂
ATMP (Peroxide + Mg(OH) ₂)	0.35% DTPA + 2.2% H ₂ O ₂ + 1.4% Mg(OH) ₂
ATMP (Bisulphite + Peroxide)	0.21% DTPA + 0.78% NaHSO ₃ + 3.5 % H ₂ O ₂ + 1.9% Mg(OH) ₂

DTPA was added at the outlet of the Impressafiner, while the rest of the process chemicals were added through the inner ring dilution water into the Fiberizer or the first stage refiner, Figure 3-1. Refiner variables used in the pilot trial are given in Table 3-2.

For ATMP (Bisulphite) and ATMP (Peroxide + Mg(OH)₂) the chemicals were added into the first stage refiner. However, for ATMP (Bisulphite + Peroxide) and ATMP (Bisulphite + Wash + Peroxide) the bisulphite was added into the Fiberizer and the peroxide added into the primary refiner. For ATMP (Bisulphite + Wash + Peroxide) there was a washing stage between the Fiberizer and the primary refiner. The pulp was washed by a pilot wire press where the pulp was first diluted and then drained through the wire press.

Table 3-2 Refining variables during the pilot trial

	Impressafiner	Fiberizer	1st stage refiner
TMP trials			
Preheating time (s)	Not used	Not used	150
Speed (rpm)	-	-	1800
Casing pressure (bars)	-	-	2,8
Casing temperature (°C)*	-	-	142
Segment pattern**	-	-	Ex
RTS trials			
Preheating time (s)	Not used	Not used	10-15
Speed (rpm)	-	-	2300
Casing pressure (bars)	-	-	5,9
Casing temperature (°C)*	-	-	164
Segment pattern**	-	-	Ex
ATMP trials			
Preheating time (s)	15	0	10-15
Speed (rpm)	38	1800	2300
Casing pressure (bars)	1,4	2,3	6,1
Casing temperature (°C)*	127	138	166
Segment pattern**	-	Ex	Ex

* Casing temperature calculated under the assumption of saturated steam conditions

** Ex (expel) segment patterns gave higher intensity compared to Hb (holdback)

The accumulated specific energy demand (SEC) in refining during the pilot trial is given in Table 3-3. The error in specific energy demand for this pilot plant has been calculated to be approximately 1,5 % (Johansson et al 2011).

Table 3-3 Accumulated electrical energy demand (in kWh/odt)

Pulp	Impressafiner	Fiberizer	1st stage refiner
TMP	-	-	1064
RTS	-	-	754
ATMP (aq.)	39	219	863
ATMP (Bisulphite)	46	236	1108
ATMP (Bisulphite + Wash + Peroxide)	37	197	1058
ATMP (Peroxide + Mg(OH) ₂)	39	219	830
ATMP (Bisulphite + Peroxide)	37	197	1023

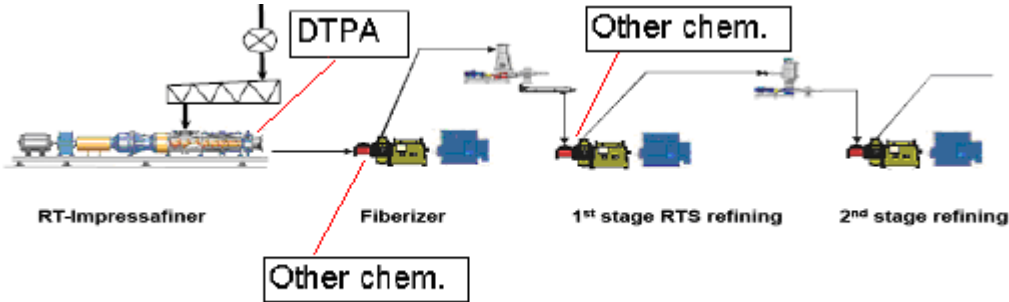


Figure 3-1 Pilot plant refiner configuration for ATMP production. No mechanical pre-treatment for TMP and RTS. ATMP (aq.) had mechanical pre-treatment but no addition of chemicals (Gorski et al 2011).

3.2 Methods

This chapter describes the different methods used for the analysis of pulps, fibres and paper sheets.

3.2.1 Total charge measurements done by methylene blue sorption

Total charge is a measurement of the total amount of anionic groups in a pulp. Methylene blue is not selective and reacts with all anionic groups in a pulp, Figure 3-2. It is known for its strong adsorption onto solids and its recognized usefulness in characterizing adsorptive material (Froix and Nelson 1975, Barton 1987, Kaewprasit 1998). As long as it is an excess of methylene blue compared to the number of anionic groups in the pulp it is possible to measure the total charge. An increase in total charge affects fibre swelling and could also serve as binding sites in for paper additives.

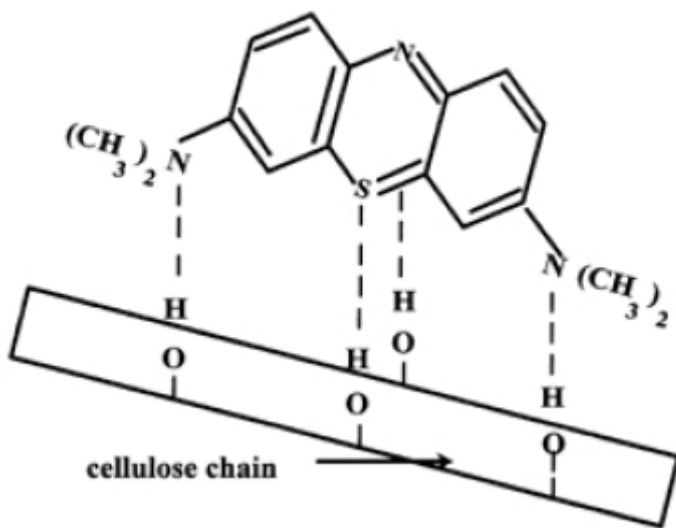


Figure 3-2 Schematic model of methylene blue and cellulose interaction (Kaewprasit 1998).

The total charge for each pulp was measured using methylene blue sorption. Conductometric titration is more accurate than methylene blue sorption, but the latter method is much faster and cheaper. One of the targets in this thesis was to implement the methylene blue sorption method to nsiFOCUS. The method is based on articles written by Fardim and some help from PFI (Fardim et al. 2002, Fardim et al. 2005a, Fardim et al 2005b)

Four parallel tests were performed on each sample to get a more accurate result. Each sample was diluted to a consistency around 1 %. The samples were prepared in a disintegrator with a temperature of 90 °C. About 70 mg (o.d.) of pulp was transferred to an Erlenmeyer bottle and mixed with 0,4 mM methylene blue dissolved in 0,6 mM phosphate buffer. The Erlenmeyer bottles were wrapped in aluminium foil and stirred for 15 min. All samples were then filtered through a Glass Microfiber Filter. The recovered filtrate was diluted 25 times with phosphate buffer before it was measured by UV-visible spectrophotometer at a wavelength of 664 nm. To get an accurate answer the amount of filtrate was measured and added to the calculation of anionic groups. The calibration curve was made using the 0,4 mM methylene blue solution diluted with a ratio of 25:250 with phosphate buffer. From the filtrate and calibration curve it was possible to calculate the concentration of methylene blue that was adsorbed to the fibres and then the amount of anionic groups in the pulp could be calculated.

3.2.2 Britt Dynamic Drainage Jar

A Britt Dynamic Drainage Jar (BDDJ) fractionates pulps with the help of a mesh screen. The pulp used for fractionation was added to the jar and agitated by the impeller at 2500 rpm. After 1 minute of stirring, the pinch clamp underneath the screen was opened to let the pulp fraction smaller than the screen opening trough. When the jar was empty 1, 5 liters of distilled water was added to wash the rest of the pulp held back by the screen plate (Britt 1973).

BDDJ was used to separate the fines fraction from the rest of the pulp. The pulps were hot disintegrated and diluted to a consistency of 3 g/l before fractionation. The disintegration was done according to the ISO 5263-3:1997 standards. Approximately 5 grams oven dry pulp was used in the fractionation for each pulp.

A screen with a mesh opening of 200 (76, μm) was used in the BDDJ. The pulps were fractionated by the screen plate and the fines were retained in a beaker under the jar. Each pulp was washed with 1,5 liters of distilled water. *Figure 3-3* shows the setup of a BDDJ.

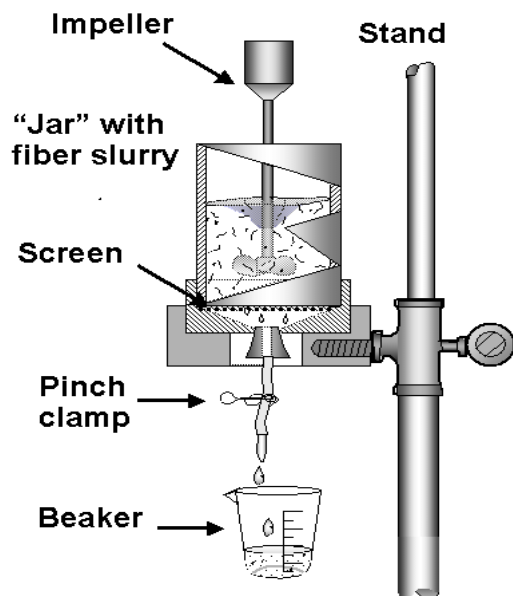


Figure 3-3 Schematic of a Britt Dynamic Drainage Jar
(http://www4.ncsu.edu/~hubbe/Essays/reten&drainage_chem.htm)

3.2.3 Bauer McNett

Bauer McNett is a device which allows separating pulps into different size fractions. The pulp is separated by screens with different mesh openings, there are 5 different screens, *Figure 3-5*. From Bauer-McNett it is possible to get 6 different fractions; R14, P14/R30, P30/R50, P50/R100, P100/R200, P200. R represent retended and P represent passed. Each chamber in the Bauer McNett does the fractionation in an identical way, *Figure 3-4*. Bauer McNett was used to separate the long and the middle fraction from each other. The fractionation was done on the pulp hold back in the jar after the BDDJ fractionation.

The fractionation was done according to the standard SCAN M6:69.

R14 retains shives and long fibres that can not pass the mesh.

P14/R50 is the long fibre fraction.

P50/R100 is the middle fraction with some long fibres and some fines.

P100/R200 is the middle fraction with some long fibres and some fines.

P200 is the fraction containing fines. The design of Bauer-McNett makes it complicated to retain this fraction.

Long fraction consisted of R14 and R14/R50.

Middle fraction consisted of P50/R100 and P100/R200.

Fines fraction consisted of P200 fractionated in the BDDJ.

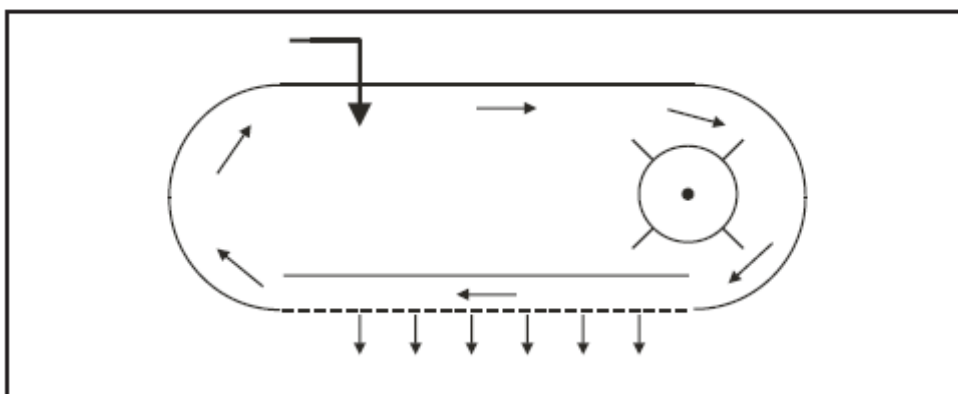


Figure 3-4 Schematic of a Bauer McNett chamber seen from the top. The inlet flow enters from the top and is driven circulatory by the rotor at the right side. Some of the flow splits up and passes through the screen at the bottom. The fraction that doesn't pass is held back by the screen mesh (Gooding and Olson, 2001)



Figure 3-5 Photograph of a Bauer McNett classifier (Gooding and Olson, 2001).

3.2.4 Sheet making

Sheets were made using two different sheet formers. The sheets produced from the long fibre fraction were produced on a larger sheet former to get a better distribution of fibres compared to the small sheet former. The small sheet former was used on the middle and the fines fraction where the distribution was much better compared to the long fibre fraction. This sheet former was also favourable due to the small amounts of middle and fines fraction available.

3.2.4.1 Long fibre fraction

Sheets from the long fibre fraction were produced on a PFI Sheet former according to the SCAN-CM-27.00 standard. There was no need to use recycled white water for the production of sheets from the long fibre fraction since there were no fines present in the pulp.

3.2.4.2 Middle and fines fraction

The sheets from the middle and fines fraction were made on a sheet former made by nsiFOCUS in cooperation with PFI. This sheet former was designed to produce smaller sheets than the sheet formers used for regular sheet making, *Figure 3-6*. The sheets are 15 cm long and 8 cm wide, before investigations the sheets are cut to become 14 cm long and 7 cm wide.

The pulp was added in the upper container and was drained over a wire, approximately 0,72 g o.d pulp was used to produce paper with a weight of 60-70 gram/m². When the upper container was empty a vacuum switch was turned on to increase drainage and make it possible to remove the sheet from the wire. For production of sheets from the fines fraction, a wire with a wire opening of 22 µm was used. Each sheet made in the Sheet Former dried in a room with 50 % relative humidity before testing.

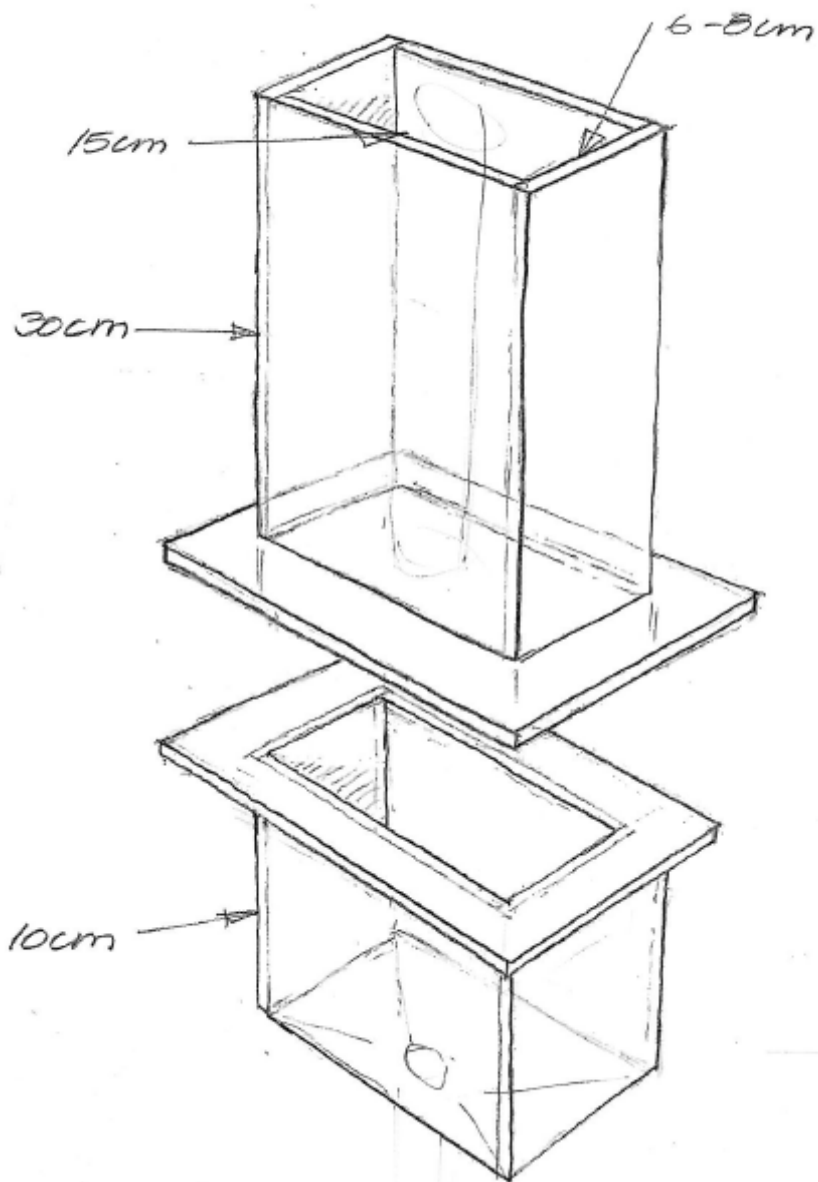


Figure 3-6 Sketch of the sheet former used for middle and fines fraction.

3.2.5 Charge decay measurements

Charge decay is a method to measure electrostatic properties of paper. Static electricity can lead to double feeds, misfeeds and paper jams in the printing works. Sparks can also be seen not only in the printing works, but also in the calander when producing paper. This happens if the resistivity is too high or the charge decay time is too long (Niskanen 1998). Highly charged sheets could also increase the accumulation of dust on paper. These measurements refer to the sensibility of a paper surface to undergo charging and the time the paper surface requires for discharging (Levlin and Söderhjelm 1999).

The charge decay measurements were done on JCI 155v5 Charge Decay Test Unit. This is a test unit where a high voltage corona discharge is sent through the material to be tested. In this study the discharge was sent through a piece of paper. The unit measures capacitance, received charge, initial peak voltage and the time it takes to discharge 90 % of the charge brought into the paper. In the tests done in this thesis there were taken 5 parallels for each sample.

3.2.6 Sheet analyses

Strength and optical properties were tested and evaluated on the sheets produced as described in section 3.2.4. The determination of grammage, sheet thickness, density, opacity, brightness, light scattering coefficient (s), light absorption (k), tensile index, and z-strength were done according to the following standards:

- ISO 534:1988, SCAN P7:96, sheet thickness, density
- ISO 536:1996, SCAN P6:75, grammage weight
- ISO 1294:1995, SCAN P38:80, tensile index, strain
- ISO 2470:1999, SCAN P3:93, ISO-brightness
- ISO 2471:1998, SCAN P8:93, optical properties, opacity, light absorption, light scattering
- TAPPI T 541 om-99, z-strength

In addition Ambertec formation was also measured.

4 Results and Discussion

It is important to notice that all of the pulps used in these investigations are 1st stage pulps. Pulp is normally refined in two stages prior to papermaking. In this case it was interesting to investigate the effect of using different chemicals in the ATMP process and primary stage pulps were studied.

4.1 Methylene blue sorption as a method for measuring total charge

Methylene blue is a fast method to measure the total amount of acidic groups in a pulp. Acidic groups are important functional groups since it affect fibre swelling, refining, strength properties and interaction with paper chemicals (Fardim et al 2005a). The methylene blue sorption method is not as accurate as conductometric titration, but since conductometric titration is much more time consuming compared to methylene blue sorption it was decided to use the last mentioned method.

Measurements were done to validate and implement the method since it had never been used before in Norske Skog, *Table 4-1*. The measurements for verification of this method were conducted on White spruce, while the rest of the measurements were conducted on Norway spruce. 2

Table 4-1 Total charge measured by methylene sorption of different pulps made by White Spruce at the Andritz Research and Development Centre in Springfield, Ohio, USA.

Name	Acidic groups (umol/g on filter)	Standard deviation
ATMP (Mg(OH) ₂ + Peroxide)	173,8	2,7
ATMP (NaOH + Peroxide)	93,8	1,3
ATMP (Peroxide)	88,8	13,1
TMP	80,5	4,1

It was expected that the number of acidic groups for ATMP pulps would be higher compared to TMP. The result for TMP was as expected, however the result for ATMP (Na + Peroxide) and ATMP (Peroxide) were lower than expected. The amount of sodium hydroxide added in the trial was low and the absence of alkali for ATMP (Peroxide) could be the reason for the low total charge.

The result of the unbleached TMP is however possible to compare with the theoretical values available in the literature. The total amount of anionic groups in unbleached TMP has been measured to be 80-110 $\mu\text{mol/g}$ (Zhang et al 1994, Fardim et al 2002). Unbleached TMP made by white spruce was measured to be 80,5 $\mu\text{mol/g}$, *Table 4-1*, which is an acceptable result compared to the values in the literature. Comparing ATMP ($\text{Mg}(\text{OH})_2$ + Peroxide) with peroxide bleached TMP in the literature gave similar results. ATMP ($\text{Mg}(\text{OH})_2$ + Peroxide) gave 173,8 $\mu\text{mol/g}$ while peroxide bleached TMP gave 178 ± 5 $\mu\text{mol/g}$ in the literature which also is an acceptable result (Fardim et al 2002, Fardim and Holmbom 2003). Based on these results the methylene blue sorption was chosen as the method to measure total charge. Measurements with conductometric titration are under procedure to better verify the results.

4.2 Total charge measured on different pulps made from Norway spruce

The amount of acidic groups was measured in $\mu\text{mol/g}$ for different pulps. Four of the pulps were produced with chemicals added and three were without addition of chemicals.

Additional tests were done on three different fractions from the various pulps; long, middle and the fines fraction.

4.2.1 Total charge measured on whole pulps

The pulps are not produced with the same energy input, but it is expected that all of the acidic groups in each pulp are receptive for methylene blue independent of the energy input. The results exhibit a large difference for pulps with addition of chemicals and for pulps without addition of chemicals, *Figure 4-1*.

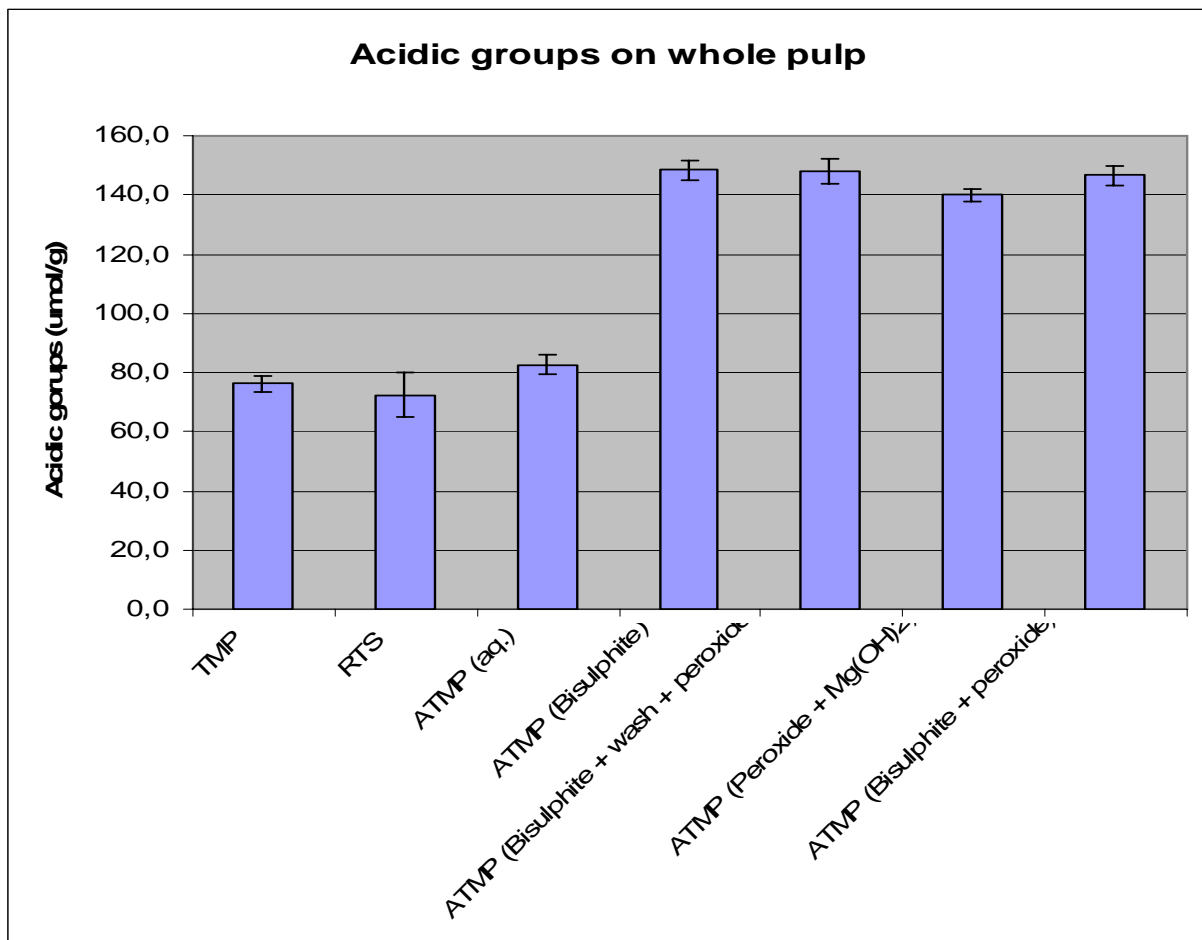


Figure 4-1 Acidic groups measured on various pulps made of Norway spruce with different chemicals added. TMP, RTS and ATMP (aq.) are not added chemicals.

Pulps with addition of the chemicals used in the pilot trial are expected to have a significantly higher total charge compared to the pulps without any addition of chemicals. This is also proven in the test results from *Table 3-1*. Alkaline hydrolysis of ester bonds in carbohydrates and pectin, and the formation of carboxyl groups in the lignin by oxidation is probably the biggest contributor to the increase in total charge for peroxide bleached pulps (Zhang et al. 1994, Fardim et al. 2002). For bisulphite bleached pulps the introduction of sulfonic acid groups in the lignin contributing to sulfonation in the pulp which is probably the biggest contributor (Westermarck and Samuelsson 1993, Fardim et al 2005a)

The three pulps treated with bisulphite had the highest amount of acidic groups. If one compare the ATMP pulps treated with bisulphite and the ATMP (Peroxide + Mg(OH)₂) there are especially two things that differ. The amount of long fibre is higher for ATMP (Peroxide + Mg(OH)₂), *Table 4-2*, and the amount of acidic groups for the long fraction is lower, *Figure 4-2* in chapter 4.2.2. Since the total amount of acidic groups are additive this results in a lower charge for the whole ATMP (Peroxide + Mg(OH)₂) pulp compared to the other ATMP pulps. ATMP (Bisulphite + Wash + Peroxide) had a high amount of long fibres compared to ATMP (Bisulphite) and ATMP (Bisulphite + Peroxide), but ATMP (Bisulphite + Wash + Peroxide) gave the highest charge for this fraction resulting in a high total charge for the whole pulp.

Table 4-2: Overview of the different distribution of different fractions in each pulp.

Sample	Pulp	Long (%)	Middle (%)	Fines (%)
A68	TMP	73,8	11,7	14,5
A31	RTS	56,2	27,1	16,7
A58	ATMP (aq.)	57,4	24,6	18,0
A47	ATMP (Bisulphite)	46,6	29,2	24,2
A53	ATMP (Peroxide + Mg(OH) ₂)	57,7	23,4	18,8
A9	ATMP (Bisulphite + Wash + Peroxide)	55,6	27,0	17,5
A3	ATMP (Bisulphite + Peroxide)	46,3	30,8	22,9

4.2.2 Total charge measured on different fractions

Fractionating the pulp in three different fractions gives an indication of which fraction in the pulp that contributes the most to the amount of acidic groups in the pulp, *Figure 4-2*.

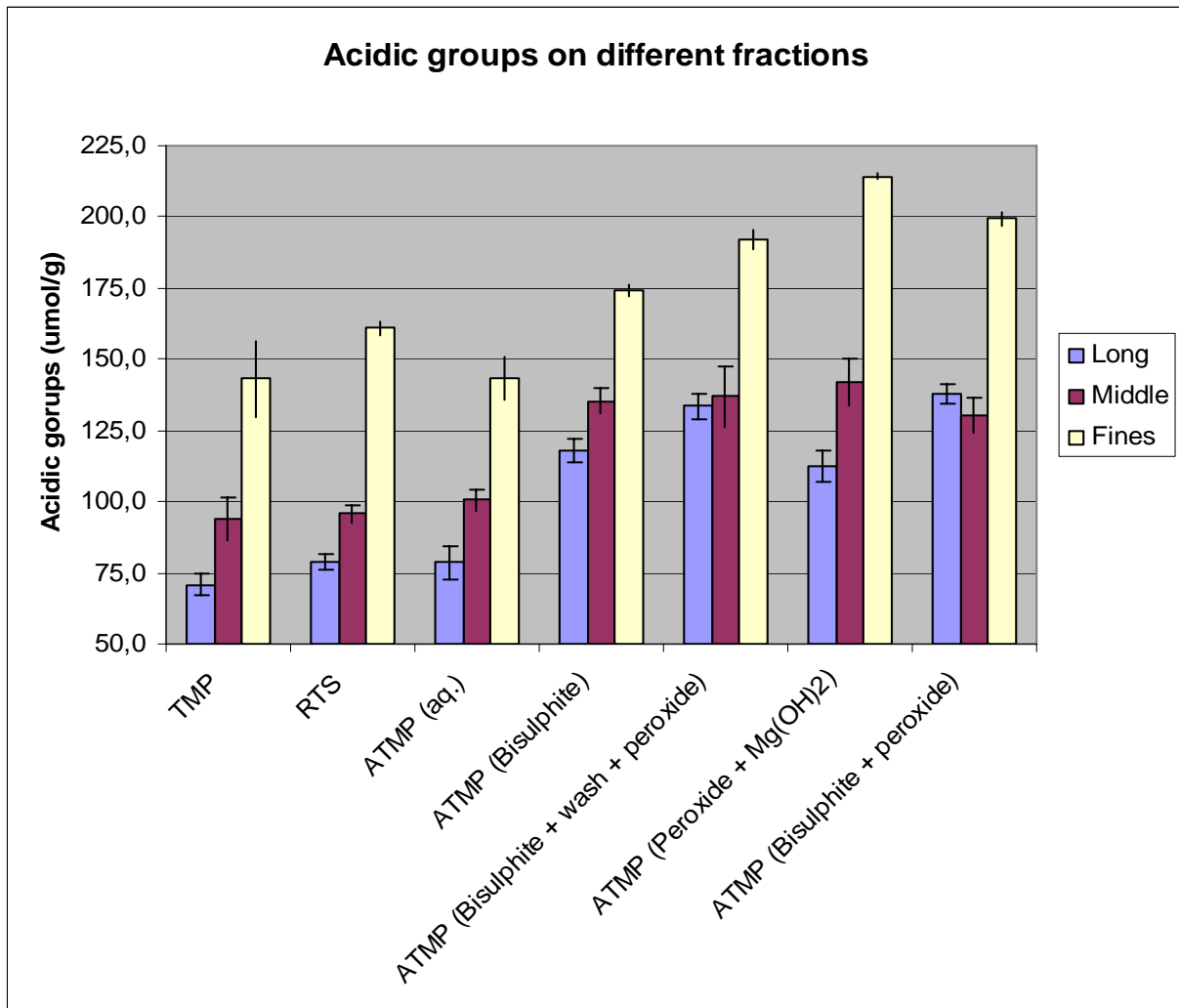


Figure 4-2 Acidic groups measured on different fractions from various pulps made of Norway spruce. TMP, RTS and ATMP (aq.) are not added chemicals.

It was expected that the fines fraction would contain more acidic groups compared to the long and middle fraction. This was also the result for all seven pulps. The middle fraction was expected to contain more acidic groups compared to the long fraction, and for all of the pulps except ATMP (Bisulphite + Peroxide) this is the result. Defibration of the chips before the addition of chemicals are most likely the reason for this. The surface area increases after defibration which make all fractions equally susceptible for chemicals.

The long fraction seems to react more with the combination of bisulphite and peroxide compared to only bisulphite or the combination of peroxide and magnesium hydroxide. The increase for the ATMP pulps are evident compared to the pulps without addition of chemicals. This shows that the long fraction in ATMP pulps is susceptible for chemical reactions due to an access to more reactive structures after defibration. The pulps are from the primary refining stage, further refining could affect the total number of anionic groups in each fraction as well as the whole pulp.

In the middle fraction there are no big differences comparing the total amount of acidic groups in the different ATMP pulps. The methylene blue method for measuring acidic groups is not accurate enough to draw any conclusions of which of the chemicals that react more or less with the middle fraction.

Comparing the fines fraction for the different pulps it is noticeable that the pulps with peroxide have a higher charge compared to ATMP (Bisulphite). ATMP (Peroxide + Mg(OH)₂) have the highest charge and this is the only ATMP pulp without bisulphite. The reason for this is probably that the reaction between peroxide and the chemicals present in fines like pectins and proteins. Also the amount of lignin present in each fines fraction affect the result since more lignin increases the reactivity with chemicals and therefore increases the number of anionic groups.

When adding the total amount of acidic groups from each fraction based on the percentage share, Table 4-3, it is possible to obtain close to the same results as for the whole pulp, *Figure 4-1*. This shows that the acidic groups are additive and gives an indication that the results are correct.

Table 4-3 Table describing how many acidic groups there is in each fraction. The amount is calculated from percentage fraction in each pulp and acidic groups (AG) in each fraction.

Sample	Pulp	Long (AG)	Middle (AG)	Fines (AG)	Total (AG)
A68	TMP	52,2	11,0	20,7	83,9
A31	RTS	44,2	25,9	26,9	97,0
A58	ATMP (aq.)	45,1	24,8	25,8	95,6
A47	ATMP (Bisulphite)	55,0	39,5	42,1	136,6
A53	ATMP (Peroxide + Mg(OH) ₂)	77,0	32,1	36,1	145,1
A9	ATMP (Bisulphite + Wash + Peroxide)	62,5	38,3	37,5	138,3
A3	ATMP (Bisulphite + Peroxide)	63,7	40,1	45,6	149,5

4.3 Optical properties

All optical properties were measured at nsiFOCUS laboratory in Halden.

4.3.1 Light absorption and brightness

The brightness is higher and the light absorption is lower for all of the ATMP pulps compared to the pulps without addition of chemicals, *Figure 4-3* and *Figure 4-4*. Since all of the chemicals are typical bleaching chemicals the results are as expected.

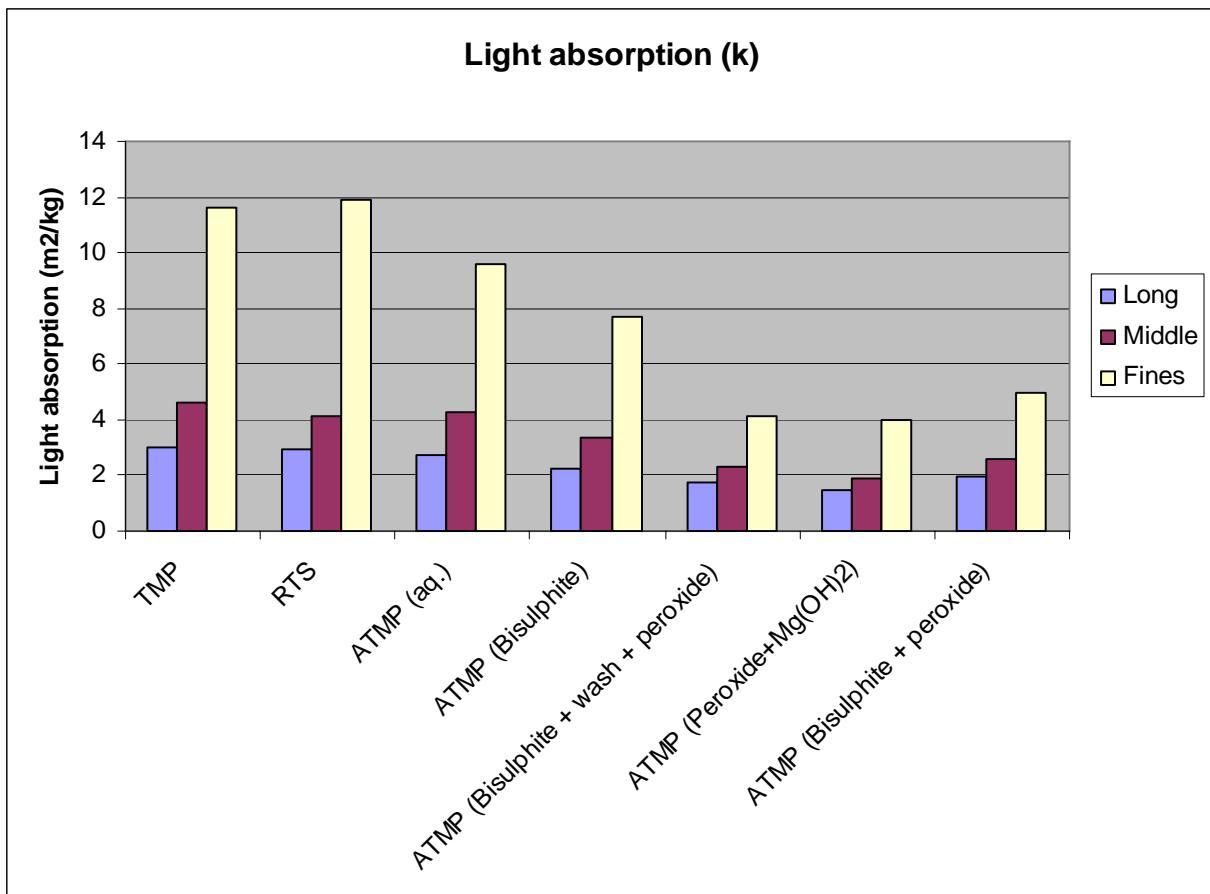


Figure 4-3 Light absorption (k) measured for three fractions from each pulp.

Light absorption (k) describes how much light is absorbed by the sheet (Fellers and Norman 1998). It is related to the molecular groups which gives colour to the paper, especially the chromophoric groups in the lignin. The higher the light absorption, the darker the material appears (Pauler 1998). The fines fraction is the fraction which the largest differences. TMP, RTS and ATMP (aq.) are the three pulps without addition of chemicals. ATMP (aq.) achieved a lower light absorption compared to TMP and RTS. This could indicate that lignin and extractives are washed out in the Impressafiner resulting in a lower light absorption. The ATMP pulps with addition of chemicals achieved a lower light absorption. This result was as expected since the primary fines fraction consists of a substantial part of lignin from the middle lamellae. Dark lignin is bleached by the chemicals resulting in a lower light absorption for the ATMP pulps with addition of chemicals. Since peroxide is generally a more efficient chemical for bleaching compared to bisulphite it was also expected that the ATMP pulps added peroxide gave lower light absorption compared to ATMP (Bisulphite).

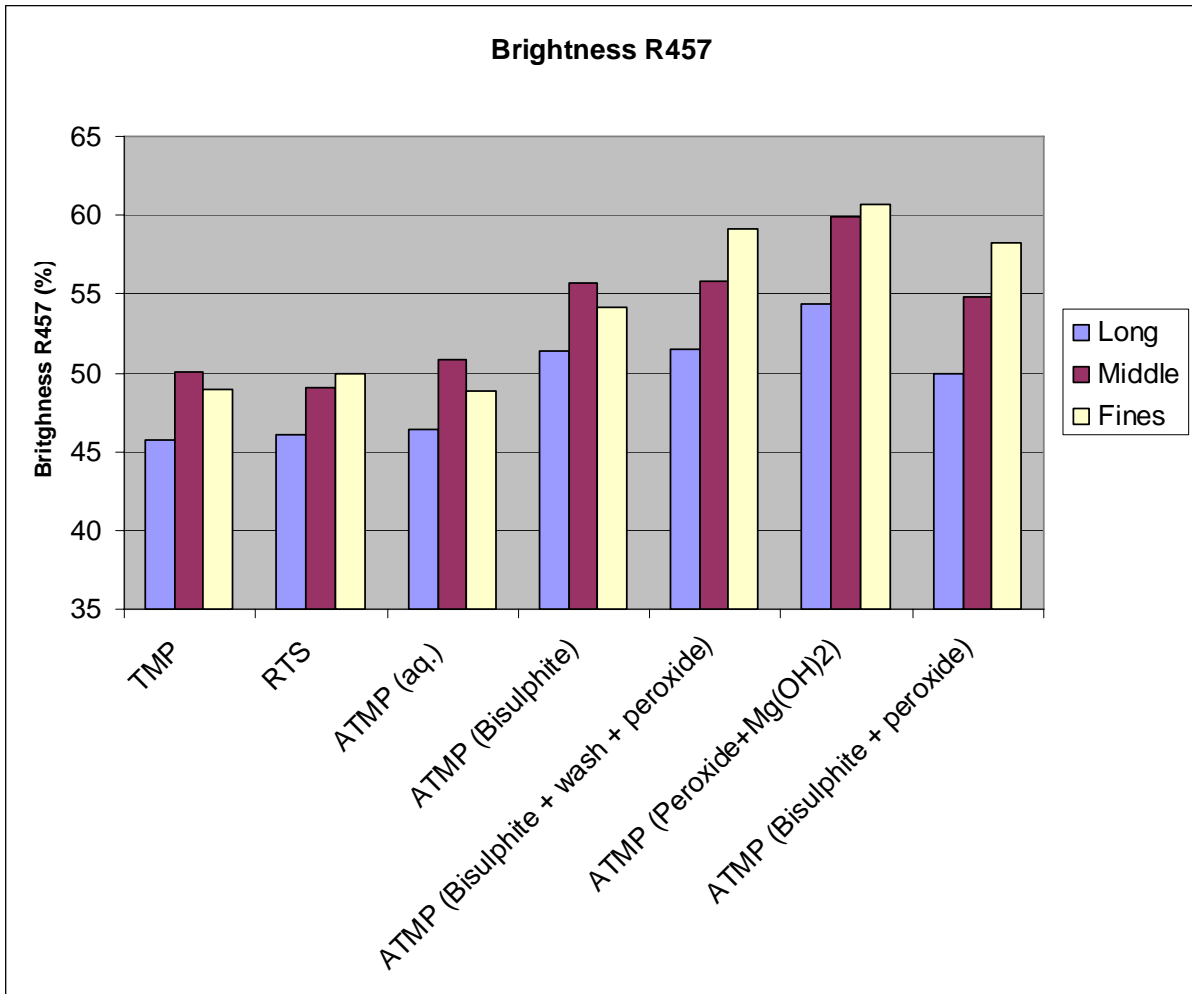


Figure 4-4 Brightness measured for three fractions from each pulp.

The trend from *Figure 4-3* can also be seen in *Figure 4-4*. The brightness of the pulp is a measure for the colour of the pulp; a higher value gives a paper looking whiter. ATMP pulps with added bleaching chemicals obtain higher values compared to the pulps without addition of chemicals. The ATMP pulps obtained the highest brightness values, this is due to the effect of the bleaching chemicals added in the process. The combination of peroxide and magnesium hydroxide gave the highest brightness and lowest light absorption for all fractions. Brightness is dependent on both light scattering (s) and light absorption (k), therefore it does not give any specific chemical or physical information (Haugan 2006).

4.3.2 Light scattering vs. SEC

Light scattering (s) is a measure of how large the free surface is in the paper (Fellers and Norman 1998). The s -value is used to describe the ability of the sheet to scatter light (Rundlöf 2002). Standard deviation in SEC is based on the calculations done for the Andritz pilot plant (Johansson et al. 2011)

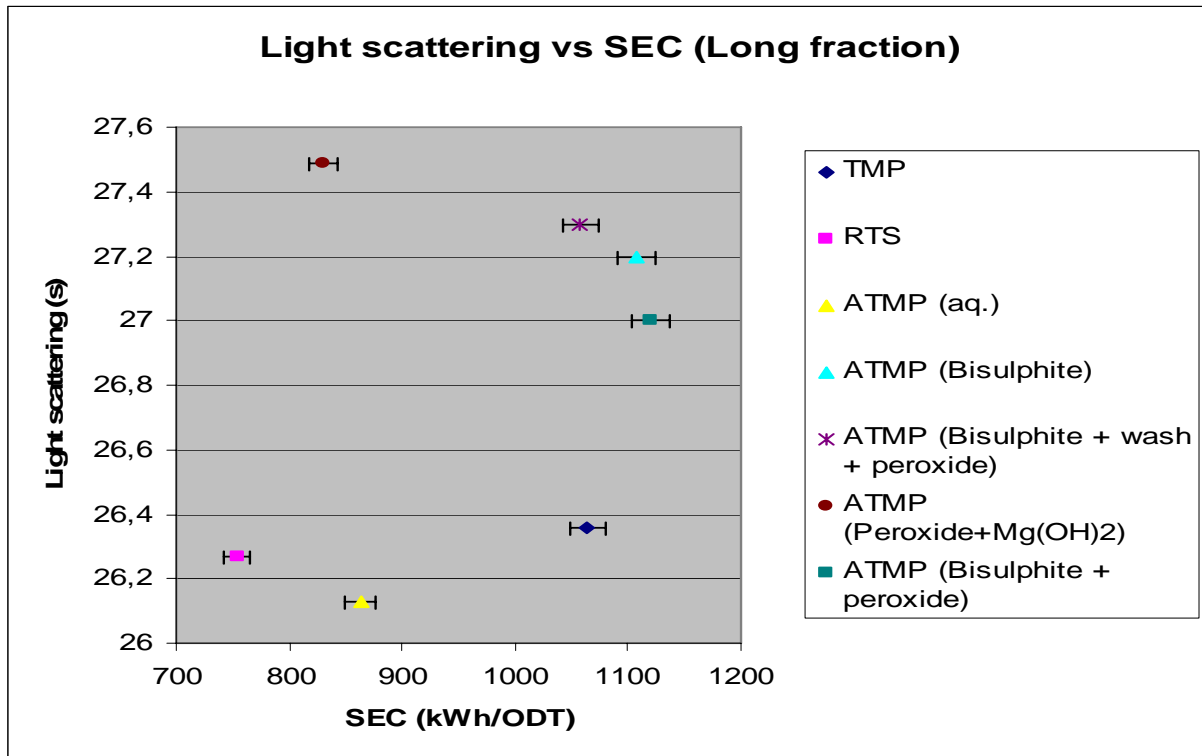


Figure 4-5 Light scattering (s) vs. SEC for long fraction of seven different pulps.

Light scattering is depended on two physical phenomenon, refraction and diffraction. Refraction occurs when light goes from one medium with a certain refraction index to another medium with a different refraction index. Diffraction occurs when the size of a particle draw near the size of the light wavelength (Young and Freedman 2004). Rundlöf stated that the light scattering coefficient (s) was related to the size of the particles in the pulp (Rundlöf 2002). This indicates that the diffraction is most probably the reason for the differences in the result in this thesis. The light scattering for the long fraction, *Figure 4-5*, shows that the ATMP pulps reaches higher light scattering compared to TMP, ATMP (aq.) and RTS. The reason for this is probably that ATMP pulps with addition of chemicals have a higher specific surface area compared to TMP, RTS and ATMP (aq.). A larger surface scatters more light. ATMP (Peroxide + Mg(OH)₂) had the highest light scattering. The low light scattering coefficient for TMP, ATMP (aq.) and RTS indicates that to preserve the size of the particles in the long fraction it is required to introduce chemicals in the production method.

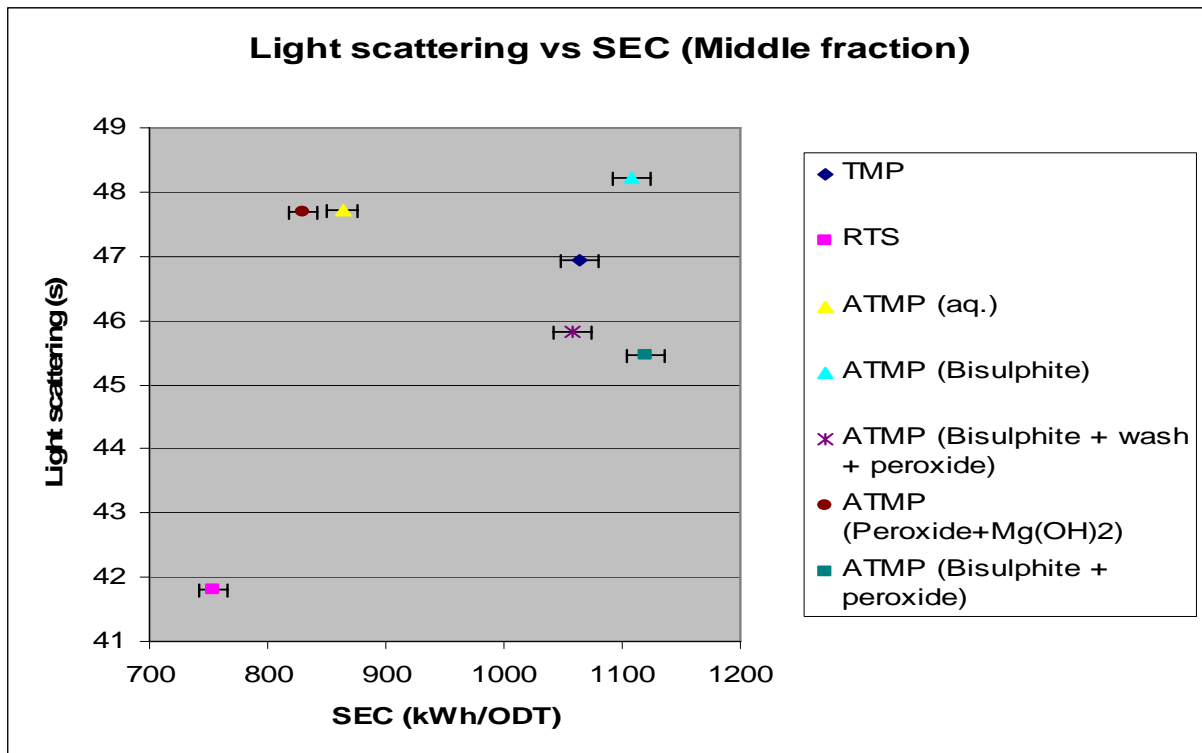


Figure 4-6 Light scattering (s) vs. SEC for middle fraction of seven different pulps.

The middle fraction from RTS stands out with low light scattering, *Figure 4-6*. This could indicate that the pulp is not ready for the high intensity refining without a mechanical and/or chemical pre-treatment. The high intensity refining most likely reduce the size of the particles in the middle fraction significantly. If the middle fraction of RTS is compared to the middle fraction of ATMP (aq.) it may indicate that the most important feature to preserve the size of the particles in the middle fraction is mechanical pre-treatment. Since the TMP pulp also reaches high light scattering coefficient it can also indicate that it is important to either have a pre-treatment of the pulp prior to high intensity refining or refine without high intensity to preserve light scattering in the middle fraction.

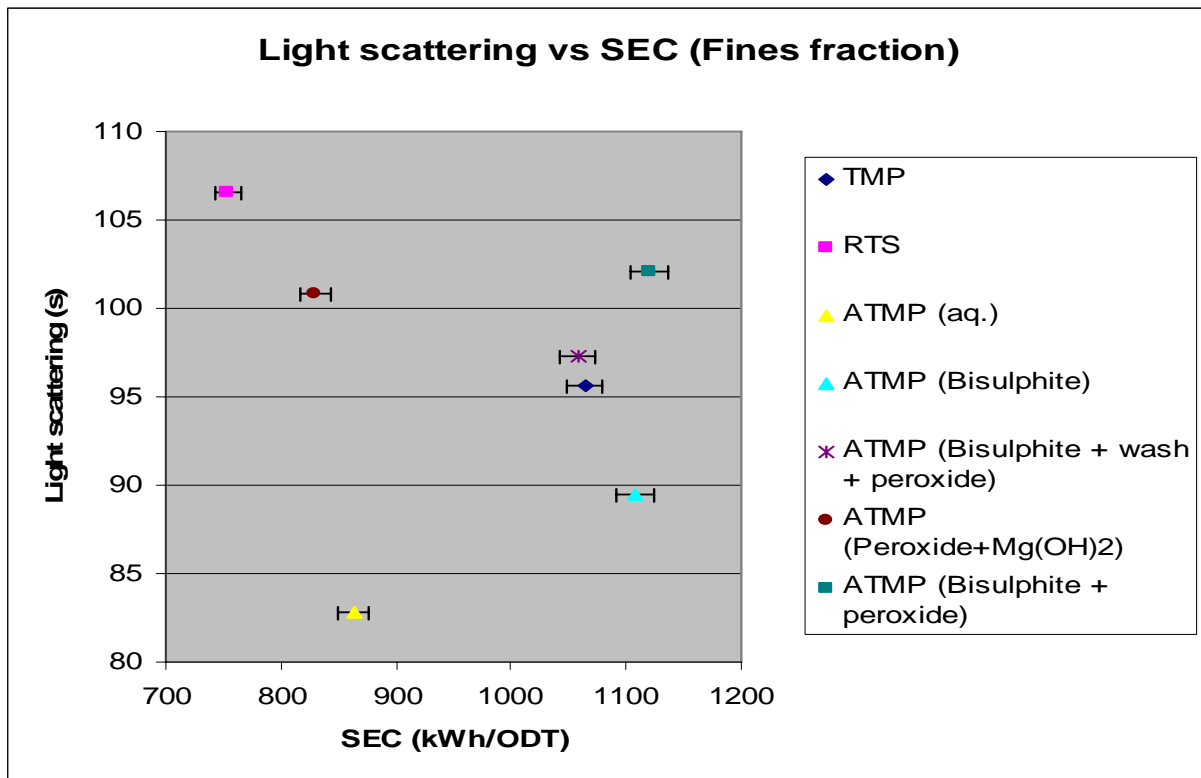


Figure 4-7 Light scattering (s) vs. SEC for fines fraction of seven different pulps.

The light scattering of fines is in addition to the size of the fines also dependent of which type of fines present. Flake-like fines increases the light scattering compared to the fibrillar-like fines (Luukko and Paulapuro 1999). The high light scattering coefficient for RTS could indicate that the fines fraction from this pulp is mostly flake-like fines from the middle lamellae. ATMP (aq.) have a low light scattering coefficient, this could be because of the mechanical defibration of the pulp prior to high intensity refining where the fines are released in the Fiberizer and refined one more time in the primary refining stage. The fines released after the primary refining stage could then consist of a higher amount of fibrillar-like fines. Fibrillar-like fines are more binding compared to flake-like fines, this could contribute to a lower specific surface index resulting in a lower light scattering. The amount of fibrillar-like fines could be investigated to find out how large the content of flake-like fines are for each pulp and see if this is the reason for the differences in light scattering. All of the ATMP pulps produce fines fraction with similar light scattering coefficient compared to TMP, this is highly preferable.

4.4 Strength properties

All strength properties were measured at PFI in Trondheim. The properties that were investigated were the tensile strength, strain and the tensile strength in z-direction. To ensure statistically significant results several laboratory sheets were tested for every pulp and fraction.

4.4.1 Stress-strain curve

The stress-strain curve is a graph describing the relationship between the force applied to a paper strip and the strain of this strip. From the endpoint of the curve it is possible to find the maximum tensile index and the maximum strain, which is where the paper strip breaks. The integral of the area under this curve gives us the TEA which is the work required to break a paper strip apart. TEA is dependent on the force applied and the strain. Mathematically the TEA has the following definition (Levlin and Söderhjelm 1999);

$$TEA = \int F dl$$

where F is the and Δl is the corresponding strain.

To draw the stress-strain curve, the force applied to the paper strip is plotted against strain. In this case the tensile index is used on the y-axis instead of force since the tensile index also takes the differences in grammage weight into consideration. The tensile index was calculated from the standard force (N/15mm) and grammage weight (g/m^2) while the strain was given straight from the instrument.

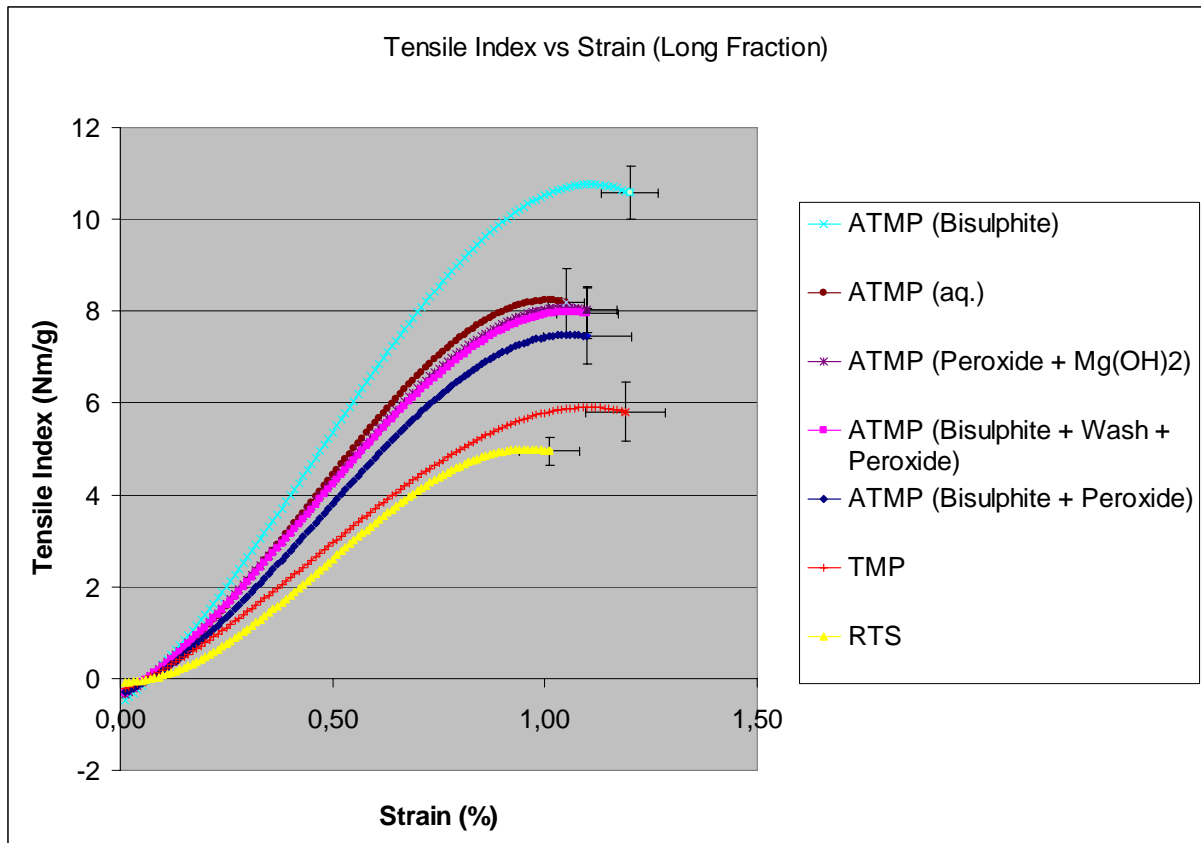


Figure 4-8 Tensile Index vs. Strain for long fraction of seven different pulps.

The long fraction of ATMP (Bisulphite) gave both the highest tensile index and strain, Figure 4-8, this also results in the highest TEA. The reason for this could be a larger specific surface area and therefore more binding sites accessible. Together with a high total charge this could affect the TEA in a positive way increasing the internal bonding for this fraction. ATMP (Bisulphite) was the only pulp where bisulphite was added to the primary refiner. Because of a short retention time in this stage it is probably better to add bisulphite here since it is known to have a faster reaction time compared to peroxide. ATMP (Bisulphite + Wash + Peroxide) achieved a higher TEA compared to ATMP (Bisulphite + Peroxide), even though it is not a big difference it could indicate that the extractives removed in the washing stage influences the strength properties adversely. This should be investigated further. Both TMP and RTS achieved a low TEA, these are the only two pulps without mechanical pre-treatment. This could indicate that the long fraction of these pulps have a lower specific surface area resulting in less binding sites and lower TEA. It could also be that the flexibility of these pulps are lower compared to the ATMP pulps

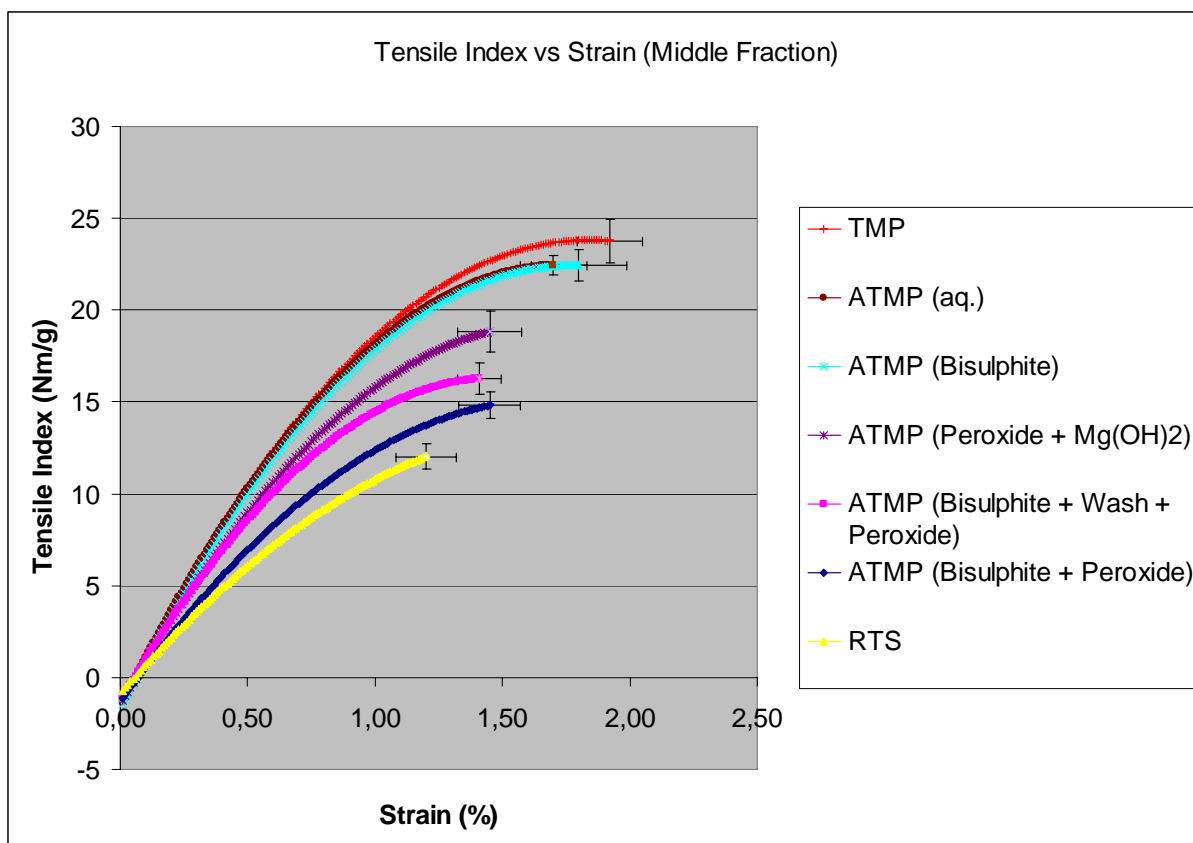


Figure 4-9 Tensile Index vs. Strain for middle fraction of seven different pulps.

The middle fraction with highest strain and tensile index is the TMP pulp, Figure 4-9. Earlier investigations have shown that increased density increases the bond strength by higher bond area and number of bonds (Retulainen et al 1993, Reutlingen et al 1998). From Table 4-4 it is shown that the density for the middle fraction of TMP is significantly higher compared to the rest of the pulps. The TEA for the middle fraction of TMP could indicate that this is true. However there is no clear relation between TEA and density for the ATMP pulps. The differences between these pulps could be because of different reaction times of the chemicals and where the chemicals are added. High intensity in the primary refining stage with addition of bisulphite could be the most efficient way to achieve high strength properties.

Table 4-4 Density measured on the different fractions from each pulp.

	TMP	RTS	ATMP (aq.)	ATMP (Bisulphite)	ATMP (Bisulphite + Wash + Peroxide)	ATMP (Peroxide+Mg(OH) ₂)	ATMP (Bisulphite + Peroxide)
	A68	A31	A58	A47	A9	A53	A3
density (kg/m³)							
Long	182	193	219	227	235	247	219
Middle	441	291	380	355	362	365	360
Fines	497	540	502	554	526	512	511

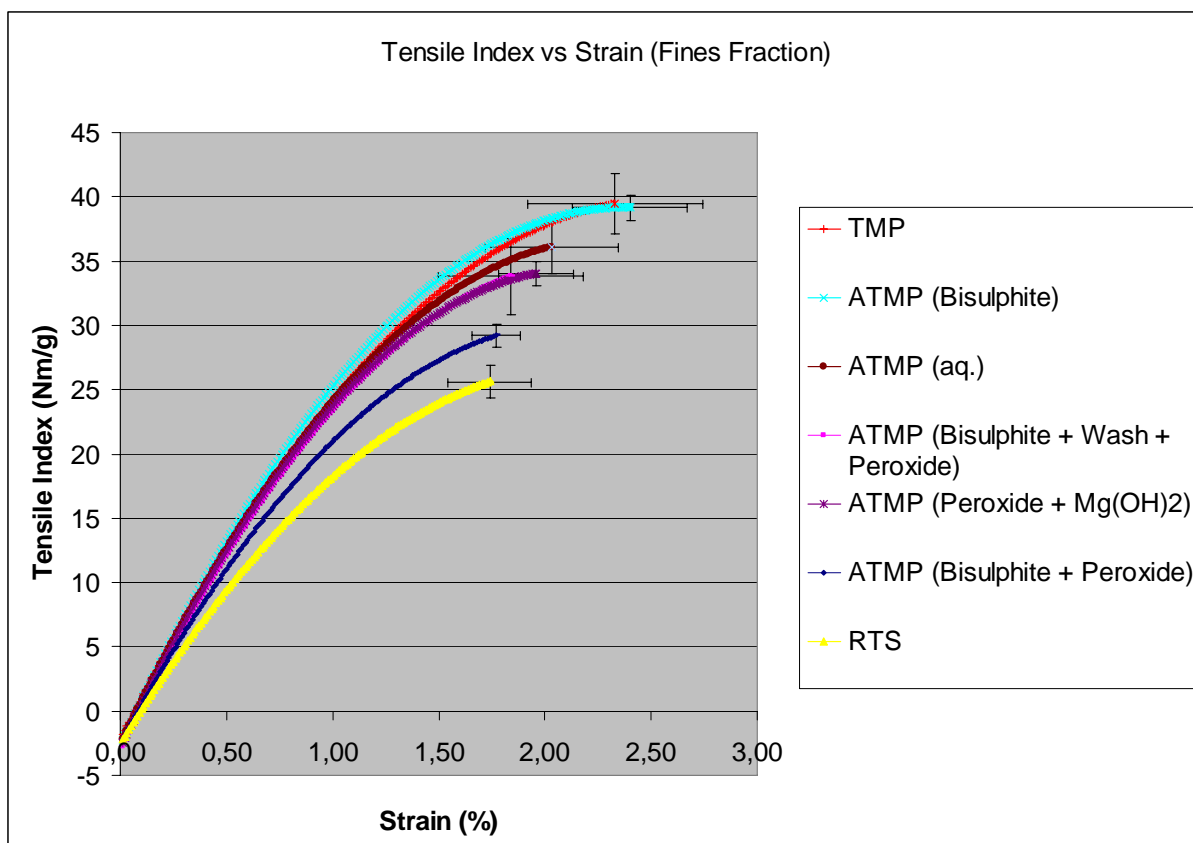


Figure 4-10 Tensile Index vs. Strain for fines fraction of seven different pulps.

TMP and ATMP (Bisulphite) produced the fines fraction with highest tensile index and strain, Figure 4-10. This could indicate that the total charge does not influence the tensile strength for the fines fraction as believed. The ATMP (Bisulphite) had $48,9 \mu\text{mol/g}$ more than TMP for the fines fraction, but achieved similar TEA. Of the ATMP pulps it was ATMP (Peroxide + $\text{Mg}(\text{OH})_2$) that achieved the highest total charge for the fines fraction, which also achieved a significantly lower TEA compared to ATMP (Bisulphite). The differences in the fines fraction could be because of differences in the composition of fines. It could be that fibrillar-like fines contribute more to increased strength properties compared to the flake-like fines and vice versa. This should be further investigated to get a better understanding of the differences in the stress-strain curve for the fines fraction.

4.4.2 Internal bond strength of paperboard (z-strength)

The z-strength is a measurement for the internal fiber bond strength, i.e. the tensile strength in z-direction of a paper sheet.

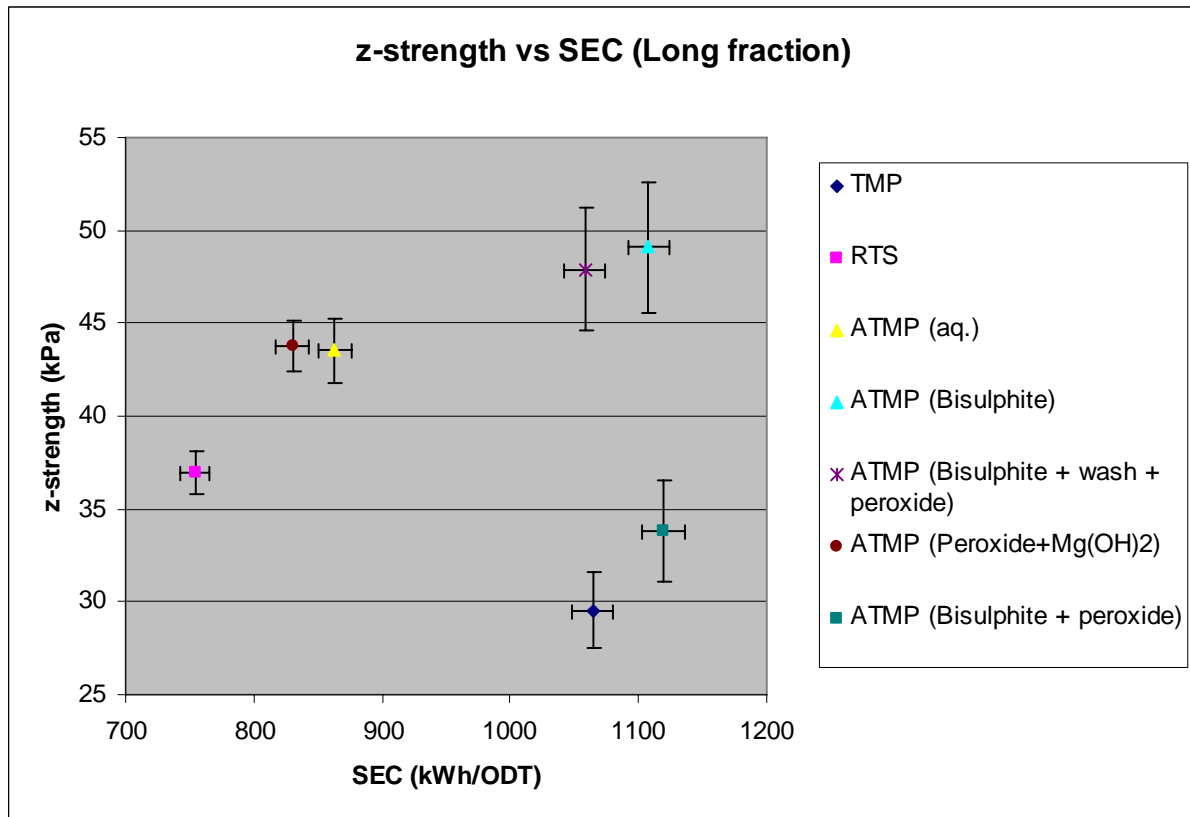


Figure 4-11 z-strength vs. SEC for long fraction of seven different pulps.

TMP and ATMP (Bisulphite + Peroxide) achieved the lowest z-strength for the long fraction, Figure 4-11. Low specific surface area index could be a reason for the differences.

Differences in the specific surface area index have been found to be significantly after the first refining stage (Gorski 2011). However, this does not describe why the ATMP (Bisulphite + Peroxide) get the low result. Gorski found no significant differences in flexibility between ATMP and TMP after the first refining stage (Gorski 2011). However, the differences in sheet density for TMP compared to the other pulps could indicate that there is a difference in flexibility for these pulps, Table 4-5. This should be investigated. The amount of shives has significance for screening of the pulp and particularly how much additional refining energy is needed to develop these fibres.

Since the ATMP (Bisulphite + Wash + Peroxide) gave significantly higher z-strength compared to ATMP (Bisulphite + Peroxide) it could show that the extractives caused the low value. A high amount of extractives gives lower strength properties and some of these are probably washed away in the washing stage for ATMP (Bisulphite + Peroxide). Another feature could be the differences in flexibility between these two pulps. Table 4-5 shows differences in sheet density for these two pulps in the long fraction. The increase in density could indicate that the ATMP (Bisulphite + Wash + Peroxide) had more flexible fibres.

Table 4-5 Density measured on the different fractions from each pulp.

	TMP	RTS	ATMP (aq.)	ATMP (Bisulphite)	ATMP (Bisulphite + Wash + Peroxide)	ATMP (Peroxide+Mg(OH) ₂)	ATMP (Bisulphite + Peroxide)
	A68	A31	A58	A47	A9	A53	A3
density (kg/m³)							
Long	182	193	219	227	235	247	219
Middle	441	291	380	355	362	365	360
Fines	497	540	502	554	526	512	511

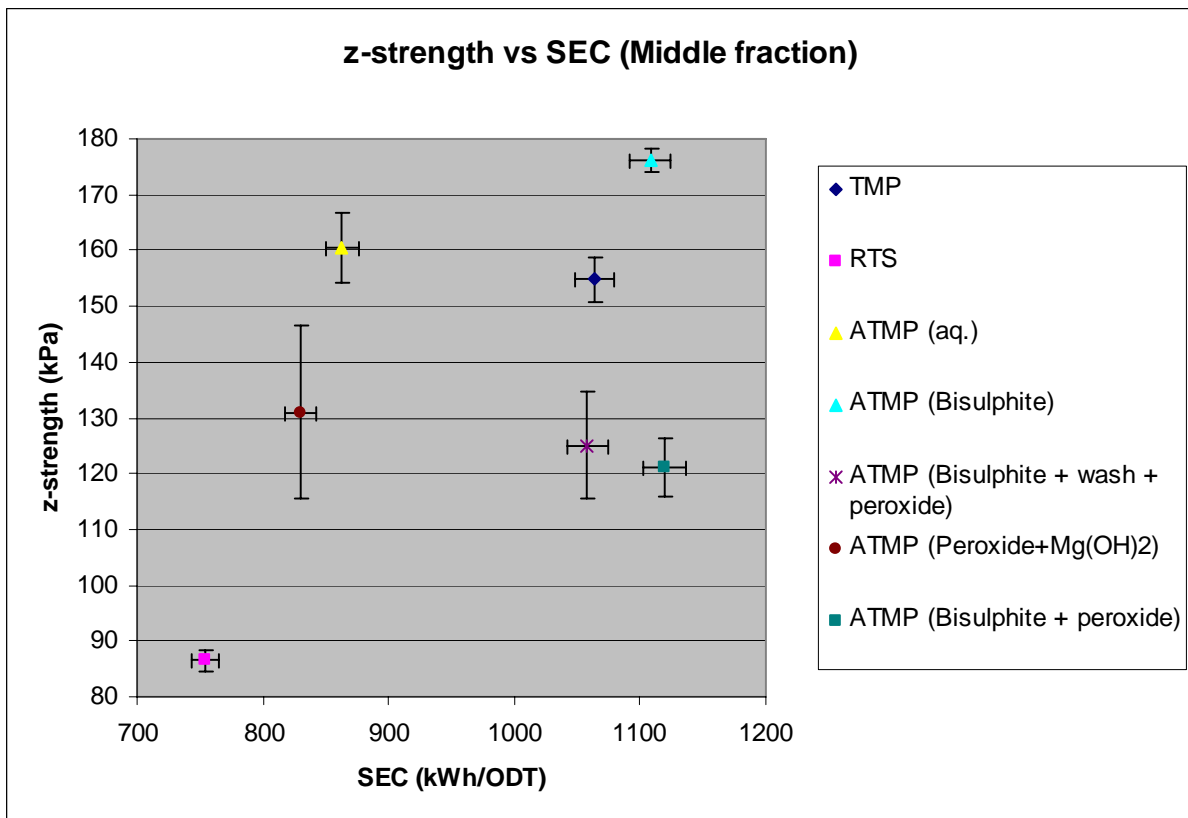


Figure 4-12 z-strength vs. SEC for middle fraction of seven different pulps.

The RTS pulp got the lowest result in z-strength for the middle fraction, Figure 4-12. From Table 4-5 it is clear that this fraction clearly has lower density compared to the other pulps. Flexible fibres contribute to high density and higher specific surface index (Gorski 2011). Low specific surface area index affects the bonding strength in the paper adversely (Niskanen 1998). This is probably the reasons for the poor z-strength for RTS.

The result of ATMP (aq.) could indicate that it is the mechanical pre-treatment that contributes the most to the z-strength compared to chemical pre-treatment. This should be investigated on pulps from other stages in the different productions methods. It is possible that the chemicals added develop the fibre more after additional refining stages.

Even though the ATMP (Bisulphite) reaches the highest z-strength for the middle fraction it is only the RTS pulp which had lower density. This could indicate that it is not only the flexibility that contributes to increased z-strength for ATMP (Bisulphite). It could be a high specific surface area index that is the reason for the good result which could improve the bonding strength in the paper. This could also indicate that it is best to add bisulphite in the primary refiner, because of the short retention time in the refiner and that bisulphite has a faster reaction time compared to peroxide.

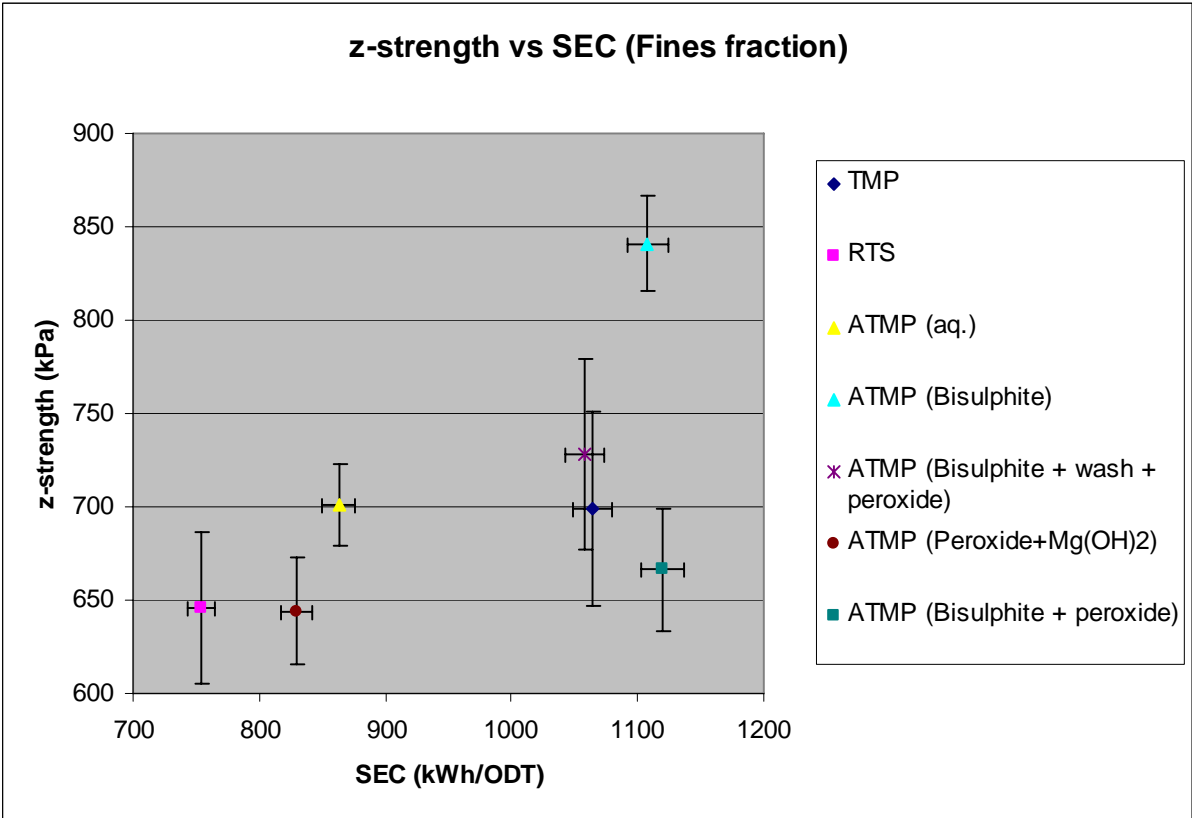


Figure 4-13 z-strength vs. SEC for middle fraction of seven different pulps.

ATMP (Bisulphite) achieved the highest z-strength for the fines fraction, Figure 4-13. It is not easy to describe why ATMP (Bisulphite) stands out like it does since there are so big differences. It is quite interesting to see how much it stands out. It could be the result of a different fines composition compared to the other pulps, this should be further investigated to better understand these results.

4.4.3 Comparisation of strength properties for all pulps

A table was put together to summarize and get an overview of all strength properties for all pulps, Table 4-6. Tensile Energy Absorption (TEA) was calculated by multiplying the tensile index and strain. The area under the curve for tensile index vs. strain is usually integrated to find the correct answer for TEA, since the product from tensile index x strain correlates strongly this value was used. TEA describes how much tensile energy the paper is able to absorb.

ATMP (Bisulphite) produced the best pulp after the primary refining stage. The chemical reaction of bisulphite and wood is known to be a fast reaction, this is believed to be the reason for the good strength properties early in the refining process.

The TMP pulp produces pulp with good strength properties in the middle and fines fraction. However, the long fraction of TMP is poor. This probably results in poorer strength properties compared to ATMP pulps when comparing the whole pulps. The poor result in tensile index and z-strength for the long fraction is probably due to the high amount of shives, low specific surface area index and low flexibility. Poor tensile index and poor strain also results in low TEA. In papermaking the strain is just as important as tensile index when talking about strength. Tensile index tells something about how much static strength there is in the paper, while strain is important because of all the speed variations in the paper machine and printing works.

The pulp produced with only high intensity like the RTS pulp got the lowest value comparing the strength properties for all pulps and fractions. It is fair to believe that the chips are not prepared for high intensity refining without any mechanical or chemical pre-treatment. This could be the reason for the poor strength properties in Table 4-6. ATMP (aq.) gave a much better result compared to RTS pulp, the only difference between these two pulps are the mechanical pre-treatment.

Peroxide is added to all ATMP pulps except ATMP (Bisulphite). It is known that the chemical reaction with peroxide is slower compared to bisulphite. It would be interesting to do the same investigations on pulps from the secondary refining stage to see how the pulps develop through at least one more refining stage.

The difference between ATMP (Bisulphite + Peroxide) and ATMP (Bisulphite + Wash + Peroxide) is that the pulp gets washed in production of ATMP (Bisulphite + Wash + Peroxide). This could indicate that some extractives are removed in the washing stage. Washing mechanical pulp with an open water circuit is a good way to remove extractives, a closed water circuit also remove extractives but this is less effective. It is mainly resin acids that can be removed from undefibrated chips while the other components can be removed from the pulp later in the process (Opedal Tanase 2011). Removal of extractives could also improve the fibre swelling which probably improves the fibre development in the refining stage. However, this is probably not the only thing that could affect the differences in these pulps. This should be investigated further by measuring at least fibre swelling, surface area index and bonding strength.

Table 4-6 Summarisation of all strength properties measured on the different pulps. Including a classification of which pulp got the best results.

	TMP	RTS	ATMP (aq.)	ATMP (Bisulphite)	ATMP (Bisulphite + Wash + Peroxide)	ATMP (Peroxide+Mg(OH) ₂)	ATMP (Bisulphite + Peroxide)
	A68	A31	A58	A47	A9	A53	A3
z-strength (kPa)							
Long	29,5	37,0	43,5	49,1	47,9	43,8	33,8
Middle	155	87	161	176	125	131	121
Fines	699	645	701	841	728	644	666
Tensile index (Nm/g)							
Long	5,9	5,0	8,2	10,8	8,0	8,1	7,5
Middle	23,8	11,9	22,4	22,4	16,2	18,6	14,8
Fines	39,3	25,5	35,9	39,2	33,0	33,9	29,0
Strain (%)							
Long	1,14	1,00	1,04	1,12	1,04	1,08	1,08
Middle	1,88	1,18	1,65	1,75	1,38	1,39	1,43
Fines	2,28	1,71	1,99	2,35	1,84	1,92	1,73
Tensile index x strain							
Long	6,7	5,0	8,5	12,1	8,3	8,8	8,1
Middle	44,7	14,0	37,0	39,2	22,4	25,9	21,2
Fines	89,6	43,6	71,4	92,1	60,7	65,1	50,2
Classification							
Long	7	5	4	1	2	3	6
Middle	3	7	2	1	5	4	6
Fines	4	6	3	1	2	7	5
Long	6	7	2	1	4	3	5
Middle	1	7	2	2	5	4	6
Fines	1	7	3	2	5	4	6
Long	1	7	5	2	5	3	3
Middle	1	7	3	2	6	5	4
Fines	2	7	3	1	5	4	6
Long	6	7	3	1	4	2	5
Middle	1	7	3	2	5	4	6
Fines	2	7	3	1	5	4	6
Sum	35	81	36	17	53	47	64
Mean	2,9	6,8	3	1,4	4,4	3,9	5,3
#	2	7	3	1	5	4	6
SEC (MWh/t)	1,06	0,75	0,86	1,11	1,06	0,83	1,12

4.5 Ambertec formation

Formation of a paper sheet describes how well the fibres are distributed throughout the sheet. It is important for paper machines that the fibres are well distributed since it affects the strength and visual impression. It is ideal that the formation is as low as possible to produce the best possible paper.

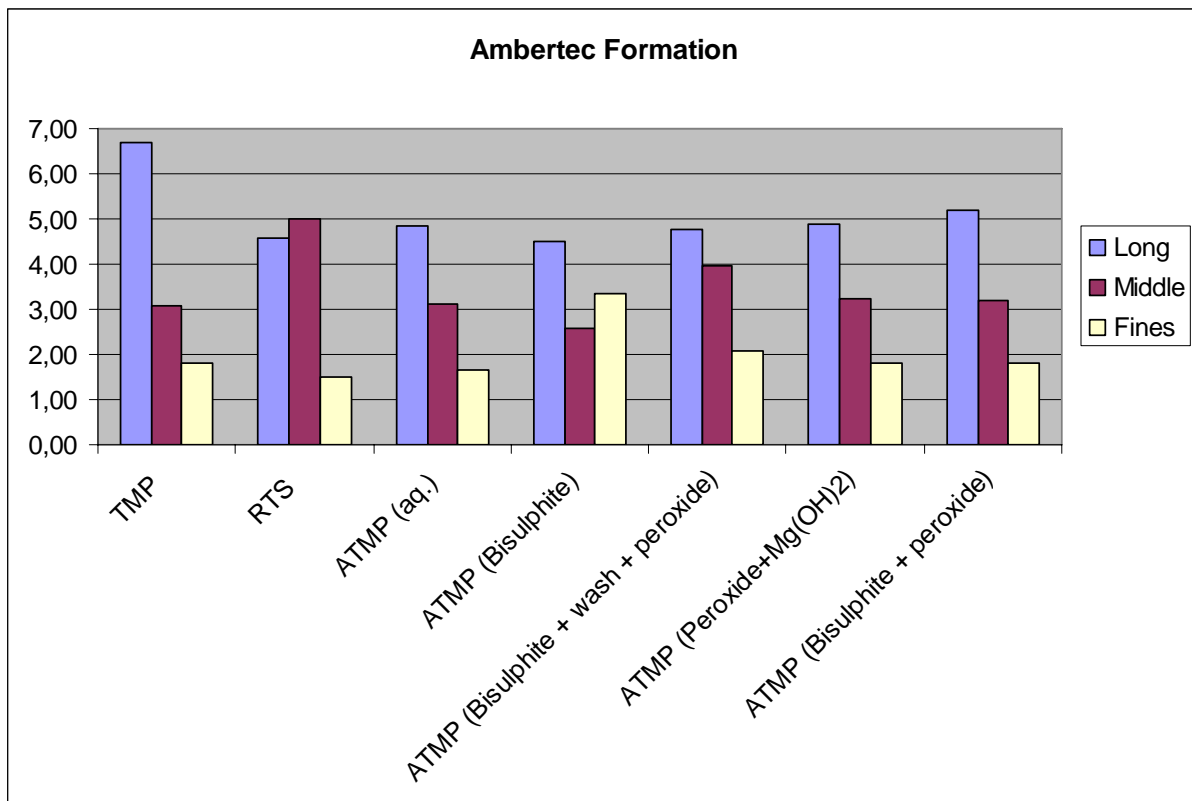


Figure 4-14 Ambertec formation measured for three fractions of each pulp.

Figure 4-14 shows that the TMP long fibre fraction has a higher formation in the long fraction compared to the other pulps. Poor formation is linked to the tendency of fibres to flocculate (Kerekes and Schell 1995, Kure 1999). It is known that long fibres flocculate easily and are therefore harmful for paper formation. It is also known that flexible fibre has a lower tendency to flocculate (Kerekes and Schell 1995, Beghello and Eklund 1997). This could indicate that the flexibility of the long fraction of TMP is poor. Since the density for long fraction of TMP is lower compared to the other pulps the flexibility and/or bendability is probably the reason for the poor formation, Table 4-5. ATMP pulps have higher bendability compared to TMP (Gorski et al 2011).

The differences in the middle and fines fraction could be that the sheets made on the small sheet former did not get agitated before forming the sheet. It seems that the differences do not have anything to do with the production method of the pulp, without any agitation of the pulp prior to the sheet formation it is difficult to compare the results.

4.6 Charge Decay

Charge decay is a method to measure the electrostatic properties of paper. This is an important feature in case of runnability and printability in the printing works. The charge decay unit measures capacitance, received charge, initial peak voltage and the time it takes to discharge 90 % of the charge brought into the paper. These measurements are highly dependent on humidity and the thickness of paper. It is also fair to believe that the total charge of the paper measured in chapter 4.2 influence the results.

The laboratory sheets were measured at 35 % RH and 50 % RH. Five parallels were done for each fraction. Initial peak voltage, received charge, capacitance and the time to reach 10 % charge was measured. The paper surface is charged with a high energy corona treatment, Figure 4-15. After a predetermined charging time, the corona wires are moved aside before measuring (Levlin and Söderhjelm 1999).

The capacitance is a measurement for how well the capacitor is able to store energy (Young and Freeman 2004). In this case the capacitor is the paper sheet. The time to decay the electrical potential to 10 % from initial peak voltage describes how fast it is possible to reduce the electrical potential in the paper. The static electricity properties are important for printability and runnability for papermaking. Highly charged sheets will adhere together and create feeding problems, accumulation of dust is could also be a problem on highly charged sheets (Levlin and Söderhjelm 1999).

Capacitance and the time are the two units considered. It seems clear that the time from initial peak voltage to 10 % is longer for the long fibre fraction compared to the fines fraction. The same trend can be seen for the capacitance only that the fines fraction has higher values compared to the long fraction. The middle fraction varies in all results.

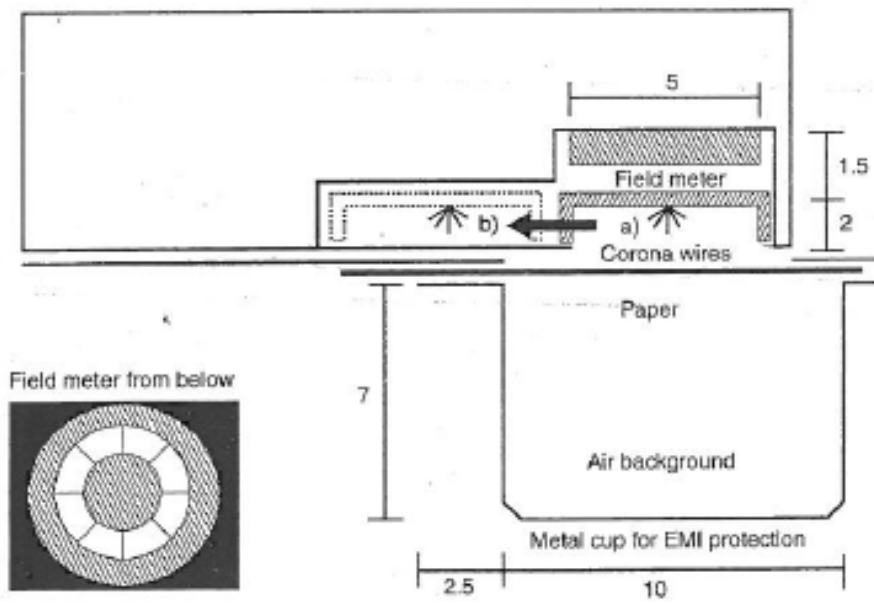


Figure 4-15 Basic principle of measurements of electric properties on a paper sheet. After the charging period the cover disc are moved from position a to position b (Niskanen 1998).

The variations in capacitance are probably because of variations in thickness of the paper.

Capacitance is calculated from the equation (Young and Freedman 2004):

$$C = \frac{Q}{V_{ab}} = \epsilon \frac{A}{d}$$

Where C is capacitance, ϵ is dependent of relative humidity, A is the area where the measurements are done and d describes the variations in thickness. Since the relative humidity and area of measurements should be constant the variations in capacitance should be because of variations in thickness of the paper.

Variations in charge decay time could be because of signal noise in the instrument. If there are any particles, dust from paper etc, in the field meter where the measurements are done, this could probably cause variations in the results. The charge decay time is also dependent on the capacitance. High capacitance gives shorter decay time.

Differences in capacitance and decay time from day to day could be the result of differences in moisture content in the paper. The sheets were first acclimatized to 50 % relative humidity, then to 35 % relative humidity and back to 50 % relative humidity. Hysteresis means that the moisture content of paper is different in absorption coming from dry conditions and in desorption when coming from humid conditions (Niskanen 1998). This phenomenon is described by a hysteresis curve of paper moisture against relative humidity, Figure 4-16. Different moisture content affects the capacitance and charge decay time.

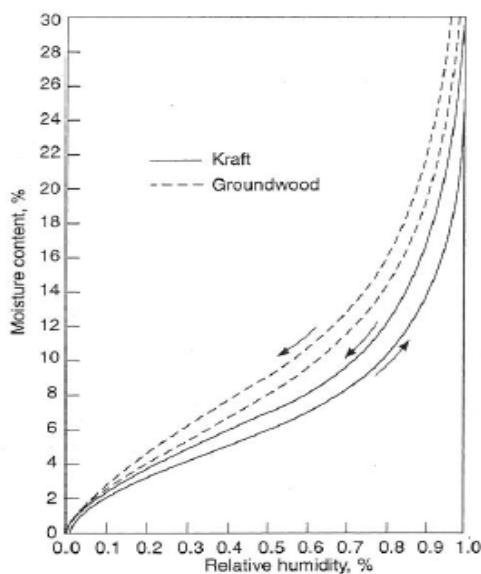


Figure 4-16 Hysteresis curve describing differences in moisture content at the same relative humidity (Prah 1968, Niskanen 1998).

4.6.1 Relative humidity 50 %

The sheets were measured two times during two different days at a relative humidity of 50%.

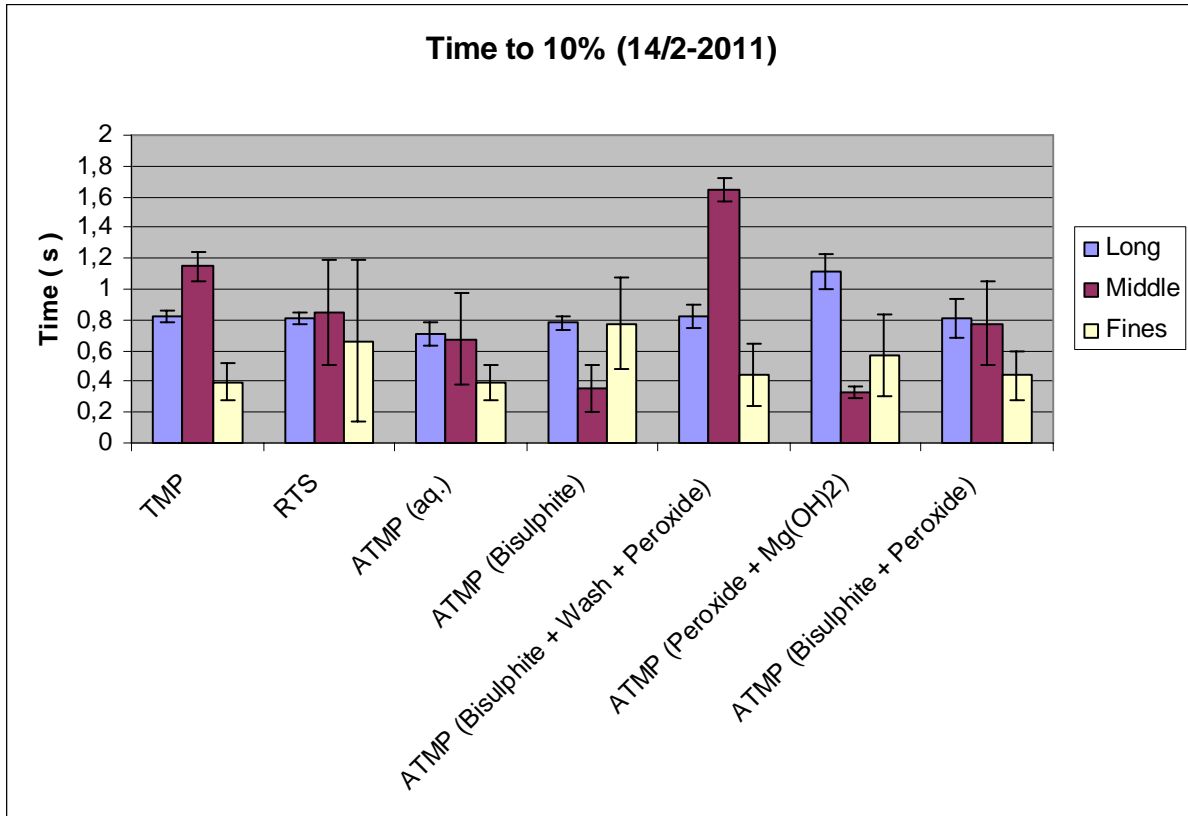


Figure 4-17 Describes the time it takes from initial peak voltage to 10 % of this.

There are big variations in the time from initial peak voltage to 10 %. The time should theoretically be the same in both results since it is measured at the same paper, temperature and relative humidity. Since the results vary so much, *Figure 4-17* and *Figure 4-18*, it is difficult to conclude anything regarding the time.

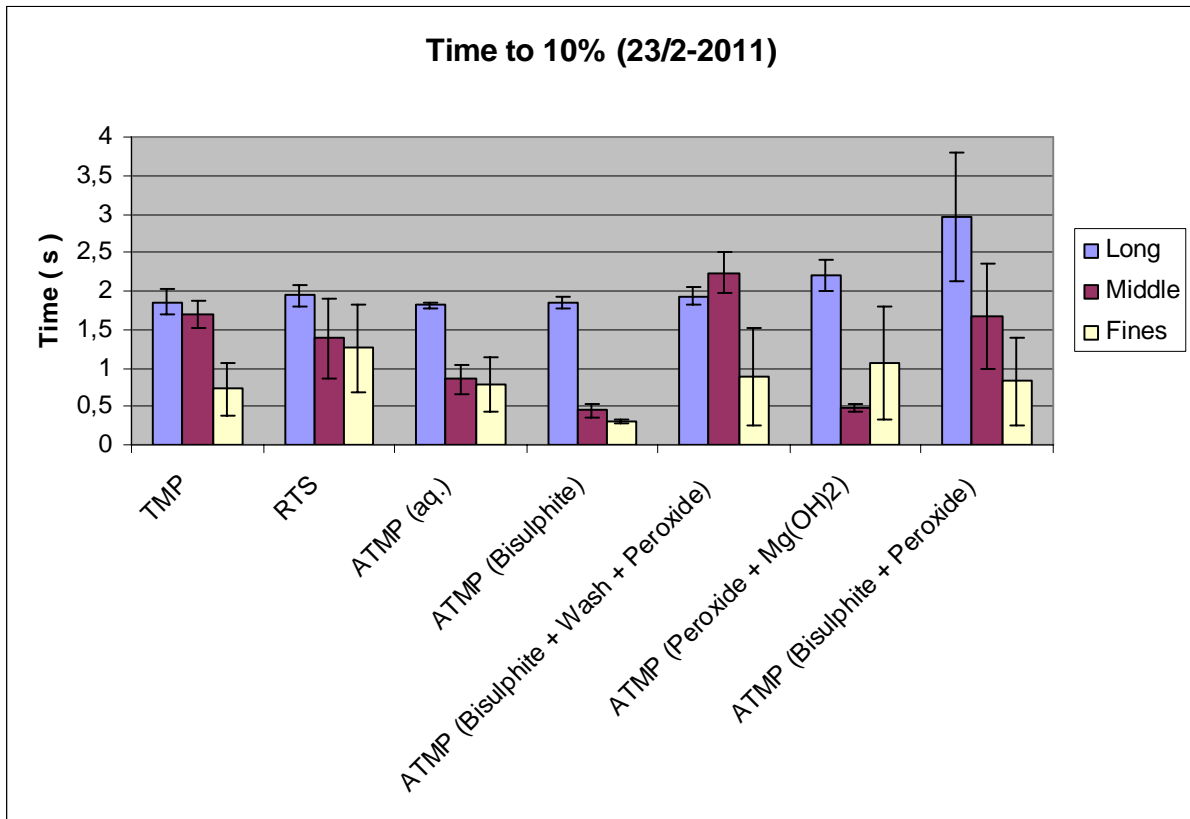


Figure 4-18 Describes the time it takes from initial peak voltage to 10 % of this.

The variations in the time from initial peak voltage to 10% are great comparing *Figure 4-17* and *Figure 4-18*. Variations like these are also seen in other tests performed at paper from Norske Skog Saugbrugs measured by nsiFOCUS. Until the reason for these variations have been unveiled it is difficult to conclude what the ideal time and capacitance for the paper is. It is also difficult to conclude with how the addition of chemicals influences the paper and which of the chemicals which provide the best results.

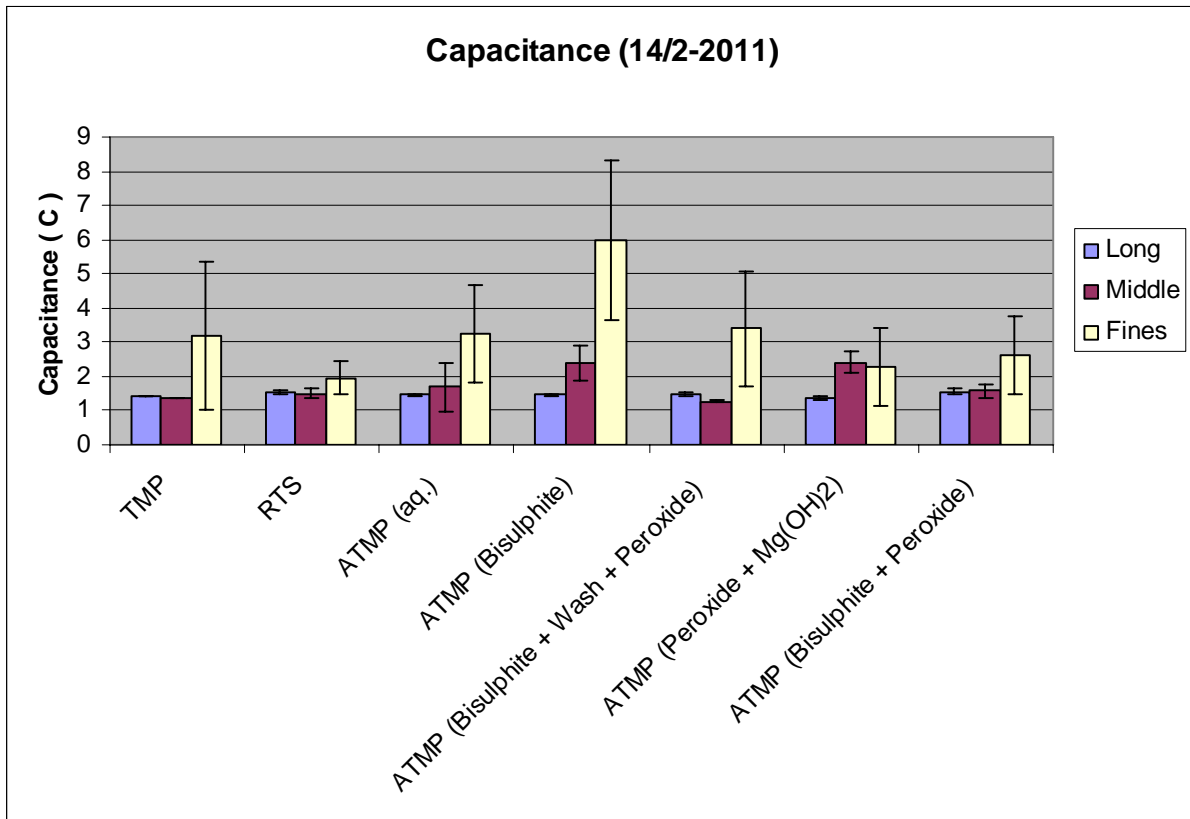


Figure 4-19 Capacitance measured on all fractions from each pulp.

Variations in capacitance are significantly measured at different time. There are not only the mean values that vary, *Figure 4-19* and *Figure 4-20*, there are huge variations inside each fraction of a pulp. The variations are especially high for capacitance measured on the fines fraction. Differences in the thickness of paper from this fraction could be the reason for this. Under sheets making from the fines fraction, special paper where used to pick up the produced paper from the sheet former. Removal of this paper from the produced paper sheet were sometimes very difficult, small pieces of this paper could have been stuck in the surface of the paper causing variations in thickness. These pieces of paper could also affect the measurements since it probably have other characteristics compared to the paper supposed to be measured.

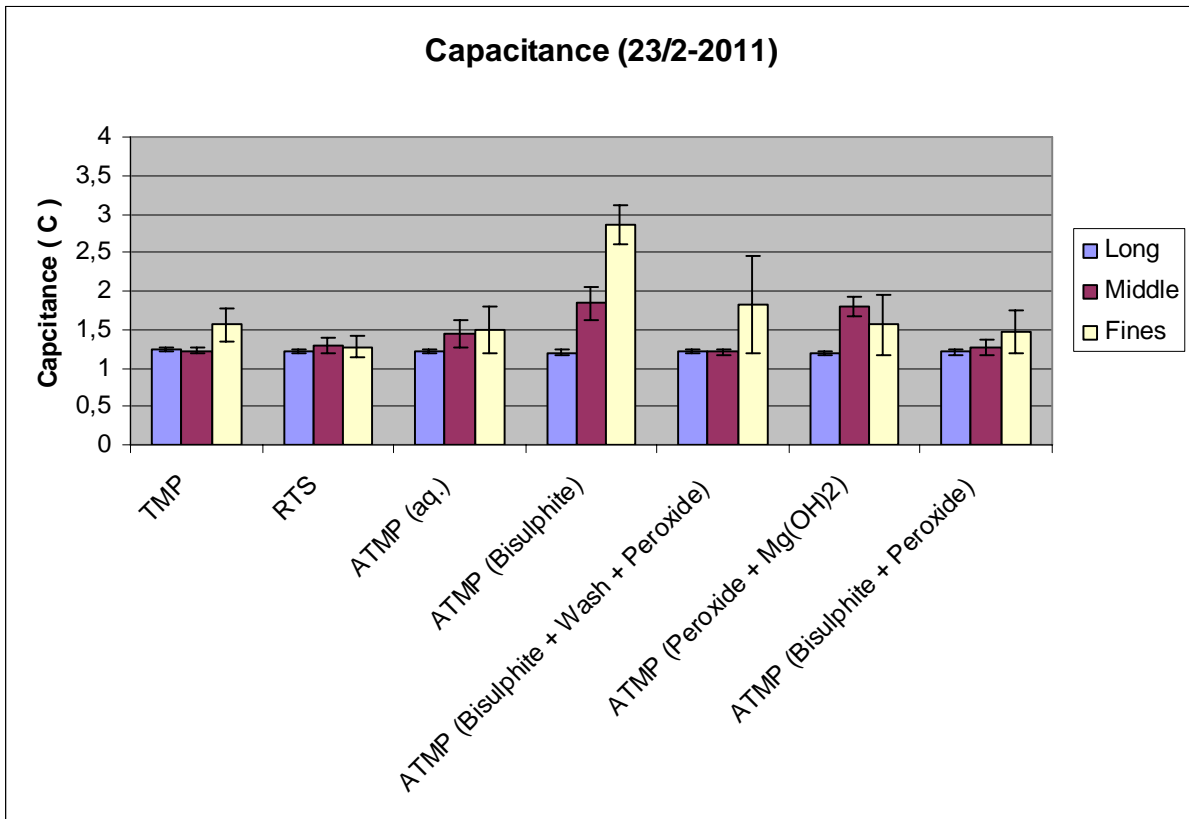


Figure 4-20 Capacitance measured on all fractions from each pulp.

4.6.2 Relative humidity 35 %

The same variations from measurements at 50 % RH can be seen when measuring the paper sheets at a relative humidity of 35 %. The individual differences are bigger for the time from initial peak voltage to 10 %, *Figure 4-21*. This makes it even more difficult to explain the results from the measurements. Differences in the time for long fiber and fines fraction can also be seen here.

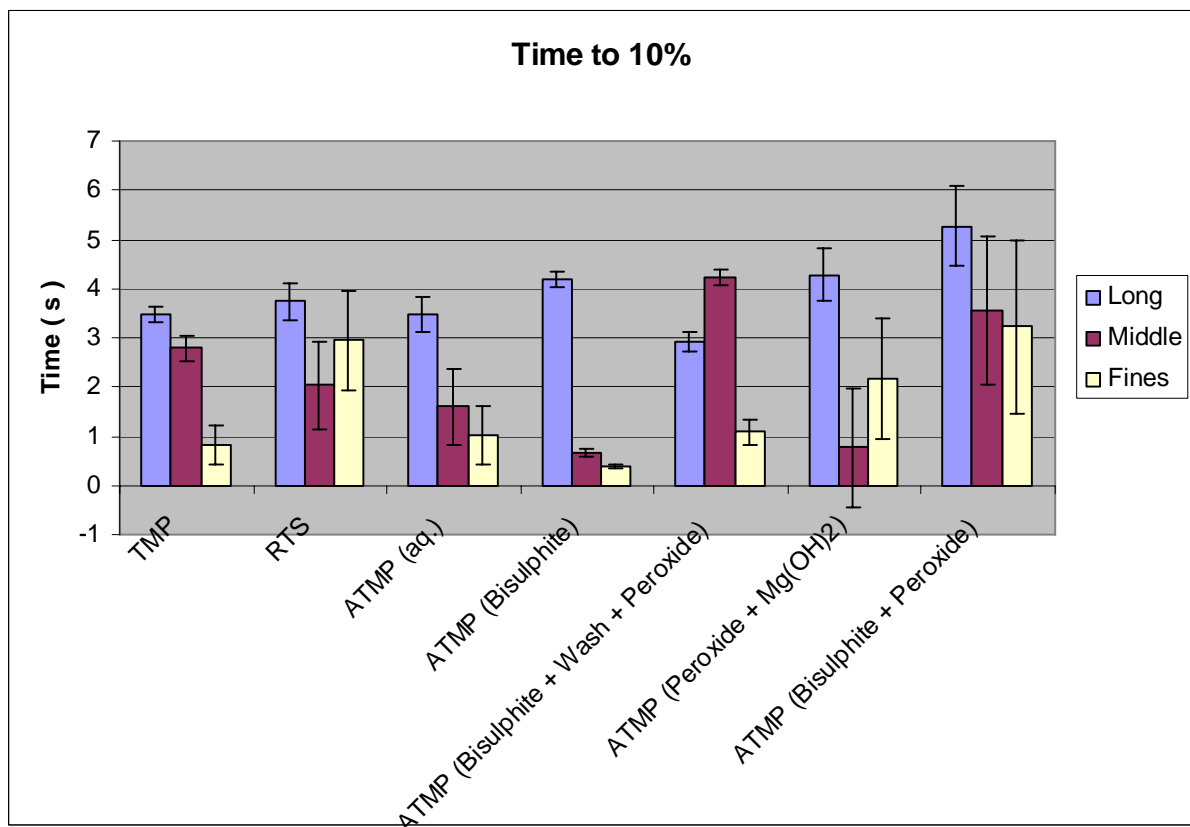


Figure 4-21 Describes the time it takes from initial peak voltage to 10 % of this.

The capacitance measured at 35 % RH seems to be low, *Figure 4-22*, but since the measurements are done only one time it is difficult to conclude from the results. Experiences from measuring the paper sheets at 50 % RH two times are that the results vary from day to day. This is also expected to be the result if the sheets are measured one more time at 35 % RH and this is the reason for only one measurement at this humidity.

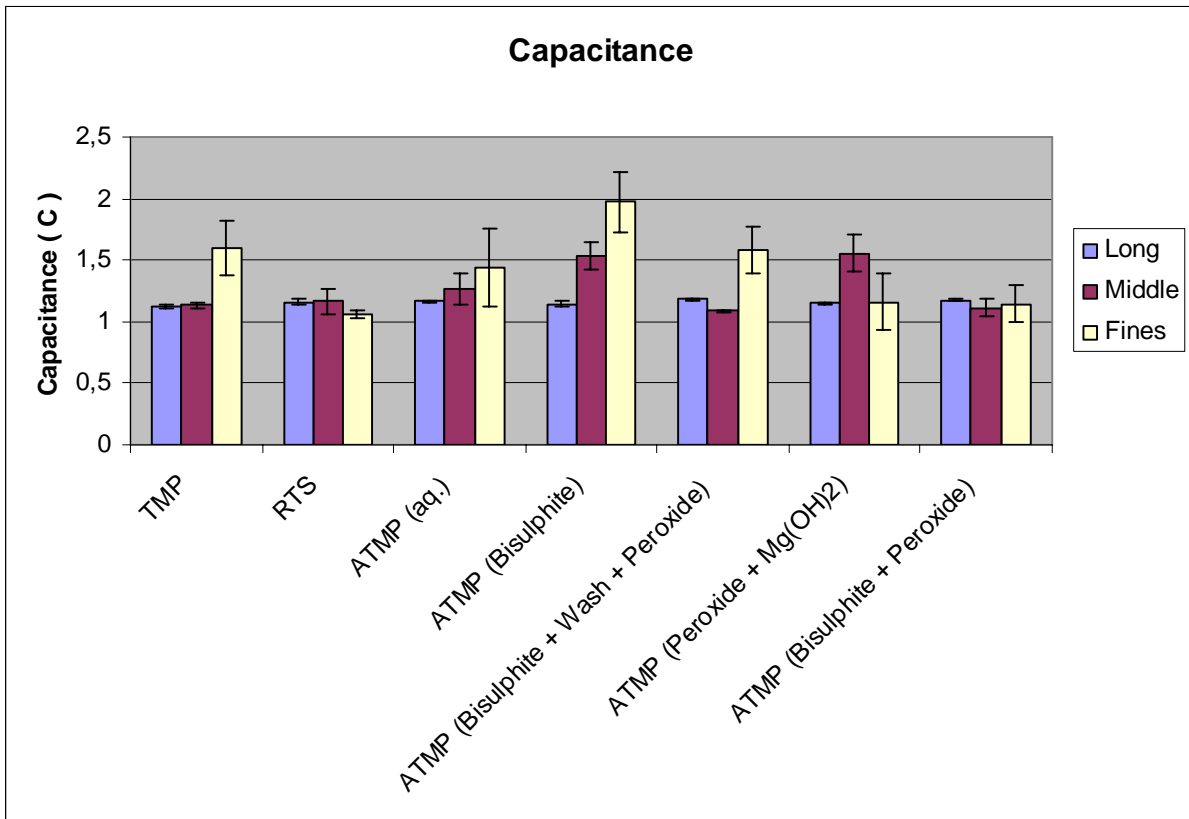


Figure 4-22 Capacitance measured on all fractions from each pulp.

5 Conclusions and recommendations

Methylene blue sorption method gave similar results compared to conductometric titration values, both obtained from the literature. It seems to be possible to use this method as an alternative to conductometric titration. Tests are now conducted using with conductometric titration to further verify the results.

ATMP had higher total charge compared to the pulps produced without addition of chemicals. This was expected. Differences between the total charges measured for whole ATMP pulps could be explained by the difference in composition of the pulp. Since the long fibre fraction contains less acidic groups compared to the middle and fines fraction, this will affect the result for the whole pulp. TMP, RTS and ATMP (aq.) contained less acidic groups compared to ATMP pulps, this is most likely the result carboxylation and/or sulphonation by the chemicals added in ATMP. Water Retention Value should be tested to see if there are any differences in swelling due to the increase in acidic group's content.

Light absorption (k) is lower and the brightness is higher for all ATMP pulps compared to the pulps produced without the addition of chemicals. This is as expected since the chemicals added are typically bleaching chemicals. Differences between the different ATMP pulps could be the result of two mechanisms. The effect of the chemicals added and how fast the bleaching reaction proceeds is one mechanism. The other is the compositions of fractions in each pulp and the compositions of each fraction. For example differences in fines quality could affect the result for the whole pulp. Pulps where bisulphite was added had the highest brightness and lowest light absorption. This indicates that bisulphite reacts faster compared to magnesium hydroxide. These tests are performed on pulps from the primary refining stage, performing the same tests on pulps from other refining stages would be interesting to see if there are any differences.

Differences in light scattering (s) are probably the result from dissimilarity in diffraction. For the long and middle fraction the differences in the size of particles are probably the reason. Differences in internal and external development of the fibre could be a reason since this affects light scattering. However, for the fines fraction the differences could also be the result of different types of fines. Flake-like and fibrillar-like fines scatter the light differently. TMP, RTS and ATMP (aq.) had lowest light scattering of the long fraction. This could be due to the

reduction of the long fraction from the high intensity refining without any chemical pre-treatment. To preserve the particle size in this fraction it seems to be dependent on softening of the fibres by addition of chemicals. The light scattering (s) for RTS in the middle fraction is significantly poorer compared to the other pulps. This could be because of little fibre development resulting in a small surface to scatter light. The difference in light scattering (s) for the fines fraction is probably caused by different types of fines for each pulp. Flake-like fines produced from the middle lamellae scatters more light compare to fibrillar-like fines. Composition of fines present in each fines fraction should be studied in the future.

The z-strength for the long fraction of TMP and ATMP (Bisulphite + Peroxide) was lower compared to the other pulps. Lower fibre bonding could be the reason for this result. Poor z-strength of the middle fraction of RTS pulp could be the result of reduced fiber development resulting in a low specific surface area index which affects the z-strength. The fines fraction gave quite similar results in z-strength for all pulps except for ATMP (Bisulphite), this could be the result of bisulphite reacting with the fines which increased the strength but also the difference in the composition of different types of fines which should be further investigated.

Tensile Energy Absorption (TEA) is dependent on both strain and tensile index. RTS has the lowest TEA for all fractions. This is probably due too poor fibre development. TMP had low TEA for the long fraction and high TEA for middle and fines fraction. This suggests reduced fibre development for the long fraction and better development for the middle and fines fraction. ATMP (Bisulphite) had the highest TEA for long and fines fraction, this could be because of the fast reaction with bisulphite. This could help ATMP (Bisulphite) fibres to develop faster compared to the other pulps. Testing the same parameters on pulps from a later refining stage could contribute to understand how the fibre development is with different chemicals.

Ambertec formation of TMP long fibre fraction stand out as poorer compared to the other pulps, low fibre flexibility could be the reason. It is not easy to see a clear result comparing the middle and fines fractions, the absence of agitation prior to sheet making on the small sheet former probably contributes to this.

The JCI 155v5 used for charge decay measurements did not give any accurate answers regarding differences between the pulps. The individual measurement differences were too big to do any definite conclusions. Differences in moisture content described by the hysteresis curve should be investigated to find out more of about the charge decay measurements act.

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8 Appendix

Appendix for strength properties contains some labelling for the different pulps, Table 8-1;

Table 8-1; Table explaining the different abbreviations used in the appendix.

Abbreviation	Explanation
F	Fines fraction
M	Middle fraction
C	Long fraction
A68	TMP
A31	RTS
A58	ATMP (aq.)
A47	ATMP (Bisulphite)
A9	ATMP (Bisulphite + Wash + Peroxide)
A53	ATMP (Peroxide + Mg(OH) ₂)
A3	ATMP (Bisulphite + Peroxide)

A68F refers to the fines fraction of TMP, A68M is the middle fraction of TMP and A68C is the long fraction of TMP and so on.

CD added in the back of this thesis contains all data used in calculations, figures and tables.

Appendix I; Table used for calculation of total charge to validate the use of methylene blue sorption for total charge measurements.

Name	Concentration Mb in the filtrate (mM)	Undiluted (mM)	Weight, wet pulp sample (kg)	Volume of water in the pulp sample, (l)	Volume, filtrate (l)	Amount of Mb in the filtrate (mmol)
ATMP (Mg(OH)₂ + Peroxide)						
1	0,005636	0,1409	0,006052	0,005981	0,055981	0,007888
2	0,005377	0,134425	0,005975	0,005905	0,055905	0,007515
3	0,004918	0,12295	0,006106	0,006029	0,056029	0,006889
4	0,00527	0,13175	0,005974	0,005902	0,055902	0,007365
ATMP (NaOH+Peroxide)						
9	0,010877	0,271925	0,00477	0,004716	0,054716	0,014879
10	0,011136	0,2784	0,004834	0,004783	0,054783	0,015252
11	0,011394	0,28485	0,004769	0,004721	0,054721	0,015587
12	0,01097	0,27425	0,004874	0,004821	0,054821	0,015035
ATMP (P)						
13	0,010029	0,250725	0,00662	0,006548	0,056548	0,014178
14	0,00966	0,2415	0,006528	0,006454	0,056454	0,013634
15	0,008184	0,2046	0,006477	0,006399	0,056399	0,011539
16	0,010084	0,2521	0,006473	0,006402	0,056402	0,014219
TMP						
17	0,009457	0,236425	0,006012	0,005924	0,055924	0,013222
18	0,009383	0,234575	0,005916	0,005836	0,055836	0,013098
19	0,009992	0,2498	0,005758	0,005682	0,055682	0,013909
20	0,009955	0,248875	0,00573	0,005651	0,055651	0,013850

Name	Mb left in the pulp (mmol)	Weight of filter (g)	Weight of filter + sample (g)	Weight of sample on the filter (g)	Acidic groups (umol/g on filter)	Standard deviation		Mean value
ATMP (Mg(OH)₂ + Peroxide)								
	1 0,012112	0,1304	0,2011	0,0707	171,3	2,652808	3 %	173,8
	2 0,012485	0,1276	0,1984	0,0708	176,3			
	3 0,013111	0,1275	0,2039	0,0764	171,6			
	4 0,012635	0,1287	0,2006	0,0719	175,7			
ATMP (NaOH+Peroxide)								
	9 0,005121	0,1302	0,1839	0,0537	95,4	1,32534	3 %	93,8
	10 0,004748	0,1284	0,1793	0,0509	93,3			
	11 0,004413	0,1279	0,1757	0,0478	92,3			
	12 0,004965	0,1277	0,1803	0,0526	94,4			
ATMP (P)								
	13 0,005822	0,1262	0,1982	0,072	80,9	13,13924	30 %	88,8
	14 0,006366	0,1272	0,2013	0,0741	85,9			
	15 0,008461	0,1262	0,2044	0,0782	108,2			
	16 0,005781	0,126	0,1979	0,0719	80,4			
TMP								
	17 0,006778	0,1259	0,2137	0,0878	77,2	4,095263	10 %	80,5
	18 0,006902	0,1256	0,2056	0,08	86,3			
	19 0,006091	0,1271	0,2028	0,0757	80,5			
	20 0,006150	0,1267	0,2055	0,0788	78,0			

Appendix II; Table used for calculation of total charge for whole pulps

Name	Concentration Mb in the filtrate (mM)	Undiluted (mM)	Weight, wet pulp sample (kg)	Volume of water in the pulp sample, (l)	Volume, filtrate (l)	Amount of Mb in the filtrate (mmol)
RTS - A31						
1	0,009385	0,234625	0,0090881	0,0090102	0,0590102	0,013845
2	0,01047	0,26175	0,0090222	0,0089503	0,0589503	0,015430
3	0,00942	0,2355	0,0090398	0,0089621	0,0589621	0,013886
4	0,009652	0,2413	0,0090672	0,008983	0,058983	0,014233
TMP - A68						
5	0,009313	0,232825	0,0080055	0,0079159	0,0579159	0,013484
6	0,008833	0,220825	0,0081323	0,0080417	0,0580417	0,012817
7	0,007836	0,1959	0,0079954	0,0078822	0,0578822	0,011339
8	0,008637	0,215925	0,0080472	0,0079486	0,0579486	0,012513
ATMP (Peroxide + Mg(OH)₂) - A53						
9	0,00228	0,057	0,0073088	0,0072029	0,0572029	0,003261
10	0,00293	0,07325	0,0073238	0,0072264	0,0572264	0,004192
11	0,00236	0,059	0,007274	0,0071712	0,0571712	0,003373
12	0,00248	0,062	0,0075689	0,0074658	0,0574658	0,003563
ATMP (aq.) - A58						
13	0,009256	0,2314	0,0073327	0,0072466	0,0572466	0,013247
14	0,00861	0,21525	0,0074635	0,007374	0,057374	0,012350
15	0,009077	0,226925	0,0072509	0,0071645	0,0571645	0,012972
16	0,008467	0,211675	0,0072569	0,0071639	0,0571639	0,012100
ATMP (Bisulphite) - A47						
17	0,005827	0,145675	0,0071375	0,0070584	0,0570584	0,008312
18	0,004732	0,1183	0,0072591	0,0071725	0,0571725	0,006764
19	0,005037	0,125925	0,0073208	0,0072328	0,0572328	0,007207
20	0,005252	0,1313	0,0071322	0,0070472	0,0570472	0,007490
ATMP (Bisulphite + wash + peroxide) - A9						
21	0,004085	0,102125	0,007229	0,0071314	0,0571314	0,005835
22	0,004983	0,124575	0,0071836	0,00709	0,05709	0,007112
23	0,004175	0,104375	0,0073295	0,0072304	0,0572304	0,005973
24	0,004175	0,104375	0,007256	0,0071525	0,0571525	0,005965
ATMP (Bisulphite + peroxide) - A3						
1	0,005382331	0,134558	0,0228167	0,0227488	0,0727488	0,009789
2	0,004521158	0,113029	0,0251702	0,0250898	0,0750898	0,008487
3	0,004922049	0,123051	0,0229839	0,0229096	0,0729096	0,008972
4	0,005011136	0,125278	0,0228556	0,0227804	0,0727804	0,009118

Name	Mb left in the pulp (mmol)	Weight of filter (g)	Weight of filter + sample (g)	Weight of sample on the filter (g)	Acidic groups (umol/g on filter)	Standard deviation		Mean value
RTS - A31								
1	0,006155	0,1284	0,2063	0,0779	79,0	7,67	21 %	72,4
2	0,004570	0,1272	0,1991	0,0719	63,6			
3	0,006114	0,1277	0,2054	0,0777	78,7			
4	0,005767	0,128	0,2122	0,0842	68,5			
TMP - A68								
5	0,006516	0,1273	0,2169	0,0896	72,7	2,69	7 %	76,1
6	0,007183	0,1291	0,2197	0,0906	79,3			
7	0,008661	0,1284	0,2416	0,1132	76,5			
8	0,007487	0,128	0,2266	0,0986	75,9			
ATMP (Peroxide + Mg(OH)₂) - A53								
9	0,016739	0,1291	0,235	0,1059	158,1	1,98	2 %	160,4
10	0,015808	0,1258	0,2232	0,0974	162,3			
11	0,016627	0,1285	0,2313	0,1028	161,7			
12	0,016437	0,1271	0,2302	0,1031	159,4			
ATMP (aq.) - A58								
13	0,006753	0,1295	0,2156	0,0861	78,4	3,30	8 %	82,5
14	0,007650	0,1281	0,2176	0,0895	85,5			
15	0,007028	0,1284	0,2148	0,0864	81,3			
16	0,007900	0,1297	0,2227	0,093	84,9			
ATMP (Bisulphite) - A47								
17	0,011688	0,1282	0,2073	0,0791	147,8	3,20	4 %	148,3
18	0,013236	0,1284	0,215	0,0866	152,8			
19	0,012793	0,129	0,217	0,088	145,4			
20	0,012510	0,1288	0,2138	0,085	147,2			
ATMP (Bisulphite + wash + peroxide) - A9								
21	0,014165	0,1287	0,2263	0,0976	145,1	4,22	6 %	140,0
22	0,012888	0,1291	0,2227	0,0936	137,7			
23	0,014027	0,129	0,2281	0,0991	141,5			
24	0,014035	0,1293	0,2328	0,1035	135,6			
ATMP (Bisulphite + peroxide) - A3								
1	0,010211	0,1289	0,1968	0,0679	150,4	3,31	5 %	146,7
2	0,011513	0,1287	0,2091	0,0804	143,2			
3	0,011028	0,128	0,2023	0,0743	148,4			
4	0,010882	0,1293	0,2045	0,0752	144,7			

Appendix III; Table used for calculation of total charge for different fractions of TMP.

Name	Concentration Mb in the filtrate (mM)	Undiluted (mM)	Weight, wet pulp sample (kg)	Volume of water in the pulp sample, (l)	Volume, filtrate (l)	Amount of Mb in the filtrate (mmol)
TMP - Long fraction						
1	0,004828	0,1207	0,0132283	0,0130642	0,0630642	0,007612
2	0,003817	0,095425	0,0140766	0,0138782	0,0638782	0,006096
3	0,002644	0,0661	0,0137483	0,01351	0,06351	0,004198
4	0,004066	0,10165	0,0134927	0,0133022	0,0633022	0,006435
TMP - Middle fraction						
5	0,008624	0,2156	0,0167548	0,0166866	0,0666866	0,014378
6	0,007833	0,195825	0,016748	0,0166781	0,0666781	0,013057
7	0,007906	0,19765	0,0168583	0,0167873	0,0667873	0,013201
8	0,007877	0,196925	0,0167516	0,0166814	0,0666814	0,013131
TMP - Fines fraction						
9	0,003868	0,0967	0,0354364	0,035364	0,085364	0,008255
10	0,004869	0,121725	0,0353895	0,0353163	0,0853163	0,010385
11	0,004511	0,112775	0,0354087	0,0353357	0,0853357	0,009624
12	0,004705	0,117625	0,0355227	0,03545	0,08545	0,010051

Name	Mb left in the pulp (mmol)	Weight of filter (g)	Weight of filter + sample (g)	Weight of sample on the filter (g)	Acidic groups (umol/g on filter)	Standard deviation	Mean value
TMP - Long fraction							
1	0,012388	0,1283	0,2924	0,1641	75,5	3,778762	11 %
2	0,013904	0,1294	0,3278	0,1984	70,1		
3	0,015802	0,1286	0,3669	0,2383	66,3		
4	0,013565	0,1279	0,3184	0,1905	71,2		
TMP - Middle fraction							
5	0,005622	0,1293	0,1975	0,0682	82,4	7,741872	16 %
6	0,006943	0,1285	0,1984	0,0699	99,3		
7	0,006799	0,1282	0,1992	0,071	95,8		
8	0,006869	0,1283	0,1985	0,0702	97,8		
TMP - Fines fraction							
9	0,011745	0,1281	0,2005	0,0724	162,2	13,46486	19 %
10	0,009615	0,1285	0,2017	0,0732	131,4		
11	0,010376	0,1285	0,2015	0,073	142,1		
12	0,009949	0,1273	0,2	0,0727	136,8		

Appendix IV; Table used for calculation of total charge for different fractions of RTS.

Name	Concentration Mb in the filtrate (mM)	Undiluted (mM)	Weight, wet pulp sample (kg)	Volume of water in the pulp sample, (l)	Volume, filtrate (l)	Amount of Mb in the filtrate (mmol)
RTS - Long fraction						
1	0,005583	0,139575	0,0099695	0,0098285	0,0598285	0,008351
2	0,004823	0,120575	0,0105982	0,0104335	0,0604335	0,007287
3	0,004659	0,116475	0,0106281	0,0104594	0,0604594	0,007042
4	0,005687	0,142175	0,0099833	0,009836	0,059836	0,008507
RTS - Middle fraction						
5	0,008638	0,21595	0,0090531	0,0089796	0,0589796	0,012737
6	0,009278	0,23195	0,0088739	0,0088045	0,0588045	0,013640
7	0,008989	0,224725	0,0089386	0,0088689	0,0588689	0,013229
8	0,009095	0,227375	0,0090674	0,0089982	0,0589982	0,013415
RTS - Fines fraction						
9	0,003946	0,09865	0,0267669	0,0266893	0,0766893	0,007565
10	0,004372	0,1093	0,0248182	0,0247456	0,0747456	0,008170
11	0,004388	0,1097	0,0249025	0,02483	0,07483	0,008209
12	0,004631	0,115775	0,0246801	0,0246082	0,0746082	0,008638

Name	Mb left in the pulp (mmol)	Weight of filter (g)	Weight of filter + sample (g)	Weight of sample on the filter (g)	Acidic groups (umol/g on filter)	Standard deviation		Mean value
RTS - Long fraction								
1	0,011649	0,1287	0,2697	0,141	82,6	2,687479	7 %	78,7
2	0,012713	0,1281	0,2928	0,1647	77,2			
3	0,012958	0,1283	0,297	0,1687	76,8			
4	0,011493	0,1283	0,2756	0,1473	78,0			
RTS - Middle fraction								
5	0,007263	0,1289	0,2024	0,0735	98,8	3,083936	6 %	95,7
6	0,006360	0,1285	0,1979	0,0694	91,6			
7	0,006771	0,129	0,1987	0,0697	97,1			
8	0,006585	0,1282	0,1974	0,0692	95,2			
RTS - Fines fraction								
9	0,012435	0,1271	0,2047	0,0776	160,2	2,301586	3 %	161,0
10	0,011830	0,1276	0,2002	0,0726	163,0			
11	0,011791	0,1269	0,1994	0,0725	162,6			
12	0,011362	0,1274	0,1993	0,0719	158,0			

Appendix V; Table used for calculation of total charge for different fractions of ATMP

(aq.).

Name		Concentration Mb in the filtrate (mM)	Undiluted (mM)	Weight, wet pulp sample (kg)	Volume of water in the pulp sample, (l)	Volume, filtrate (l)	Amount of Mb in the filtrate (mmol)
ATMP (aq.) - Long fraction							
	1	0,004843	0,121075	0,0128148	0,0126705	0,0626705	0,007588
	2	0,004857	0,121425	0,0129183	0,0127637	0,0627637	0,007621
	3	0,003641	0,091025	0,0130578	0,0128594	0,0628594	0,005722
	4	0,005649	0,141225	0,0121205	0,0119726	0,0619726	0,008752
ATMP (aq.) - Middle fraction							
	5	0,008489	0,212225	0,0088354	0,0087635	0,0587635	0,012471
	6	0,008695	0,217375	0,008897	0,0088244	0,0588244	0,012787
	7	0,008901	0,222525	0,0088246	0,0087526	0,0587526	0,013074
	8	0,008563	0,214075	0,0087855	0,0087127	0,0587127	0,012569
ATMP (aq.) - Fines fraction							
	9	0,005467	0,136675	0,0249532	0,0248834	0,0748834	0,010235
	10	0,00478	0,1195	0,0261878	0,0261141	0,0761141	0,009096
	11	0,005094	0,12735	0,0248408	0,0247714	0,0747714	0,009522
	12	0,005527	0,138175	0,0248144	0,02474262	0,07474262	0,010328

Name		Mb left in the pulp (mmol)	Weight of filter (g)	Weight of filter + sample (g)	Weight of sample on the filter (g)	Acidic groups (umol/g on filter)	Standard deviation		Mean value
ATMP (aq.) - Long fraction									
	1	0,012412	0,1289	0,2732	0,1443	86,0	5,990021	15 %	78,5
	2	0,012379	0,1288	0,2834	0,1546	80,1			
	3	0,014278	0,1289	0,3273	0,1984	72,0			
	4	0,011248	0,1281	0,276	0,1479	76,1			
ATMP (aq.) - Middle fraction									
	5	0,007529	0,1263	0,1982	0,0719	104,7	3,653851	7 %	100,6
	6	0,007213	0,1274	0,2	0,0726	99,4			
	7	0,006926	0,1276	0,1996	0,072	96,2			
	8	0,007431	0,1271	0,1999	0,0728	102,1			
ATMP (aq.) - Fines fraction									
	9	0,009765	0,1282	0,198	0,0698	139,9	7,420803	10 %	143,4
	10	0,010904	0,1287	0,2024	0,0737	148,0			
	11	0,010478	0,1274	0,1968	0,0694	151,0			
	12	0,009672	0,1279	0,19968	0,07178	134,8			

Appendix VI; Table used for calculation of total charge for different fractions of ATMP (Bisulphite).

Name	Concentration Mb in the filtrate (mM)	Undiluted (mM)	Weight, wet pulp sample (kg)	Volume of water in the pulp sample, (l)	Volume, filtrate (l)	Amount of Mb in the filtrate (mmol)
ATMP (Bisulphite) - Long Fraction						
1	0,006094	0,15235	0,0057203	0,005622	0,055622	0,008474
2	0,007885	0,197125	0,0056174	0,0055379	0,0555379	0,010948
3	0,007839	0,195975	0,0061574	0,0060845	0,0560845	0,010991
4	0,008765	0,219125	0,0059921	0,0059264	0,0559264	0,012255
ATMP (Bisulphite) - Middle Fraction						
5	0,008264	0,2066	0,0068306	0,0067667	0,0567667	0,011728
6	0,008355	0,208875	0,006551	0,0064912	0,0564912	0,011800
7	0,007869	0,196725	0,006683	0,0066198	0,0566198	0,011139
8	0,008143	0,203575	0,0066527	0,0065895	0,0565895	0,011520
ATMP (Bisulphite) - Fines Fraction						
9	0,003928	0,0982	0,0254114	0,0253394	0,0753394	0,007398
10	0,003793	0,094825	0,0254268	0,0253535	0,0753535	0,007145
11	0,003838	0,09595	0,0257501	0,0256758	0,0756758	0,007261
12	0,003853	0,096325	0,025337	0,025264	0,075264	0,007250

Name	Mb left in the pulp (mmol)	Weight of filter (g)	Weight of filter + sample (g)	Weight of sample on the filter (g)	Acidic groups (umol/g on filter)	Standard deviation	Mean value
ATMP (Bisulphite) - Long Fraction							
1	0,011526	0,1296	0,2279	0,0983	117,3	4,029793	7 %
2	0,009052	0,1295	0,209	0,0795	113,9		
3	0,009009	0,1288	0,2017	0,0729	123,6		
4	0,007745	0,1285	0,1942	0,0657	117,9		
ATMP (Bisulphite) - Middle Fraction							
5	0,008272	0,1298	0,1937	0,0639	129,5	4,580399	7 %
6	0,008200	0,1281	0,1879	0,0598	137,1		
7	0,008861	0,1282	0,1914	0,0632	140,2		
8	0,008480	0,129	0,1922	0,0632	134,2		
ATMP (Bisulphite) - Fines Fraction							
9	0,012602	0,1306	0,2026	0,072	175,0	1,806094	2 %
10	0,012855	0,1294	0,2027	0,0733	175,4		
11	0,012739	0,1308	0,2051	0,0743	171,5		
12	0,012750	0,1291	0,2021	0,073	174,7		

Appendix VII; Table used for calculation of total charge for different fractions of

ATMP (Bisulphite + wash + peroxide).

Name	Concentration Mb in the filtrate (mM)	Undiluted (mM)	Weight, wet pulp sample (kg)	Volume of water in the pulp sample, (l)	Volume, filtrate (l)	Amount of Mb in the filtrate (mmol)
ATMP (Bisulphite + wash + peroxide) - Long fraction						
1	0,00611	0,15275	0,0062992	0,006211	0,056211	0,008586
2	0,006823	0,170575	0,0063457	0,0062674	0,0562674	0,009598
3	0,004972	0,1243	0,00653	0,0064373	0,0564373	0,007015
4	0,007794	0,19485	0,0064372	0,0063686	0,0563686	0,010983
ATMP (Bisulphite + wash + peroxide) - Middle fraction						
5	0,007551	0,188775	0,0080503	0,0079827	0,0579827	0,010946
6	0,007237	0,180925	0,0080359	0,0079635	0,0579635	0,010487
7	0,006413	0,160325	0,0080488	0,0079786	0,0579786	0,009295
8	0,007461	0,186525	0,0081236	0,0080531	0,0580531	0,010828
ATMP (Bisulphite + wash + peroxide) - Fines fraction						
9	0,00279	0,06975	0,0289825	0,0289079	0,0789079	0,005504
10	0,002775	0,069375	0,0290407	0,0289634	0,0789634	0,005478
11	0,002596	0,0649	0,0290389	0,0289628	0,0789628	0,005125
12	0,002626	0,06565	0,0290768	0,0289991	0,0789991	0,005186

Name	Mb left in the pulp (mmol)	Weight of filter (g)	Weight of filter + sample (g)	Weight of sample on the filter (g)	Acidic groups (umol/g on filter)	Standard deviation	Mean value
ATMP (Bisulphite + wash + peroxide) - Long fraction							
1	0,011414	0,1295	0,2177	0,0882	129,4	4,641325	7 % 133,4
2	0,010402	0,128	0,2063	0,0783	132,9		
3	0,012985	0,1299	0,2226	0,0927	140,1		
4	0,009017	0,1288	0,1974	0,0686	131,4		
ATMP (Bisulphite + wash + peroxide) - Middle fraction							
5	0,009054	0,129	0,1966	0,0676	133,9	10,46137	15 % 137,0
6	0,009513	0,1292	0,2016	0,0724	131,4		
7	0,010705	0,1278	0,198	0,0702	152,5		
8	0,009172	0,1288	0,1993	0,0705	130,1		
ATMP (Bisulphite + wash + peroxide) - Fines fraction							
9	0,014496	0,1296	0,2042	0,0746	194,3	3,479324	4 % 192,1
10	0,014522	0,1295	0,2068	0,0773	187,9		
11	0,014875	0,1295	0,2056	0,0761	195,5		
12	0,014814	0,1296	0,2073	0,0777	190,7		

Appendix VIII; Table used for calculation of total charge for different fractions of ATMP (Peroxide + Mg(OH)₂).

Name	Concentration Mb in the filtrate (mM)	Undiluted (mM)	Weight, wet pulp sample (kg)	Volume of water in the pulp sample, (l)	Volume, filtrate (l)	Amount of Mb in the filtrate (mmol)
ATMP (Peroxide + Mg(OH)₂) - Long fraction						
1	0,0053	0,1325	0,0071352	0,007031	0,057031	0,007557
2	0,002946	0,07365	0,0083233	0,0081817	0,0581817	0,004285
3	0,002767	0,069175	0,0082091	0,0080578	0,0580578	0,004016
4	0,003572	0,0893	0,0078223	0,0076917	0,0576917	0,005152
ATMP (Peroxide + Mg(OH)₂) - Middle fraction			0			
5	0,006566	0,16415	0,0076589	0,0075833	0,0575833	0,009452
6	0,006566	0,16415	0,0077186	0,0076408	0,0576408	0,009462
7	0,006253	0,156325	0,0077124	0,0076332	0,0576332	0,009010
8	0,005448	0,1362	0,0076661	0,0075872	0,0575872	0,007843
ATMP (Peroxide + Mg(OH)₂) - Fines fraction			0			
9	0,00128	0,032	0,0248642	0,0247816	0,0747816	0,002393
10	0,001478	0,03695	0,0244663	0,0243858	0,0743858	0,002749
11	0,001722	0,04305	0,0238476	0,023769	0,073769	0,003176
12	0,001661	0,041525	0,0237614	0,0236829	0,0736829	0,003060

Name	Mb left in the pulp (mmol)	Weight of filter (g)	Weight of filter + sample (g)	Weight of sample on the filter (g)	Acidic groups (umol/g on filter)	Standard deviation		Mean value
ATMP (Peroxide + Mg(OH)₂) - Long fraction								
1	0,012443	0,1272	0,2314	0,1042	119,4	5,732531	10 %	112,4
2	0,015715	0,1286	0,2702	0,1416	111,0			
3	0,015984	0,1262	0,2775	0,1513	105,6			
4	0,014848	0,128	0,2586	0,1306	113,7			
ATMP (Peroxide + Mg(OH)₂) - Middle fraction								
5	0,010548	0,1287	0,2043	0,0756	139,5	8,27207	12 %	142,0
6	0,010538	0,1281	0,2059	0,0778	135,5			
7	0,010990	0,1293	0,2085	0,0792	138,8			
8	0,012157	0,1292	0,2081	0,0789	154,1			
ATMP (Peroxide + Mg(OH)₂) - Fines fraction								
9	0,017607	0,1285	0,2111	0,0826	213,2	1,097105	1 %	214,3
10	0,017251	0,1284	0,2089	0,0805	214,3			
11	0,016824	0,1277	0,2063	0,0786	214,0			
12	0,016940	0,1292	0,2077	0,0785	215,8			

Appendix IX; Table used for calculation of total charge for different fractions of ATMP (Bisulphite + peroxide).

Name	Concentration Mb in the filtrate (mM)	Undiluted (mM)	Weight, wet pulp sample (kg)	Volume of water in the pulp sample, (l)	Volume, filtrate (l)	Amount of Mb in the filtrate (mmol)
ATMP (Bisulphite + peroxide) - Long fraction						
5	0,007891611	0,19729	0,0144081	0,0143545	0,0643545	0,012697
6	0,007371938	0,184298	0,0144743	0,0144165	0,0644165	0,011872
7	0,00918337	0,229584	0,0141009	0,0140612	0,0640612	0,014707
8	0,005768374	0,144209	0,0182528	0,0181803	0,0681803	0,009832
ATMP (Bisulphite + peroxide) - Middle fraction						
9	0,004773571	0,119339	0,0223113	0,0222289	0,0722289	0,008620
10	0,004936897	0,123422	0,0259214	0,0258347	0,0758347	0,009360
11	0,006956199	0,173905	0,0233236	0,0232678	0,0732678	0,012742
12	0,005308092	0,132702	0,0231439	0,0230645	0,0730645	0,009696
ATMP (Bisulphite + peroxide) - Fines fraction						
13	0,00281366	0,070341	0,0291621	0,0290889	0,0790889	0,005563
14	0,002828508	0,070713	0,028109	0,0280375	0,0780375	0,005518
15	0,002991834	0,074796	0,0279306	0,0278599	0,0778599	0,005824
16	0,003021529	0,075538	0,028274	0,0282025	0,0782025	0,005907

Name	Mb left in the pulp (mmol)	Weight of filter (g)	Weight of filter + sample (g)	Weight of sample on the filter (g)	Acidic groups (umol/g on filter)	Standard deviation	Average
ATMP (Bisulphite + peroxide) - Long fraction							
5	0,007303	0,1294	0,183	0,0536	136,3	3,479355	5 % 137,6
6	0,008128	0,1292	0,187	0,0578	140,6		
7	0,005293	0,1293	0,169	0,0397	133,3		
8	0,010168	0,1299	0,2024	0,0725	140,2		
ATMP (Bisulphite + peroxide) - Middle fraction							
9	0,011380	0,1285	0,2109	0,0824	138,1	6,288273	10 % 130,2
10	0,010640	0,1289	0,2156	0,0867	122,7		
11	0,007258	0,1278	0,1836	0,0558	130,1		
12	0,010304	0,1274	0,2068	0,0794	129,8		
ATMP (Bisulphite + peroxide) - Fines fraction							
13	0,014437	0,1291	0,2023	0,0732	197,2	2,653662	3 % 199,3
14	0,014482	0,1282	0,1997	0,0715	202,5		
15	0,014176	0,1288	0,1995	0,0707	200,5		
16	0,014093	0,1301	0,2016	0,0715	197,1		

Appendix X; Optical properties measured on all fractions from each pulp.

Fraction					
Long	TMP	RTS	ATMP (aq.)	ATMP (B)	ATMP (B+W+P)
	A68	A31	A58	A47	A9
Grammage weight 7*14 cm sheet (g)	67,8	59,5	66,6	62,4	62,1
Thickness (µm)	372,8	307,9	304,2	274,4	264,7
Density (kg/m3)	182	193	219	227	235
Brightness R457 (%)	45,7	46,1	46,4	51,4	51,5
Opacity C2 (%)	88,7	85,4	87,4	84,4	82,5
Light scattering (m2/kg)	26,36	26,27	26,13	27,2	27,3
Light absorption (m2/kg)	3,04	2,93	2,76	2,26	1,72
Middle	TMP	RTS	ATMP (aq.)	ATMP (B)	ATMP (B+W+P)
	A68	A31	A58	A47	A9
Grammage weight 7*14 cm sheet (g)	65,9	64,1	65,45	64,4	63,9
Thickness (µm)	149,5	220,5	172,2	181,2	176,5
Density (kg/m3)	441	291	380	355	362
Brightness R457 (%)	50,1	49,1	50,8	55,7	55,8
Opacity C2 (%)	96,4	94,7	96,1	94,8	92,3
Light scattering (m2/kg)	46,93	41,82	47,73	48,22	45,81
Light absorption (m2/kg)	4,62	4,15	4,25	3,36	2,33
Fines	TMP	RTS	ATMP (aq.)	ATMP (B)	ATMP (B+W+P)
	A68	A31	A58	A47	A9
Grammage weight 7*14 cm sheet (g)	66,4	65,7	65,7	71,3	65,1
Thickness (µm)	133,5	121,6	131	128,7	123,7
Density (kg/m3)	497	540	502	554	526
Brightness R457 (%)	49	50	48,8	54,1	59,1
Opacity C2 (%)	99,1	99,9	100	99,7	98,9
Light scattering (m2/kg)	95,62	106,57	82,8	89,48	97,31
Light absorption (m2/kg)	11,62	11,88	9,57	7,71	4,14

Fraction		
Long	ATMP (P+Mg(OH) ₂)	ATMP (B+P)
	A53	A3
Grammage weight 7*14 cm sheet (g)	60,2	68,3
Thickness (µm)	244,2	312,5
Density (kg/m ³)	247	219
Brightness R457 (%)	54,4	49,9
Opacity C2 (%)	80,6	85,7
Light scattering (m ² /kg)	27,49	27
Light absorption (m ² /kg)	1,5	1,97
Middle	ATMP (P+Mg(OH) ₂)	ATMP (B+P)
	A53	A3
Grammage weight 7*14 cm sheet (g)	65,9	69,4
Thickness (µm)	180,7	192,6
Density (kg/m ³)	365	360
Brightness R457 (%)	59,9	54,8
Opacity C2 (%)	92,1	94
Light scattering (m ² /kg)	47,69	45,47
Light absorption (m ² /kg)	1,9	2,58
Fines	ATMP (P+Mg(OH) ₂)	ATMP (B+P)
	A53	A3
Grammage weight 7*14 cm sheet (g)	66,2	66,2
Thickness (µm)	129,2	129,6
Density (kg/m ³)	512	511
Brightness R457 (%)	60,7	58,2
Opacity C2 (%)	99	99,3
Light scattering (m ² /kg)	100,85	102,11
Light absorption (m ² /kg)	4,01	4,99

Appendix XI; Charge decay measurements done at 50 % RH taken the 14/2-2011.

Long fraction		t to %	Q(nC)	CL	Vpk
67111741	ATMP (B+P)	0,864844	4,96166	1,53211	-1390,63
67111742	ATMP (B+P)	0,663672	5,31562	1,6359	-1395,31
67111743	ATMP (B+P)	0,892187	4,9294	1,50859	-1403,13
67111744	ATMP (B+P)	0,93125	4,78312	1,46709	-1400
67111745	ATMP (B+P)	0,675391	5,1429	1,63776	-1348,44
	Mean value	0,805469	5,02654	1,55629	-1387,5
67111746	RTS	0,835547	4,89244	1,53139	-1371,88
67111747	RTS	0,80625	4,99993	1,54915	-1385,94
67111748	RTS	0,739844	5,0268	1,57165	-1373,44
67111749	RTS	0,817969	4,8563	1,49287	-1396,88
67111750	RTS	0,821875	4,64437	1,42932	-1395,31
	Mean value	0,804297	4,883968	1,514876	-1384,69
67111751	ATMP (aq.)	0,616797	4,76997	1,51199	-1354,69
67111752	ATMP (aq.)	0,636328	4,88688	1,50902	-1390,63
67111753	ATMP (aq.)	0,800391	4,60036	1,40476	-1406,25
67111754	ATMP (aq.)	0,767187	4,62925	1,42626	-1393,75
67111755	ATMP (aq.)	0,728125	4,64484	1,43751	-1387,5
	Mean value	0,709766	4,70626	1,457908	-1386,56
67111756	TMP	0,784766	4,65305	1,4548	-1373,44
67111757	TMP	0,855078	4,67753	1,43471	-1400
67111758	TMP	0,855078	4,62579	1,4284	-1390,63
67111759	TMP	0,798437	4,71815	1,4504	-1396,88
67111760	TMP	0,819922	4,71944	1,42373	-1423,44
	Mean value	0,822656	4,678792	1,438408	-1396,88
67111761	ATMP (B)	0,728125	4,68519	1,43866	-1398,44
67111762	ATMP (B)	0,767187	4,71906	1,4572	-1390,63
67111763	ATMP (B)	0,798437	4,70751	1,45855	-1385,94
67111764	ATMP (B)	0,765234	4,84897	1,48563	-1401,56
67111765	ATMP (B)	0,843359	4,71847	1,45538	-1392,19
	Mean value	0,780468	4,73584	1,459084	-1393,75
67111766	ATMP (B+W+P)	0,841406	4,7562	1,45397	-1404,69
67111767	ATMP (B+W+P)	0,839453	4,74539	1,46861	-1387,52
67111768	ATMP (B+W+P)	0,884375	4,71759	1,4502	-1396,9
67111769	ATMP (B+W+P)	0,694922	4,98549	1,56229	-1370,31
67111770	ATMP (B+W+P)	0,853125	4,80401	1,48343	-1390,63
	Mean value	0,822656	4,801736	1,4837	-1390,01
67111771	ATMP (P+Mg(OH) ₂)	1,20859	4,44957	1,33206	-1434,4
67111772	ATMP (P+Mg(OH) ₂)	1,17344	4,42219	1,33113	-1426,56
67111773	ATMP (P+Mg(OH) ₂)	1,11875	4,49296	1,348	-1431,25
67111774	ATMP (P+Mg(OH) ₂)	1,16172	4,55955	1,35908	-1440,63
67111775	ATMP (P+Mg(OH) ₂)	0,923437	4,7753	1,43577	-1428,2
	Mean value	1,117187	4,539914	1,361208	-1432,21

Middle fraction		t to %	Q(nC)	CL	Vpk
67111776	ATMP (B+P)	1,11094	4,52081	1,34753	-1440,63
67111777	ATMP (B+P)	0,751562	4,8605	1,50085	-1390,65
67111778	ATMP (B+P)	0,99375	4,65135	1,40473	-1421,88
67111779	ATMP (B+P)	0,472266	6,07786	1,89596	-1376,56
67111780	ATMP (B+P)	0,554297	5,30823	1,68647	-1351,59
	Mean value	0,776563	5,08375	1,567108	-1396,26
67111782	ATMP (P+Mg(OH)2)	0,382422	5,88487	2,01149	-1256,3
67111783	ATMP (P+Mg(OH)2)	0,335547	6,4308	2,29226	-1204,69
67111784	ATMP (P+Mg(OH)2)	0,308203	6,89107	2,53186	-1168,75
67111785	ATMP (P+Mg(OH)2)	0,339453	6,58563	2,29973	-1229,69
67111786	ATMP (P+Mg(OH)2)	0,271094	7,53996	2,85421	-1134,38
	Mean value	0,327344	6,666466	2,39791	-1198,76
67111787	ATMP (B)	0,310156	6,52357	2,3621	-1185,94
67111788	ATMP (B)	0,616797	5,24875	1,64479	-1370,31
67111789	ATMP (B)	0,251563	7,8276	3,0644	-1096,88
67111790	ATMP (B)	0,286719	6,77646	2,49977	-1164,06
67111791	ATMP (B)	0,296484	6,68796	2,41526	-1189,06
	Mean value	0,352344	6,612868	2,397264	-1201,25
67111792	ATMP (aq.)	0,540625	5,29249	1,6854	-1348,44
67111793	ATMP (aq.)	1,15391	4,57309	1,36757	-1435,94
67111794	ATMP (aq.)	0,704687	4,8763	1,51769	-1379,69
67111795	ATMP (aq.)	0,358984	6,39859	2,22311	-1235,94
67111796	ATMP (aq.)	0,599219	5,06402	1,61078	-1350
	Mean value	0,671485	5,240898	1,68091	-1350
67111797	ATMP (B+W+P)	1,70078	4,3509	1,26399	-1478,13
67111798	ATMP (B+W+P)	1,67734	4,28887	1,2715	-1448,44
67111799	ATMP (B+W+P)	1,65	4,36218	1,2863	-1456,25
67111800	ATMP (B+W+P)	1,63047	4,36053	1,27351	-1470,31
67111801	ATMP (B+W+P)	1,68516	4,39597	1,28387	-1470,31
67111802	ATMP (B+W+P)	1,49375	4,41671	1,29959	-1459,38
	Mean value	1,639583	4,362527	1,279793	-1463,8
67111803	TMP	1,04453	4,64265	1,39291	-1431,25
67111804	TMP	1,30625	4,54517	1,33739	-1459,38
67111805	TMP	1,11875	4,59262	1,37791	-1431,25
67111806	TMP	1,12266	4,55566	1,36831	-1429,69
67111807	TMP	1,14609	4,64996	1,38904	-1437,5
	Mean value	1,147656	4,597212	1,373112	-1437,81
67111808	RTS	0,907812	4,85887	1,44049	-1448,44
67111809	RTS	0,499609	5,52029	1,74782	-1356,25
67111810	RTS	0,708594	4,94792	1,52103	-1396,88
67111811	RTS	1,4	4,46219	1,30461	-1468,73
67111812	RTS	0,722266	4,94195	1,51078	-1404,66
	Mean value	0,847656	4,946244	1,504946	-1414,99

Fines fraction		t to %	Q(nC)	CL	Vpk
67111813	ATMP (B+P)	0,605078	5,29776	1,63958	-1387,5
67111814	ATMP (B+P)	0,509375	5,43498	1,76139	-1325
67111815	ATMP (B+P)	0,276953	7,36287	2,87428	-1100
67111816	ATMP (B+P)	0,325781	9,40242	4,40957	-915,625
67111817	ATMP (B+P)	0,622656	5,10445	1,63309	-1342,19
67111818	ATMP (B+P)	0,290625	7,9638	3,29614	-1037,5
	Mean value	0,438411	6,761047	2,602342	-1184,64
67111819	RTS	0,673437	4,972	1,54398	-1382,81
67111820	RTS	0,441016	5,63572	1,85934	-1301,56
67111821	RTS	0,304297	6,7544	2,45863	-1179,69
67111822	RTS	1,56797	4,64274	1,4482	-1376,64
67111823	RTS	0,323828	6,73075	2,44679	-1181,25
	Mean value	0,66211	5,747122	1,951388	-1284,39
67111824	ATMP (B)	0,679297	11,8666	6,37105	-799,814
67111825	ATMP (B)	1,12266	12,7086	7,14255	-764,044
67111826	ATMP (B)	0,975195	14,1145	8,31941	-728,528
67111827	ATMP (B)	0,751562	11,2118	5,8691	-820,313
67111828	ATMP (B)	0,347266	6,29245	2,16706	-1246,88
	Mean value	0,775196	11,23879	5,973834	-871,916
67111829	ATMP (P+Mg(OH)2)	0,290625	8,87092	3,75564	-1014,28
67111830	ATMP (P+Mg(OH)2)	0,798437	4,81454	1,47828	-1398,54
67111831	ATMP (P+Mg(OH)2)	0,276953	8,2401	3,26749	-1082,91
67111832	ATMP (P+Mg(OH)2)	0,675391	4,95144	1,53906	-1381,49
67111833	ATMP (P+Mg(OH)2)	0,810156	4,63788	1,42535	-1397,24
	Mean value	0,570312	6,302976	2,293164	-1254,89
67111834	ATMP (aq.)	0,540625	5,25952	1,68918	-1337,04
67111835	ATMP (aq.)	0,261328	8,87207	3,72973	-1021,46
67111836	ATMP (aq.)	0,464453	5,62112	1,84925	-1305,27
67111837	ATMP (aq.)	0,470313	10,7262	5,60369	-821,948
67111838	ATMP (aq.)	0,302344	8,2527	3,42604	-1034,38
67111839	ATMP (aq.)	0,294531	8,12286	3,28763	-1060,96
	Mean value	0,388932	7,809078	3,264253	-1096,84
67111840	ATMP (B+W+P)	0,253516	9,24526	4,22764	-939,063
67111841	ATMP (B+W+P)	0,284766	9,63395	4,52587	-914,063
67111842	ATMP (B+W+P)	0,651953	5,02208	1,57735	-1367,19
67111843	ATMP (B+W+P)	0,661719	5,06535	1,60748	-1353,13
67111844	ATMP (B+W+P)	0,364844	10,1825	5,02403	-870,313
	Mean value	0,44336	7,829828	3,392474	-1088,75
67111845	TMP	0,251563	7,4649	2,86927	-1117,19
67111846	TMP	0,505469	12,9403	7,44762	-746,106
67111847	TMP	0,403906	5,85137	1,99022	-1262,5
67111848	TMP	0,257422	7,64452	3,24212	-1012,5
67111849	TMP	0,444922	5,53026	1,88333	-1260,94
67111850	TMP	0,521094	5,3968	1,74081	-1331,25
	Mean value	0,397396	7,471358	3,195562	-1121,75

Appendix XII; Charge decay measurements done at 50 % RH taken the 23/2-2011.

Long Fraction		t to %	Q(nC)	CL	Vpk
75	TMP	2,09531	4,24337	1,21959	1494,07
76	TMP	1,86094	4,24117	1,24092	1467,63
77	TMP	1,84922	4,38336	1,23061	1529,54
78	TMP	1,63828	4,45265	1,26517	1511,28
79	TMP	1,82578	4,44938	1,23628	1545,46
	Mean value	1,853906	4,353986	1,238514	1509,596
80	ATMP (P+Mg(OH)2)	2,275	4,23299	1,19388	1522,51
81	ATMP (P+Mg(OH)2)	1,86094	4,21422	1,22807	1473,56
82	ATMP (P+Mg(OH)2)	2,22813	4,31352	1,2038	1538,7
83	ATMP (P+Mg(OH)2)	2,39219	4,25118	1,16971	1560,64
84	ATMP (P+Mg(OH)2)	2,25938	4,29925	1,17969	1564,94
	Mean value	2,203128	4,262232	1,19503	1532,07
85	ATMP (B+W+P)	1,73594	4,46873	1,25044	1534,59
86	ATMP (B+W+P)	1,93711	4,31939	1,25175	1481,76
87	ATMP (B+W+P)	1,94687	4,34982	1,21202	1541,11
88	ATMP (B+W+P)	1,97812	4,21698	1,18199	1532,01
89	ATMP (B+W+P)	2,03477	4,26202	1,20313	1521,17
	Mean value	1,926562	4,323388	1,219866	1522,128
90	RTS	1,99375	4,33065	1,24486	1493,85
91	RTS	1,69297	4,34418	1,23666	1508,45
92	RTS	2,00938	4,40322	1,24862	1514,31
93	RTS	2,06406	4,23299	1,19205	1524,85
94	RTS	1,9332	4,28941	1,1957	1540,45
	Mean value	1,938672	4,32009	1,223578	1516,382
95	ATMP (aq.)	1,86289	4,30981	1,23741	1495,61
96	ATMP (aq.)	1,84922	4,27014	1,20463	1522,17
97	ATMP (aq.)	1,77109	4,33607	1,19565	1557,28
98	ATMP (aq.)	1,82969	4,36711	1,24368	1507,86
99	ATMP (aq.)	1,77109	4,37636	1,20431	1560,45
	Mean value	1,816796	4,331898	1,217136	1528,674
100	ATMP (B+P)	3,88047	4,2101	1,14281	1574,51
101	ATMP (B+P)	3,87656	4,15069	1,16211	1533,72
102	ATMP (B+P)	2,37656	4,2611	1,23641	1479,91
103	ATMP (B+P)	2,42344	4,28262	1,22882	1496,56
104	ATMP (B+P)	2,29063	4,29413	1,24644	1479,37
	Mean value	2,969532	4,239728	1,203318	1512,814
105	ATMP (B)	1,84141	4,1863	1,23769	1452,42
106	ATMP (B)	1,91758	4,17984	1,13805	1577,15
107	ATMP (B)	1,80625	4,28582	1,2193	1509,38
108	ATMP (B)	1,95469	4,22396	1,23862	1464,38
109	ATMP (B)	1,75156	4,24228	1,16149	1568,41
	Mean value	1,854298	4,22364	1,19903	1514,348

Middle fraction		t to %	Q(nC)	CL	Vpk
39	ATMP (B+P)	2,38438	4,22153	1,18244	1533,08
40	ATMP (B+P)	2,36875	4,23374	1,19609	1519,97
41	ATMP (B+P)	0,882422	4,68709	1,41856	1418,82
42	ATMP (B+P)	1,52109	4,27803	1,23498	1487,5
43	ATMP (B+P)	1,17734	4,54929	1,3278	1471,24
	Mean value	1,666796	4,393936	1,271974	1486,122
44	ATMP (P+Mg(OH)2)	0,409766	5,93262	1,94127	1312,3
45	ATMP (P+Mg(OH)2)	0,439063	5,80868	1,85782	1342,6
46	ATMP (P+Mg(OH)2)	0,546484	5,38387	1,63282	1415,89
47	ATMP (P+Mg(OH)2)	0,4625	5,60248	1,75921	1367,53
48	ATMP (P+Mg(OH)2)	0,513281	5,39614	1,79348	1291,99
	Mean value	0,474219	5,624758	1,79692	1346,062
49	ATMP (B)	0,505469	5,38676	1,72328	1342,29
50	ATMP (B)	0,536719	5,28171	1,6112	1407,67
51	ATMP (B)	0,421484	5,65287	1,82411	1330,74
52	ATMP (B)	0,427344	5,60758	1,85089	1300,98
53	ATMP (B)	0,327734	6,51498	2,18146	1282,45
	Mean value	0,44375	5,68878	1,838188	1332,826
54	ATMP (aq.)	1,00547	4,57648	1,3324	1474,93
55	ATMP (aq.)	0,833594	4,66532	1,39221	1438,96
56	ATMP (aq.)	0,883398	4,70649	1,36912	1476,15
57	ATMP (aq.)	0,513281	5,6254	1,75494	1376,46
58	ATMP (aq.)	1,00547	4,67828	1,36348	1473,36
	Mean value	0,848243	4,850394	1,44243	1447,972
59	ATMP (B+W+P)	2,57969	4,35586	1,23396	1515,82
60	ATMP (B+W+P)	2,11094	4,27043	1,22453	1497,53
61	ATMP (B+W+P)	1,87656	4,3455	1,2524	1489,94
62	ATMP (B+W+P)	2,34531	4,13818	1,16753	1522
63	ATMP (B+W+P)	2,25156	4,20268	1,18319	1525,27
	Mean value	2,232812	4,26253	1,212322	1510,112
64	TMP	1,73984	4,18766	1,20531	1491,92
65	TMP	2,00156	4,15179	1,17896	1512,21
66	TMP	1,62266	4,18626	1,236	1454,39
67	TMP	1,55625	4,31454	1,26306	1466,85
68	TMP	1,57187	4,29003	1,23892	1486,94
	Mean value	1,698436	4,226056	1,22445	1482,462
69	RTS	1,34141	4,3376	1,28359	1451,1
70	RTS	0,93418	4,58421	1,3953	1410,82
71	RTS	0,966406	4,62741	1,37067	1449,71
72	RTS	1,02891	4,55688	1,27149	1538,96
73	RTS	2,01719	4,12886	1,17476	1509,23
74	RTS	2,03281	4,14613	1,19665	1487,82
	Mean value	1,386818	4,396848	1,282077	1474,607

Fines fraction		t to %	Q(nC)	CL	Vpk
0	ATMP (B+P)	0,601172	4,65514	1,45055	1378,08
1	ATMP (B+P)	0,585547	4,68174	1,49299	1346,56
2	ATMP (B+P)	1,82969	3,94918	1,13304	1496,7
3	ATMP (B+P)	0,415625	5,42186	1,90096	1224,76
5	ATMP (B+P)	0,716406	4,58305	1,41144	1394,34
	Mean value	0,829688	4,658194	1,477796	1368,088
6	RTS	2,11875	3,8931	1,11317	1501,78
7	RTS	0,694922	4,59763	1,46333	1349,17
8	RTS	1,07187	4,23882	1,25804	1446,85
9	RTS	0,878516	4,43108	1,34131	1418,58
10	RTS	1,54062	4,14655	1,20681	1475,44
	Mean value	1,260936	4,261436	1,276532	1438,364
11	ATMP (B)	0,317969	6,77382	2,49922	1163,87
13	ATMP (B)	0,304297	7,86558	2,99942	1126,07
14	ATMP (B)	0,316016	8,04658	3,17693	1087,62
15	ATMP (B)	0,282813	7,60882	2,8995	1126,86
16	ATMP (B)	0,302344	7,27564	2,77789	1124,68
	Mean value	0,304688	7,514088	2,870592	1125,82
17	ATMP (P+Mg(OH) ₂)	1,9625	4,24479	1,22714	1485,38
18	ATMP (P+Mg(OH) ₂)	1,65391	4,28971	1,23785	1488,11
19	ATMP (P+Mg(OH) ₂)	0,439063	5,64887	1,86294	1302,08
20	ATMP (P+Mg(OH) ₂)	0,425391	5,74544	1,95816	1259,94
21	ATMP (P+Mg(OH) ₂)	1,53672	3,97952	1,15956	1473,71
22	ATMP (P+Mg(OH) ₂)	0,384375	5,82009	1,94986	1281,74
	Mean value	1,066993	4,954737	1,565918	1381,827
23	ATMP (aq.)	0,823828	4,53159	1,34183	1450,2
24	ATMP (aq.)	1,00156	4,38436	1,31578	1430,86
25	ATMP (aq.)	0,384375	5,8079	1,91141	1304,79
26	ATMP (aq.)	1,23984	4,18586	1,19387	1505,57
27	ATMP (aq.)	0,452734	5,43613	1,73171	1348
	Mean value	0,780467	4,869168	1,49892	1407,884
28	ATMP (B+W+P)	0,329688	6,64659	2,4595	1160,45
29	ATMP (B+W+P)	0,327734	6,68423	2,45468	1169,31
30	ATMP (B+W+P)	1,16953	4,46811	1,32413	1449
31	ATMP (B+W+P)	0,351172	6,4546	2,25639	1228,37
32	ATMP (B+W+P)	1,60703	4,50528	1,25564	1540,75
33	ATMP (B+W+P)	1,55234	4,23286	1,18856	1529,27
	Mean value	0,889582	5,498612	1,82315	1346,192
34	TMP	1,24375	4,33417	1,2664	1469,63
35	TMP	0,444922	5,48763	1,74272	1352,17
36	TMP	0,911719	4,65129	1,41908	1407,47
37	TMP	0,489844	5,39856	1,73981	1332,45
38	TMP	0,526953	5,25467	1,66429	1355,79
	Mean value	0,723438	5,025264	1,56646	1383,502

Appendix XIII; Charge decay measurements done at 35 % RH.

Long fraction		t to %	Q(nC)	CL	Vpk
67111851	TMP	3,42344	3,87604	1,137	1463,87
67111852	TMP	3,7125	3,93995	1,12677	1501,51
67111853	TMP	3,54063	3,80783	1,1051	1479,61
67111854	TMP	3,43906	3,90937	1,13352	1480,98
67111855	TMP	3,31406	4,0564	1,14983	1514,89
	Mean value	3,485938	3,917918	1,130444	1488,172
67111856	ATMP (P+Mg(OH)2)	4,86875	4,07261	1,1529	1516,89
67111857	ATMP (P+Mg(OH)2)	4,275	4,01889	1,14168	1511,6
67111858	ATMP (P+Mg(OH)2)	4,25938	3,98961	1,14559	1495,46
67111859	ATMP (P+Mg(OH)2)	4,55625	3,9918	1,15486	1484,28
67111860	ATMP (P+Mg(OH)2)	3,43906	4,00066	1,1492	1494,9
	Mean value	4,279688	4,014714	1,148846	1500,626
67111861	ATMP (B+W+P)	2,93906	4,00345	1,16538	1475,17
67111862	ATMP (B+W+P)	2,95469	4,06518	1,17483	1485,86
67111863	ATMP (B+W+P)	3,13438	4,17982	1,18596	1513,43
67111864	ATMP (B+W+P)	2,57969	4,14137	1,19551	1487,52
67111865	ATMP (B+W+P)	2,95469	4,16636	1,18243	1513,06
	Mean value	2,912502	4,111236	1,180822	1495,008
67111866	RTS	3,75938	4,02844	1,13953	1518,04
67111867	RTS	3,47031	4,04924	1,17267	1482,76
67111868	RTS	3,23594	4,00761	1,14744	1499,78
67111869	RTS	3,97813	4,0606	1,14695	1520,26
67111870	RTS	3,80625	4,10651	1,19116	1480,4
67111871	RTS	4,16563	4,14503	1,17253	1518,02
	Mean value	3,73594	4,066238	1,161713	1503,21
67111872	ATMP (aq.)	3,16563	4,06426	1,16575	1497,09
67111873	ATMP (aq.)	3,06406	4,11207	1,17592	1501,61
67111874	ATMP (aq.)	3,89219	4,08827	1,15079	1525,51
67111875	ATMP (aq.)	3,7125	4,15249	1,16631	1528,86
67111876	ATMP (aq.)	3,56406	4,03122	1,16716	1483,13
	Mean value	3,479688	4,089662	1,165186	1507,24
67111877	ATMP (B+P)	5,35313	4,09076	1,16257	1510,99
67111878	ATMP (B+P)	4,38438	4,14543	1,17329	1517,19
67111879	ATMP (B+P)	5,36875	4,11601	1,18071	1496,95
67111880	ATMP (B+P)	6,49375	4,04439	1,16876	1485,94
67111881	ATMP (B+P)	4,74375	4,14612	1,19684	1487,57
	Mean value	5,268752	4,108542	1,176434	1499,728
67111882	ATMP (B)	4,11875	3,9653	1,14228	1490,65
67111883	ATMP (B)	4,04063	3,98048	1,15393	1481,25
67111884	ATMP (B)	4,25938	3,88116	1,11456	1495,31
67111885	ATMP (B)	4,10313	3,92829	1,13635	1484,45
67111886	ATMP (B)	4,43125	4,07376	1,17851	1484,35
	Mean value	4,190628	3,965798	1,145126	1487,202

Middle fraction		t to %	Q(nC)	CL	Vpk
67111910	ATMP (B+P)	5,38438	3,72709	1,04841	1526,56
67111911	ATMP (B+P)	3,3375	3,77446	1,06608	1520,34
67111912	ATMP (B+P)	4,80625	3,90028	1,08711	1540,63
67111913	ATMP (B+P)	1,88047	4,15363	1,2248	1456,25
67111914	ATMP (B+P)	2,40781	3,95846	1,14514	1484,38
	Mean value	3,563282	3,902784	1,114308	1505,632
67111916	ATMP (P+Mg(OH)2)	1,04062	4,35615	1,32915	1407,35
67111917	ATMP (P+Mg(OH)2)	0,855078	4,84	1,42928	1454,13
67111918	ATMP (P+Mg(OH)2)	0,726172	4,93544	1,47175	1440,01
67111919	ATMP (P+Mg(OH)2)	0,851172	4,89244	1,46518	1433,86
	Mean value	0,868261	4,756008	1,42384	1433,838
67111920	ATMP (B)	0,698828	5,02313	1,48896	1448,66
67111921	ATMP (B)	0,763281	4,86048	1,45787	1431,64
67111923	ATMP (B)	0,525	5,39802	1,71655	1350,37
67111924	ATMP (B)	0,642187	4,95246	1,51729	1401,61
67111925	ATMP (B)	0,698828	4,8995	1,49429	1407,96
	Mean value	0,665625	5,026718	1,534992	1408,048
67111926	ATMP (aq.)	1,25547	4,4068	1,28415	1473,61
67111927	ATMP (aq.)	2,84531	4,02416	1,11473	1550,17
67111928	ATMP (aq.)	1,72031	4,32481	1,2288	1511,33
67111929	ATMP (aq.)	0,765234	4,82781	1,46115	1418,82
67111930	ATMP (aq.)	1,43516	4,3613	1,25234	1495,43
	Mean value	1,604297	4,388976	1,268234	1489,872
67111931	ATMP (B+W+P)	4,44688	4,11163	1,1032	1600,42
67111932	ATMP (B+W+P)	4,275	4,01006	1,08889	1581,4
67111933	ATMP (B+W+P)	4,10313	4,01388	1,08669	1586,11
67111934	ATMP (B+W+P)	4,07188	4,02159	1,08142	1596,9
67111935	ATMP (B+W+P)	4,25938	4,07825	1,09552	1598,56
	Mean value	4,231254	4,047082	1,091144	1592,678
67111936	TMP	2,45469	4,11526	1,15163	1534,47
67111937	TMP	3,17344	3,98928	1,12101	1528,13
67111938	TMP	2,76719	4,14796	1,1538	1543,75
67111939	TMP	2,73594	4,06435	1,12029	1557,89
67111940	TMP	2,78281	4,03751	1,11402	1556,3
	Mean value	2,782814	4,070872	1,13215	1544,108
67111941	RTS	2,11094	4,16112	1,17652	1518,75
67111942	RTS	1,09531	4,43061	1,3107	1451,56
67111943	RTS	1,66953	4,13094	1,18753	1493,75
67111944	RTS	3,4625	3,73854	1,02742	1562,52
67111945	RTS	1,83359	4,07518	1,12789	1551,51
	Mean value	2,034374	4,107278	1,166012	1515,618

Fines fraction		t to %	Q(nC)	CL	Vpk
67111946	ATMP (B+P)	5,11875	4,0766	1,09946	1592,19
67111947	ATMP (B+P)	4,0875	3,96281	1,07405	1584,35
67111948	ATMP (B+P)	1,70859	3,99221	1,1264	1521,92
67111949	ATMP (B+P)	1,01328	4,71313	1,40488	1440,6
67111950	ATMP (B+P)	4,19688	3,78906	1,01991	1595,31
	Mean value	3,225	4,106762	1,14494	1546,874
67111951	RTS	2,56406	3,87729	1,08956	1528,1
67111952	RTS	4,05625	4,07708	1,10176	1589,04
67111953	RTS	2,38438	3,8543	1,06565	1553,13
67111954	RTS	1,35312	3,97373	1,12123	1521,88
	Mean value	2,589453	3,9456	1,09455	1548,038
67111956	ATMP (B)	0,466406	5,41857	1,6752	1388,96
67111957	ATMP (B)	0,423438	5,60981	1,82444	1320,36
67111958	ATMP (B)	0,374609	6,07198	2,07038	1259,38
67111959	ATMP (B)	0,327734	6,73401	2,28759	1264,06
67111960	ATMP (B)	0,331641	6,31334	2,18525	1240,6
67111961	ATMP (B)	0,409766	5,73544	1,78908	1376,61
	Mean value	0,388932	5,980525	1,97199	1308,328
67111962	ATMP (P+Mg(OH)2)	0,624609	4,87671	1,45839	1435,91
67111963	ATMP (P+Mg(OH)2)	2,82969	3,72956	1,01886	1571,88
67111964	ATMP (P+Mg(OH)2)	0,646094	4,99219	1,44413	1484,42
67111965	ATMP (P+Mg(OH)2)	2,54844	3,8197	1,03834	1579,66
67111966	ATMP (P+Mg(OH)2)	3,09531	3,73644	1,0177	1576,56
67111967	ATMP (P+Mg(OH)2)	3,29063	3,45402	0,963671	1539,11
	Mean value	2,172462	4,101437	1,156849	1531,257
67111968	ATMP (aq.)	1,91562	4,1681	1,17124	1528,15
67111969	ATMP (aq.)	0,548437	4,99396	1,55607	1378,13
67111970	ATMP (aq.)	1,48594	4,04665	1,16446	1492,26
67111971	ATMP (aq.)	1,19297	4,29626	1,26682	1456,3
67111972	ATMP (aq.)	0,382422	5,9921	1,9937	1290,6
67111973	ATMP (aq.)	0,632422	4,98987	1,48896	1439,06
	Mean value	1,026302	4,747823	1,440208	1430,75
67111974	ATMP (B+W+P)	0,515234	5,2023	1,65485	1349,93
67111975	ATMP (B+W+P)	0,482031	5,29858	1,72156	1321,63
67111978	ATMP (B+W+P)	0,425391	5,67227	1,8816	1294,51
67111979	ATMP (B+W+P)	0,427344	5,88116	1,90919	1322,78
	Mean value	0,4625	5,513578	1,7918	1322,213
67111980	TMP	0,648047	4,83133	1,48371	1398,27
67111982	TMP	1,19687	4,64669	1,2835	1554,61
67111983	TMP	0,610937	5,15359	1,54098	1436,11
67111984	TMP	1,35312	4,39344	1,24087	1520,39
	Mean value	0,952244	4,756263	1,387265	1477,345