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Composition and application potential of fibre-rich side streams from the forest industry

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Abstract

Circular economy and material efficiency are strong influencers in the forest industry. Nevertheless, the forest industry generates substantial quantities of waste and side streams that are mainly incinerated or disposed in landfills. Fibre-rich side streams are generated in different stages of pulp, paper, and board production. Significant amounts of valuable components such as fibres and minerals are lost in form of fibre-rich side streams as their complex compositions are not fully known and the current uses are limited.

In this master's thesis, a selection of fibre-rich side streams from pulp, board and tissue paper mills are characterized in order to outline their suitability as raw material sources for side products in terms of chemical composition and physical properties. Two knot rejects, a fibre sludge, a fibre clay, and a deinking sludge were selected for this study. The chemical composition analyses determined the carbohydrate, lignin, extractives, ash, metal, and elemental contents. The fibre characteristics and fine material species within these side streams were analysed using both laboratory analyses and microscopy. Additionally, the feasibility of analysing these side streams using these methods was evaluated. As a result, this master's thesis provides a rough overview of the chemical composition and physical properties of the studied side streams, guidance on how to perform the analyses more reliably and conclusions on the most potential new uses.

The studied fibre-rich side streams are heterogenous materials containing 47-85% carbohydrates, 0.2-2.4% extractives, 0.5-2.0% acid soluble lignin, 1.7-50% ash and 13-32% acid insoluble material. In terms of chemical composition, the fibre sludge showed highest potential as feedstock in sugar platform or in agricultural uses, the fibre clay as a reinforcement material in composites and the deinking sludge as a source of fillers and pigments. In case of the knot reject, it was estimated that the most profitable use would be to recycle the side stream back into the digester and use it for pulp production. Further research on the applicability of fibre-rich side streams is still required to assess the viability of these materials for specific applications.

Keywords Forest industry, side streams, knot reject, fibre sludge, fibre clay, deinking sludge

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Tiivistelmä

Kiertotalous ja materiaalitehokkuus ovat voimakkaita vaikuttajia metsäteollisuuden keskuudessa. Metsäteollisuuden toiminnoissa syntyy siitä huolimatta huomattavia määriä jätettä ja sivuvirtoja, jotka päätyvät pääasiassa poltettavaksi tai sijoitetaan kaatopaikoille. Kuitupitoisia sivuvirtoja syntyy sellun, paperin, ja kartongin tuotannon eri vaiheissa. Kuitupitoisten sivuvirtojen mukana menetetään merkittäviä määriä arvokkaita komponentteja, kuten kuituja ja mineraaleja, koska näiden sivuvirtojen koostumusta ei täysin tunneta ja nykyiset hyötykäyttökohteet ovat rajalliset.

Tämän diplomityön tarkoituksena on tutkia valittujen sellu-, kartonki- ja pehmopaperitehtaiden kuitupitoisten sivuvirtojen koostumusta, jotta niiden soveltuvuutta sivutuotteiden raaka-ainelähteiksi voidaan arvioida kemiallisen koostumuksen ja fysikaalisten ominaisuuksien osalta. Tähän tutkimukseen valittiin näytteet kuitulietteestä, kuitusavesta, siistauslietteestä sekä kahden eri tehtaan oksarejektistä. Kemiallisen koostumuksen analyyseissä määritettiin näiden sivuvirtojen hiilihydraatti-, ligniini-, uuteaine-, tuhka-, metalli- ja alkuainepitoisuudet. Kuitujen ominaisuudet ja hienoaineslajit analysoitiin sekä laboratorioanalyyseillä, että mikroskopoimalla. Työssä tutkittiin myös sivuvirtojen analysoitavuutta mainituilla menetelmillä. Tämä diplomityö tarjoaa karkean yleiskuvan tutkittujen sivuvirtojen kemiallisesta koostumuksesta ja fysikaalisista ominaisuuksista, ohjeita analyysien suorittamiseen, sekä yhteenvedon potentiaalisimmista käyttökohteista.

Tutkitut kuitupitoiset sivuvirrat ovat heterogeenisiä materiaaleja, jotka sisältävät 47-85% hiilihydraatteja, 0,2-2,4% uuteaineita, 0,5-2,0% happoliukoista ligniiniä, 1,7-50% tuhkaa ja 13-32 % happoon liukenematonta ainetta. Kemiallisen koostumuksen perusteella kuituliete osoittautui potentiaalisimmaksi raaka-aineeksi sokerialustan tai maatalouden tuotteisiin, kuitusavi lujitemateriaaliksi komposiitteihin ja siistausliete täyteaineiden ja pigmenttien lähteeksi. Oksarejektin kohdalla arvioitiin, että kannattavinta olisi kierrättää sivuvirta takaisin keittoon ja hyödyntää se sellun tuotannossa. Kuitupitoisten sivuvirtojen soveltuvuutta on vielä tutkittava lisää, jotta voidaan arvioida näiden materiaalien soveltuvuutta tiettyihin käyttökohteisiin.

Avainsanat Metsäteollisuus, sivuvirrat, oksarejekti, kuituliete, kuitusavi, siistausliete

Contents

Preface

This master's thesis was carried out for Metsä Spring Oy. The experimental analyses were performed at Aalto University School of Chemical Engineering in the Department of Bioproducts and Biosystems. I am very thankful to Metsä Spring for giving me the opportunity of doing this thesis.

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Helsinki, 29 May 2023
Mia Sandberg

Abbreviations

ASL	Acid soluble lignin
DMC	Dry matter content
HDPE	High-density polyethylene
HPLC	High-performance liquid chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
LOI	Loss on ignition
MFC	Micro-fibrillated cellulose
PHA	Polyhydroxyalkanoates
PLA	Polylactic acid
TOC	Total organic carbon
WPC	Wood plastic composite
wt%	Percentage by weight

1 Introduction

The forest industry plays a critical role in the global economy, providing a range of essential products and services. From building materials and paper products to renewable energy and carbon sequestration, the forest industry is a key driver of economic growth, environmental sustainability, and social progress (Presas and Mensink, 2011). In Finland, nearly 20% of the value of Finnish exports come from the forest industry. A total of 141 production facilities operates in this sector, of which over a third are pulp, paper, and board mills.(Metsäteollisuus ry, 2023) With the increasing demand for sustainable products and renewable energy sources, the forest industry is continuously improving its operations. In recent years, the forest industry has placed a strong emphasis on research and development, exploring new uses for forest-based raw materials, improving production processes, and finding ways to reduce waste and emissions (Presas and Mensink, 2011).

The forest industry companies are strongly driven by circular economy and material efficiency, where raw materials and energy are used in the most sustainable way and the formation of waste is minimized (Virolainen, 2017). In line with the circular economy model, wood materials should be used resource-efficiently to produce versatile products and the generated side streams utilized to their highest potential (Presas and Mensink, 2011). Typically, wood logs are used to make timber and wood products and thinner trees and treetops as pulpwood to produce pulp and fibres. Bark and branches are burned to produce renewable energy (ForestBioFacts, 2022a). Regardless to the carefully planned raw material utilization, the production of pulp and pulp-based products still generates large quantities of waste and side streams (Presas and Mensink, 2011).

In Europe, the forest industry generates around 11 million tons of waste and side streams every year (Amândio et al., 2022). In pulp and paper mills, various types of side streams are generated along the process stages, mainly consisting of wood residues (bark, sawdust, fines, rejects), spent pulping liquors, ash, and sludge (Amândio et al. 2022; Hassan et al. 2018). Organic side streams are commonly burned or subjected to traditional waste management methods, such as composting, landfilling, or anaerobic digestion (Virolainen, 2017). The growing importance of the circular economy in the forest industry as well as taxes and regulations on waste management have led to an increased focus on the recovery of waste materials (Leppänen et al., 2020). According to the European Council Waste Framework Directive 2008/98/EC, a side stream can be classified as a by-product if there is an existing use and demand for the product. The by-product is generated by a production process whose primary purpose is not the manufacture of the substance and it must be available as such or modified in accordance with normal industrial practices. In addition, the by-product must meet the criteria for its intended use and its use must not pose a risk or harm to health or the environment.

Fibre-rich side streams, generated in pulp, paper and board production, contain valuable cellulosic material, that do not end up in the final product. These side streams include rejects from different process units, such as wood residues and various wastewater sludges. Currently, fibre-rich side streams are mostly treated as waste, as several challenges limit their use as raw materials for by-products. Fibre-rich side streams are complex mixtures of organic and inorganic compounds. Their composition varies depending on the source and the production process, making their utilization challenging.(Amândio et al., 2022) Fibre-rich side streams may also contain chemicals and heavy metals which may pose a risk to human health and the environment. In addition, the collection and transportation of pulp and paper industry side streams can be logistically challenging, especially when the source is located in a remote area. This can increase the cost of utilization and reduce its economic viability.

Despite of the challenges, fibre-rich side streams carry a great deal of underutilized potential. These side streams are rich in cellulose and do not compete with food production. Fibre-rich side streams are attractive feedstocks in the production of a range of materials, including biofuels, biochemicals and other biobased materials. (Amândio et al., 2022) The production of biofuels and biomaterials from these side streams would potentially reduce the reliance on fossil resources and decrease carbon emissions. However, the utilization of fibre-rich side streams requires a comprehensive understanding of their composition, treatment, logistics, and market demand. Addressing these challenges can help to maximize the value of these resources and reduce their environmental impact.

1.1 Research objectives

In this master's thesis, selected fibre-rich side streams from Metsä Group's pulp, board and tissue paper mills were characterized in order to outline their suitability as raw material sources for side products. The chemical composition and physical properties of knot reject, fibre sludge, fibre clay and deinking sludge were studied.

This thesis aims to answer the following research questions:

> **RQ1:** What is the chemical composition of knot reject, fibre sludge, fibre clay and deinking sludge? How comprehensively can industrial samples with high ash content be characterized and what are the limitations?
> **RQ2:** What is the physical appearance of the side streams?
> **RQ3:** What kind of new uses have been investigated for fibre-rich side streams? Which applications seem the most promising based on the results of this thesis?

1.2 Hypothesis

The hypothesis of this thesis is that the studied fibre-rich side streams contain components that could be utilized as raw materials for value-added products.

2 Literature review

2.1 Fibre-rich side streams and their availability

Fibre-rich side streams are generated in pulp, paper, and board production. Typically, short fibres and wood residues are screened in the early stage of wood handling and after pulping or they end up into process effluents. In addition to organic compounds, inorganic substances accumulate in wastewater at different stages of pulp, paper, and board production such as in wood debarking and chipping, pulp screening and processing, filler production, paper and board coating and sometimes during process disturbances.

2.1.1 Wood as raw material

Wood fibres are long and thin cells that form the basic building blocks of wood. They are composed of three main constituents: cellulose, hemicellulose, and lignin. Cellulose is the most abundant component in wood and is organized as cellulose microfibrils in the cell wall. The cellulose microfibrils are embedded in a matrix of hemicellulose and lignin. Hemicellulose helps to hold the cellulose microfibrils together by filling the spaces between the microfibrils. Lignin acts as an adhesive substance for wood fibres binding the cellulose and hemicellulose fibres together. This gives wood its overall structure and mechanical properties. Cellulose and hemicellulose are the main components of kraft pulp fibres and can be processed into different high-value products. Lignin is attempted to be removed during pulping in order to separate the individual fibres.(Gullichsen and Fogelholm, 2000)

The composition and structure of wood depends on the type of the tree and on environmental factors. The major types of trees are softwood and hardwood. In general, softwood contains 41-46% cellulose, 25-32% hemicellulose and 26-31% lignin. Respectively, hardwood contains 42-49% cellulose, 23-34% hemicellulose and 20-26% lignin.(Gullichsen and Fogelholm, 2000) In addition to the main polymers, wood contains extractives (i.e. resin and fatty acids), inorganic substances and ash that comprises less than 5% (Ma, 2018). The amount of extractives varies among the type of trees, species and single trees and is also affected by the time of year and how much of the extractives has evaporated during storage (Lehr et al., 2021).

2.1.2 Availability and status of fibre-rich side streams

Fibre-rich side streams contain cellulose fibres that do not end up in the final product. Typically, the fibres in these side streams are shorter and no longer suitable for paper and board production. The fibres originate from wood or recycled papers that are used as feedstock for pulp production. Depending on the raw material and manufacturing process, the amount of carbohydrates in fibre-rich side streams varies between 25–75% (Gurram et al., 2015). Fibre-rich side streams contain minor amounts of extractives that have not been removed during chemical pulping and bleaching (Lehr et al., 2021). Typically, the inorganic content (ash) in fibre-rich side streams ranges from 10% to 50% (Park et al., 2022) and consists of minerals and various residues from chemicals used in pulp production, metallic substances accumulated from piping and machinery as well as fillers, pigments, coatings, or residues from various additives (ISO 1762:2015). It must be noted that the composition of different fibre-rich side streams is strongly affected by the raw material, manufacturing process, the chemicals used, the operational conditions, and the aimed final products (Amândio et al. 2022; Wikström et al. 2018). Thereby, great variations exist in different properties like in the composition of organic material, ash content, pH, and heating values (Branco et al., 2019).

The fibre-rich side streams from wastewaters are mainly obtained in the primary clarification of process effluents and defined as primary sludge. The effluents can origin from a pulp, paper, or board mill. Generally, primary sludge contains most of the solids from the effluents, with large amounts of cellulosic fibres (Gottumukkala et al., 2016). Secondary sludge is formed after primary clarification during aerobic wastewater treatment. In secondary sludge, the fibre content is low and microbial content high.(Branco et al., 2019) Primary sludge is often mixed with secondary sludge due to difficulties associated with dewatering secondary sludge (Wikström et al., 2018). Fibres are commonly used in sludge dewatering processes to improve the efficiency of the process and achieve better dewatering results (Mäkinen et al., 2013; Steffen et al., 2018). In addition to sludges, the pulping industry generates different organic rejects. These side streams are obtained for example during wood debarking and wood log washing as well as in pulp screening and washing stages.

In this thesis, the studied side streams are limited to knot reject, fibre sludge, fibre clay, and deinking sludge. Currently, these side streams are mainly incinerated or disposed in landfills. However, the incineration of fibre-rich side streams is not feasible as the energy required for incineration is generally greater than the energy obtained. Furthermore, incineration of sludge and reject side streams generates harmful nitrogen oxide (NO_x) and sulfur dioxide (SO_2) gases, which can have adverse effects on both human health and the environment. The remaining ash after incineration also needs to be landfilled and may contain various toxic metals that can lead to ground water contamination.(Zambare and Christopher, 2020) According to the interviewed experts, generally only side streams that cannot be incinerated, e.g. those generated during process disturbances and have a composition of which varies greatly from its typical composition, are landfilled. The following chapters focus on the studied fibre-rich side streams and their generation in the forest industry.

2.2 Knot reject

2.2.1 Definition

Knot reject is a side stream generated in a pulp mill after the chemical cooking process. Knot reject consist of insufficiently cooked parts of wood chips, sticks, knots, and low-quality fibre bundles that are separated from the pulp in a screening process.(Gullichsen and Fogelholm, 2000) The amount of generated knot reject accounts for approximately 0.5-3% of the mass flow from the digester. The dry matter content of the side stream is low (30-35%), and pH is alkaline (pH 9).(Anonymous, 2022)

2.2.2 Generation of knot reject

Knot reject is obtained in a pulp mill after the cooking stage of the Kraft process (Figure 1). Woodchips are cooked at high temperature (150-170°C) and pressure in so called white liquor. White liquor is a mixture of the active cooking chemicals sodium hydroxide (NaOH) and sodium sulphide (Na_2S), water and minor amounts of accumulated salts (ForestBioFacts, 2022b). During the digestion of woodchips, the hydroxide and hydrosulphide anions of the cooking chemicals (NaOH and Na_2S)

react with lignin, causing the polymer to degrade into smaller alkali-soluble fragments enabling cellulose fibres to separate (Haile et al., 2021). However, since the production of kraft pulp is not selective, only about 90-95% of the lignin can be removed in the cooking phase without significantly reducing the strength properties of the pulp fibres (Vilarinho et al., 2022). The lignin left in the pulp makes the mass light brown. A simplified process diagram of the chemical pulp mill that uses the sulfate process (Kraft) can be seen in Figure 1.

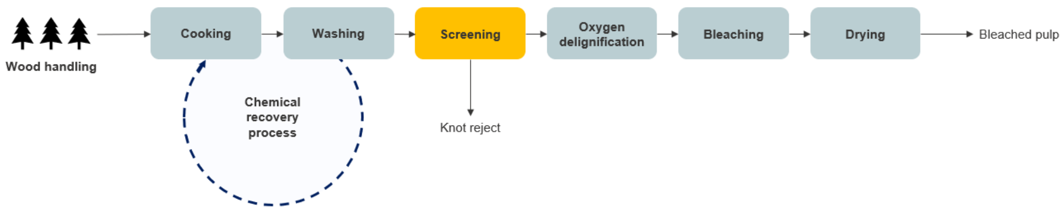


Figure 1. The main fiberline process steps in sulfate process consist of wood handling, cooking, brown stock washing, screening, oxygen delignification (optional), bleaching (optional), and pulp drying. The knot reject is obtained in the brown stock screening.

After delignification, the pulp, i.e. brown stock, is washed and screened. The general purpose of the brown stock washing is to recover dissolved substances from the pulp while cleaning the pulp for further processing. In mills where bleached pulp is produced, the brown stock is generally also treated in an oxygen delignification stage. Oxygen delignification reduces the lignin content of the pulp before bleaching. In a modern pulp mill, pulp screening is placed between pulp washing steps before or after oxygen delignification.(Gullichsen and Fogelholm, 2000).

Pulp screening can be divided into two major phases, which are coarse screening and fine screening. In coarse screening, knots and other poorly dissolved parts of woodchips are separated into a reject stream which is small in relation to the incoming stream (inject stream).(Gullichsen and Fogelholm, 2000) Knots origin mainly from denser parts of branches, which are usually the parts of branches that are embedded in the stem (Willför et al., 2003). Other uncooked parts of woodchips are mainly larger or over-thick chips that have not absorbed the cooking liquid properly. In general, knots are returned to the digester and recooked. In fine screening, smaller pieces of uncooked wood fractions as well as sand that has ended up in the digester are removed from the pulp. The reject is washed and screened to recover good wood fibres which can be returned to the main pulp stream. The material that is rejected by these screens is known as knot reject.(Gullichsen and Fogelholm, 2000) Depending on the mill, knot reject may also contain the knots separated in coarse screening (Anonymous, 2022).

2.2.3 Current use and processing of knot reject

Depending on the mill, knot reject is either recycled back into the digester or collected as a separate side stream. In modern pulp mills, knot reject is typically recycled back into the digester to enhance lignin dissolution. At these mills, knot reject is obtained as a separate side stream only during start-ups and shutdowns of the digester or during process disruptions. Knot reject can be classified as a by-product as there are existing uses for it. This side stream can be used for example as a component in soil preparation, as a supporting material in soil improvement and as a composting material. As a soil improver material, knot reject adds looseness and some nutrients to the soil. Due to the high moisture and alkaline content, the incineration of knot reject to produce energy is not favoured.(Anonymous, 2022)

2.3 Fibre sludge

2.3.1 Definition

Fibre sludge is considered as one of the main side streams in the pulp and paper industry (Haile et al., 2021). According to the interviewed experts, fibre sludge is a generic term used to describe fibre waste from mechanical separation and sludges containing fibres, fillers, and coatings. The sludge can be obtained both from a pulp and paper mill and the wastewater treatment plant can be either municipal or industrial. In Finland, a total of approximately 750 000 tonnes of fibre sludge is produced each year (Kuokkanen et al., 2018). Depending on the mill, fibre sludge may also be called as primary sludge (generic term for any sludge generated in the primary clarifier of a wastewater treatment plant), paper sludge (primary sludge obtained from a paper mill), zero fibre or classified as fibre clay (Anonymous, 2022). The main difference between pulp and paper mill fibre sludge is that the pulp mill fibre sludge does not contain such inorganic filler materials and other additives that are used in paper production (Syamsudin and Rizaluddin, 2021).

In this thesis, fibre sludge refers to the primary sludge obtained in the chemical wastewater treatment process of a pulp mill. The sludge concerned is not combined with the secondary sludge. Pulp mill fibre sludge consists mainly of short wood fibres, minerals and residual chemicals that are mechanically separated from the wastewater stream (Leppänen et al., 2020). The dry matter content of fibre sludge after mechanically dewatering is about 30-40% (Louhiniva et al., 2001). The amount of ash in fibre sludge depends strongly on the mill and production process and ranges between 10 and 50wt% (Park et al., 2022). Fibre sludge is slightly alkaline with a pH of 8-9 due to the presence of alkaline substances remaining from the pulping process (Dunkat et al., 2020).

2.3.2 Generation of fibre sludge

Fibre sludge is generated at the primary wastewater treatment plant, which aims at reducing the solids content of process effluents (Leppänen et al., 2020). Process effluents are generated throughout the pulping process such as in wood preparation, brown stock washing and pulp bleaching (Pöykiö et al., 2018). The wastewater typically contains a range of organic material including lignin, cellulose, hemicellulose, and other organic compounds as well as inorganic compounds such as suspended solids, dissolved metals, and other chemicals. Wastewater treatment generally consists of screening, sedimentation, neutralization, and flotation steps. The fibre sludge is obtained in primary wastewater treatment during the sedimentation phase (Figure 2). (De Azevedo et al. 2020; Pöykiö et al. 2018)

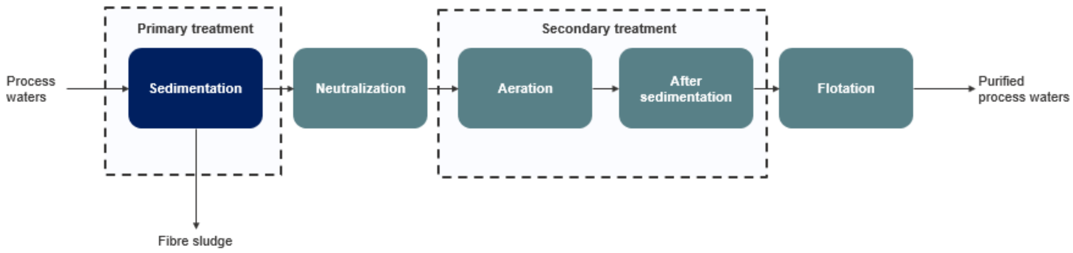


Figure 2. Example of wastewater treatment process consisting of sedimentation, neutralization, aeration and flotation steps (Adabted from Pöykiö et al., 2018)

In primary treatment, large particles and organic materials such as bark, sand, suspended and floating solids, and fibres are removed from the process effluents. In paper and board mills, also fillers, pigments and coating materials are removed in this step.(Pöykiö et al., 2018) The fibrous effluents from the mill is discharged through a screen to a clarifier, where the fibres in the clarification basin are deposited at the bottom of the basin and collected as a separate side stream (Brown et al., 2021). Clarifiers have an automatically rotating scraper installed above the basins and a mixer at the bottom of the basins to enhance the sedimentation of the solids and to prevent them from clogging to the bottom of the basin. The settled solids, i.e. the sludge, are collected in the middle of the basin as the scraper rotates around the basin. The sludge is pumped from the central part by a screw pump to the sludge treatment plant (Anonymous, 2022). Usually, over 80% of the suspended solids can be removed in the primary treatment of wastewater (Thompson et al., 2001).

The generated primary sludge is subjected to mechanical dewatering aiming to increase the dry matter content of the sludge. Cellulose fibres possess a high-water retention capacity, which limits the extent of water removal from the sludge. (Donkor et al., 2021) After primary treatment, the wastewaters from primary clarifier are mixed with the non-fibrous effluents from the mill for further purification. According to the interviewed experts, the wastewaters can be neutralized with acid, lime or sodium hydroxide after which it is generally discharged to a secondary treatment plant for sludge aeration and after sedimentation. The wastewater is then discharged into a flocculation tank, where nutrients, dissolved organic compounds and colloidal particles are removed from the wastewaters by biological methods (Pöykiö et al., 2018). Finally, the purified process water is discharged into a natural water system.

2.3.3 Current use and processing of fibre sludge

The further processing of fibre sludge depends largely on the mill. Traditionally, fibre sludge is dried and incinerated with, e.g., bark and other wood residues. However, converting fibre sludge into energy is relatively inefficient due to its high moisture content and low calorific value (4-6 MJ/kg) (Louhiniva et al., 2001). Incineration of sludge side streams is generally considered as a method to avoid disposal costs. Typically, only excessive wet sludge, that is not suitable for incineration, is landfilled. In addition to traditional uses, fibre sludge has also shown potential as a soil amendment agent and as a fertilizer product.(Pöykiö et al., 2018)

2.4 Fibre clay

2.4.1 Definition

Fibre clay is a generic term for sludge side streams containing fibres and fillers. This side stream is generated during the chemi-mechanical treatment of wastewater from the paper, paperboard, and board production process (Matilainen et al. 2013; Lohiniva et al. 2001; Saari 1998). Depending on the origin, fibre clay can be further classified as fibre sludge or deinking sludge. In this context, fibre sludge is obtained from the chemical wastewater treatment plant of a paper or board mill, whereas deinking sludge is generated in the deinking process of recycled papers. In this thesis, fibre clay refers to fibre and pigment-containing sludge side streams that originates from the board production process. The composition and generation of deinking sludge is discussed in chapter 2.5.

Fibre clay contains mainly short fibres, fillers, coating materials and other substances that are separated from the process effluents (Virolainen, 2017). The inorganic composition contains mainly calcium carbonate $CaCO_3$ (50-65%), kaolin (25-40%) and talc (< 10%). Calcium carbonate is used as the main filler and coating pigment in the board production process, whereas kaolin and talc are used as filler substances.(Tourunen, 2016)

2.4.2 Generation of fibre clay

Fibre clay is generated at the wastewater treatment plant of a board mill. In this thesis, the studied fibre clay is the only sludge side stream produced at the mill and accounts for about 1% of the board production. The process effluents origin from all process steps and contain fibres to some extent. The wastewater purification process of a board mill can be divided into following steps: screening, flocculation, sedimentation, and solids concentration. The incoming wastewaters are screened to remove the larger particles of the wastewaters. After this, the fibrous wastewater is treated with aluminum sulfate (alum), which is a cleaning chemical used in wastewater treatment. The alum flocculates impurities and solids together, which can be removed later as they settle to the bottom of the clarifier. After this, a polymer is added. The polymer is a chemical designed to flocculate the fibres in the clarifier, which facilitate the separation of the fibres from the wastewater. The solids are separated into a separate side stream in the clarifier.(Anonymous, 2022) The operating principle of the clarifier is similar to that of a primary wastewater treatment plant of a pulp mill and described in chapter 2.3.2.

After clarification, the sludge is concentrated and dried. The dewatering can be carried out for example with a suction strainer. The suction strainer is a large cylinder on the surface of which a fibrous clay mat (see Figure 3) is formed by sucking the sludge from a small pool on the surface of the cylinder. The fibrous mat is dewatered on the strainer by suction and removed from the surface of the cylinder. This fraction is known as fibre clay.(Anonymous, 2022)

Figure 3. The formation of a fibrous clay mat onto the suction strainer.

2.4.3 Current use and processing of fibre clay

Fibre clay is mainly burned, for example in the power plant of the mill. It can also be used as a soil construction material or seasonally as a soil improver material. Fibre clay is difficult to screen, which is why it is important to ensure that in the intermediate storage stones and other substances are not mixed with the side stream. The current utilization of fibre clay is limited by the high production volumes in relation to feasible uses and the challenges of transportation. Transportation costs are often very high compared to the value of the side stream.(Anonymous, 2022)

2.5 Deinking sludge

2.5.1 Definition

Deinking sludge is a major side stream of paper mills that use recycled paper as feedstock for recycled fibre production. It is formed in the deinking process, where ink and other contaminants are removed from the recycled papers and the formed sludge is mechanically dried. The chemical composition of deinking sludge depends greatly on the recycled paper feedstock. This residue contains mainly short fibres, fillers, and coating materials (i.e., kaolin, talc, and calcium carbonite) as well as small quantities of printing ink, pigments, and adhesives.(Deviatkin et al. 2015; Haddar et al. 2018; Saha et al. 2019) Deinking sludge is generally dried to a dry matter content of 40-60%. The ash content of this side stream on a dry basis is significantly higher than in other sludges from pulp and paper industry and varies from 35% to 65%.(Deviatkin et al., 2015)

2.5.2 Generation of deinking sludge

Deinking sludge is generated as a side stream in the deinking process, when printing inks, filler pigments, and coating materials are removed from the recycled paper fibres. Deinking consists of two steps. In the first step, ink is detached from the surface of the disintegrated fibres during pulping. The second step removes the detached ink particles from the pulp slurry either by washing or flotation. The ink detachment is achieved by a combination of mechanical forces and chemical actions in the pulping process. In simplicity, the chemicals added to the pulper accelerate the degradation of the recycled paper into fibres while agitation during slushing rinses away contaminants. The chemical environment can be controlled either by alkaline agents or it can be neutral. Typically, alkaline deinking is favored as it removes the non-fibrous contaminants more efficiently.(Bajpai, 2014; ForestBioFacts, 2023a)

The detached ink particles are usually removed by flotation. In this process, the pulp slurry is sent to a flotation tank, where air bubbles are injected into the slurry. The ink and other hydrophobic particles attach to the air bubbles and rise to the surface forming a foam carpet in the flotation cells. This foam is skimmed off and removed from the tank, leaving behind a cleaner pulp slurry. It is important that the printing inks are completely detached from the fibres so that they adhere to the air bubbles and can be separated from the fibres.(ForestBioFacts, 2023a) After deinking, the chemical contaminants and fines are separated from the wastewaters and the formed sludge is mechanically dried, finalizing the form of the deinking sludge (Bajpai, 2014).

2.5.3 Current use and processing of deinking sludge

Deinking sludge is generated from 50 kg to 250 kg per tonne of recycled pulp produced (Anonymous, 2022). The side stream is mostly burned in the mills own power plant. As with other sludges, the incineration of deinking sludge is not economically viable. According to the interviewed expert, the ash from the incineration process is perceived to be easier to recover than the side stream itself, which is why the sludge is usually incinerated.

Deinking sludge can also be used as a composting, construction, and landfill capping material (Vodovnik et al., 2018). For example, the side stream has been used as a substitute for natural soil fill material and for the closure of old landfills. The good mouldability and sealing properties of deinking sludge makes it also a suitable feedstock for other applications such as field structures, embankments, and noise barriers.(Nurmesniemi et al., 2007) Deinking sludge has also been utilized as a construction material in geotechnical construction. One application example is presented in the KUMARA-project, where deinking sludge was used in base layers of sports fields (MW-Kehitys Oy). However, the utilization of this side stream as a construction material is limited by general decline of interest and that potential application locations are further away from the mills. According to the interviewed experts, high transportation costs are one major limitation for a versatile utilization of this side stream.

2.6 Potential new uses

Over the last decade, more attention has been paid on exploiting various side streams as raw materials instead of incineration or landfilling. The valorization routes of fibre-rich side streams of the forest industry can be based on applications that utilize their carbohydrate content as a raw material or where a high mineral content combined with organic matter is beneficial. Fibre-rich side streams are also sources of fillers and pigments that could be utilized in the pulp and paper industry. Fibre-rich side streams have potential to be used for example as reinforcement materials in composites or their organic matter can be processed through sugar platform into renewable fuels, chemicals, or polymers. Some of the recent studies that focus on valorization possibilities for fibre-rich side streams are reviewed in this chapter. The focus is on finding potential new end-uses for side streams from pulp, tissue paper, and board mills.

2.6.1 Sugar platform products

Side streams from pulp, paper and board mills are a desirable source of carbohydrates and fermentable compounds because they are rich in lignocellulosic material and considered as zero cost raw materials. The primary approach for valorization of their organic matter is through a so-called sugar platform, where the carbohydrates are saccharified and fermented to products with wider application possibilities (Taylor et al., 2015). In the sugar platform, cellulose and hemicellulose are first hydrolyzed to sugars after which the sugars are fermented into the aimed primary product. (Brown et al 2021). These fermented primary products can either serve as the final product (e.g., alcohols) or be used as building blocks for more complex chemicals and polymers (Taylor et al., 2015). A schematic outline of the utilization pathways of lignocellulosic feedstocks, such as side streams from forest industry, via sugar platform can be seen in Figure 4.

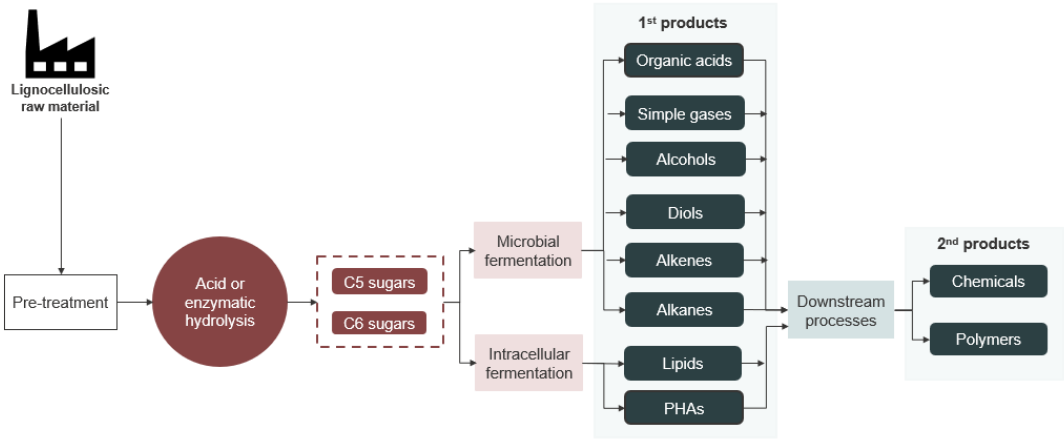


Figure 4. A schematic outline of the refining process of lignocellulosic raw materials to a product via sugar platform. The layout consists of pretreatment of the raw material, enzymatic or acid hydrolysis, fermentation, downstream processing, and final formulation to a product (Adapted from Taylor et al., 2015)

In hydrolysis, fibres are degraded into a mixture of C5 (xylose and arabinose) and C6 (glucose, galactose, mannose, and rhamnose) sugars (Taylor et al., 2015). Enzymatic hydrolysis is often preferred over acidic hydrolysis for lignocellulosic feedstocks as it results in higher sugar yields and lower energy demand. Furthermore, no fermentation inhibitors and unwanted by-products are, generally, formed during enzymatic hydrolysis of biomass.(Duncan et al 2020; Zambare and Christopher 2020) In general, the celluloses and hemicelluloses in fibre-rich side streams with low lignin content are considered to be more accessible than in untreated biomass, as the lignocellulose content has already been disrupted during chemical pulping and most of the lignin removed.(Gurram et al., 2015) However, side streams with high lignin content may lead to lower enzymatic hydrolysis yield. According to Steffen et al. (2018), lignin physically hinders the accessibility of enzymes to cellulose, and soluble lignin-derived substances may cause enzyme inhibition.(Steffen et al., 2018) The presence of inorganic material such as calcium carbonate, clay and titanium oxide may also limit especially the use of sludge as a feedstock in many applications (Duncan et al., 2020). As mentioned in chapter 2.1.2, the amount of ash in sludge side streams ranges from 10 to 50 wt% and it is essential to be removed before enzymatic hydrolysis to obtain reasonable sugar yields (Park et al., 2022).

After hydrolysis, sugars are fermented into the aimed primary product. Microbial fermentation is the most used method to turn sugars into alcohols, organic acids, alkenes, lipids and other chemicals. Either bacteria, fungi or yeast can be used in fermentation and the process conditions (e.g., pH, nutrients, oxygen demand) may vary depending on the selected fermentation process. The product of interest can be produced either intracellularly or extracellularly.(Taylor et al., 2015)

Bioethanol production

Bioethanol is the dominant sugar platform product (Taylor et al., 2015) and the production of it from industrial side streams has been widely studied (Kang et al 2010; Kemppainen et al 2012; Sebastiao et al 2016; Branco et al 2018; Tawalbeh et al 2021). Bioethanol has a wide range of applications. It can be used as transportation fuel or fermented into various chemicals. In bioethanol production, the carbohydrate content and composition in the feedstock sets the limits for the obtainable bioethanol yield (Kemppainen et al., 2012). High cellulose content of fibre sludge makes it an attractive feedstock for enzymatic hydrolysis (Alkasrawi et al., 2021). This side stream is obtained from a primary clarifier, so no additional unit operation is generally required to remove inhibitor compounds from the stream (Gurram et al., 2015). The downside is that neutralizing and dewatering the fibre sludge solely for producing bioethanol can be economically unfeasible (Wang et al., 2014). According to Wang et al (2014), fibre sludge could be used as an alkaline catalyst for bioethanol production in the pre-treatment process of other biomass feedstock such as rice straw.

Side streams with a high ash content, i.e., fibre clay and deinking sludge, have many disadvantages when considering bioethanol production. High ash content in sludges significantly influences the solid loading capacity and enzyme efficiency in a bioprocess affecting the final bioethanol concentrations (Kang et al., 2010). The presence of inorganic substances such as $CaCO_3$, kaolin, $Al_2(SO_4)_3$, TiO_2, or SiO_2 associated with cellulosic fibers may inhibit cellulase activity (Gurram et al., 2015). $CaCO_3$, which is the main ash component in fibre clay and deinking sludge, buffers pH and possibly lowers the conversion during enzymatic hydrolysis.(Kang et al. 2010; Park et al. 2022) Studies on direct production of bioethanol from deinking sludge have shown that this side streams resulted in significantly lower ethanol yields when compared to virgin pulp mill sludges (Williams, 2017).

The use of fibre-rich side streams with a high ash content as sugar platform products would most likely require that the ash would be removed first. According to Gurram et al. (2015), de-ashing refers to chemical pre-treatment or mechanical fractionation methods, where $CaCO_3$ is removed from the material. In chemical pre-treatment, the sludge sample is neutralized by washing with acid (i.e., hydrochloric acid) as a result of which $CaCO_3$ is converted into calcium chloride ($CaCl_2$). $CaCl_2$ is highly soluble in water and can be separated from the fibres by filtering and washing.(Duncan et al. 2020; Gurram et al. 2015) However, using large amounts of chemicals for the pre-treatment of side streams with high ash content prior to the enzymatic hydrolysis is both expensive and environmentally undesirable (Steffen et al., 2018).

Chemical and biomaterial production

A wide range of chemicals and polymers can be produced from the primary products of the sugar platform. Bioethanol can be converted for example into lactic acid, acetic acid, ethylene, and ammonia.(Taylor et al., 2015) According to Gottumukkala et al. (2016), fibre sludge from a pulp mill could potentially be used as a raw material in lactic acid production. Lactic acid is an industrially valuable chemical with high potential applications in the food, pharmaceutical, cosmetic, textile and packaging industries (Ahmad et al., 2020). Lactic acid is mainly produced by a bacterial fermentation using sugars or starch as a raw material (Gottumukkala et al., 2016). One of the key drivers for lactic acid production is that it is the intermediate product in polylactic acid (PLA) production. PLA is one of the most researched renewable polymers as it is fully biobased and biodegradable.(Taylor et al., 2015) This makes PLA a sustainable alternative to petroleum-based plastics and usually utilized to produce packaging materials, foams and fibres (Ahmad et al. 2020; Gigante et al. 2021) The high cost of producing lactic acid and thus also PLA, is one of the main factors limiting the widespread use of these materials. Thereby, low-cost industrial side streams are interesting options for lactic acid production and their use for this application is worth exploring further.(Gottumukkala et al., 2016)

Pulp mill fibre sludge could also serve as a potential feedstock to produce polyhydroxyalkanoates (PHAs) (Singh et al. 2021). PHAs are a class of biodegradable polymers that are synthesized naturally by various microorganisms. PHAs are often referred to as bioplastics because they are biodegradable and derived from renewable resources. The current industrial PHA production processes rely on expensive raw materials, and waste streams are of great interest as substitutes for these feedstocks (Brown et al., 2021) PHAs can be used as ingredients in plastics, chemicals, composite materials and as fish feed to provide pre/pro-biotic benefits in aquaculture.(Gottumukkala et al., 2016) Fibre sludge has also been studied as a carbon source in the synthesis of bacterial cellulose (Cavka et al., 2013) and cellulase (Prasetyo et al. 2011; Wang et al. 2010). However, further research on using fibre sludge as a carbon source in different applications is needed to optimize the process and to develop cost-effective strategies for commercial-scale production.

2.6.2 Biocomposites and coatings

Thermoplastic composites

Reject fibres from industrial waste streams are attractive alternatives for composite materials (Immonen et al., 2017) The incorporation of short fibres as reinforcements or fillers is commonly used in thermoplastic composites as a natural alternative to improve the mechanical and thermal properties of products, while offering a low cost and density (Yu et al., 2009). Furthermore, the mineral components present in sludge side streams have been used as fillers in thermoplastic products, such as in polylactic acid (PLA)-based composites with various loadings. The inorganic components present in fibre-rich side streams may increase the stiffness of thermoplastic products, improve their processing properties, and reduce production costs. (Immonen et al. 2017; Murariu and Dubois 2016) Composite materials made of wood fibres and thermoplastic polymers are often referred to as wood plastic composites (WPCs) (Vandi et al., 2018). The incorporation of different side streams into WPCs can be achieved for example with extrusion or injection moulding (Gigante et al., 2021).

Fibre sludge has been studied as a filler material in high-density polyethylene (HDPE) composites (Migneault et al., 2014). In the study of Migneault et al. (2014), the WPCs made with fibre sludge, obtained from a pulp mill that uses the Kraft process, had superior properties in terms of tensile strength, thickness swelling, water swelling, and impact energy absorption compared to those made with virgin birch and spruce fibres. Fibre clay and deinking sludge have been investigated as reinforcement materials for composites based on PLA (Immonen et al., 2017) and HDPE (Elloumi et al. 2016; Haddar et al. 2017; Haddar et al. 2018). Deinking sludge has found to increase the rigidity, tensile strength, thermal stability, and crystallinity of HDPE composites (Elloumi et al. 2016; Haddar et al. 2018; Migneault et al. 2014). In the study of Immonen et al. (2017), the incorporation of fibre clay in PLA-based composites was studied. The results of the study were promising, as the mechanical strength properties in the PLA-fibre clay composites were comparable to pine cellulose-PLA materials (Immonen et al., 2017) opening a possibility to utilize the side stream as a raw material instead of virgin feedstock.

High $CaCO_3$ content of side streams may affect the reinforcing capacity of the material for example in PLA-composites. $CaCO_3$ particles have shown to form aggregates which may result in weaker bonding between $CaCO_3$ particles and the used polymer.(Rosa et al., 2021) The formation of aggregates is due to flocculation of fillers, which causes the filler particles to clump together. This can be caused by several different factors, including changes in pH, ionic strength, and the presence of other chemicals or additives. In the study of Rosa et al. (2021), it was suspected that the aggregates acted as failure initiation points, where stress concentrations generated microcracks, leading to lower tensile strength and elongation properties of PLA composites.

Mineral/MFC composites

Paper and board applications are often coated to improve, for example, the mechanical properties, the printing properties, and the appearance of the product. The coating process involves the application of a slurry consisting of pigments and binders suspended in water. The pigments are selected to obtain, e.g., good opacity, brightness, density, barrier, and printing properties and can be adjusted for different printing operations.(Nazari and Bousfield, 2016) For instance, kaolin can be used to increase the shape factor of paper webs (Skuse et al. 2021) while $CaCO_3$ can be added to optimize the ink-jet print quality of papers and boards (Nazari and Bousfield, 2016).

Side streams with high fines and pigment content are interesting sources for nanocellulose and pigments containing composites and coatings to get improved bonding and ash content. Micro-fibrillated cellulose (MFC) and nanofibrillated cellulose (NFC) have been studied as co-binder in paper and board coating formulations to replace natural and synthetic carboxymethyl cellulose and polyacrylic thickeners in pigment coating formulations (Dimic-Misic et al. 2014; Salo et al. 2015). Typically, these nanoscale materials are chemically or mechanically produced from pulp (Dimic-Misic et al. 2014; Salo et al. 2015), but the possible utilization of low value side streams would offer a more cost-effective raw material.

Mineral/MFC composites can be used as an additive in paper and packaging applications, e.g., as wet- and dry-strength aids in paper and board production (Skuse et al., 2021). Mineral/MFC composites offer performance enhancements through several different mechanisms: increased bonding in fiber-based structures, thickening polar liquids, and reinforcement of objects. The selection of both the mineral and the fiber source used to produce mineral/MFC composites are highly diverse (Scuse et al., 2021). In the study of Skuse et al (2021), mineral/MFC composites were prepared from recycled fibres using kaolin as the mineral material. The mineral/MFC composites made with recycled fibres were shown to offer at least equivalent strength aid performance to composites made using virgin fibres (Skuse et al. 2021) opening a possibility that deinking sludge could also potentially be utilized as a feedstock in these kinds of composite materials.

2.6.3 Agricultural use

Pulp and paper mill side streams have been studied as organic soil amendments to prevent erosion and leaching of nutrients. The carbon (C) content of different side streams can improve soil hydrology giving the soil a better resistance to extreme weather conditions. The addition of organic matter has also been found to improve crop production and soil microbial activity. As microbes break down the fibres, adhesives are released into the soil, improving the soil structure.(Rasa et al., 2020).

One of the main limitations related to agricultural use of industrial side streams is whether they contain heavy metals or other harmful elements that may accumulate into the soil and end up in plants. Especially high cadmium (Cd) content may limit the use of certain side streams in agriculture. The Cd content for soil amendments under Finnish legislation is 1.5 mg kg^{-1} DM.(Rasa et al., 2020) As a soil improvement material, the amount of nitrogen, phosphorus and potassium affect the suitability of the material (Leppänen et al., 2020).

Fibre sludge has been studied as a soil amendment agent and as a fertilizer product (Pöykiö et al., 2018). In the KUITU project, launched by the Finnish Environment Institute, fibre sludge was used as a soil improver to enhance water protection in agriculture. The studied fibre sludge reduced the leaching of nutrients and bound phosphorus by more than 60%.(Rasa et al., 2021) As fibre sludge does not contain microbes, it can be used as such without biological or chemical treatment as a fertilizer, taking into account that all other fertilizer requirements are met (Matilainen et al., 2013).

2.6.4 Construction and landscaping material

Side streams with high inorganic and lower organic matter content have been found to be beneficial in construction materials as opposed to other waste types. The mineral content may provide hardness and low biodegradability in construction materials that are generally desired in cement, bricks, and ceramic products. (Deviatkin et al. 2015; Elloumi et al. 2016; Krigstin 2008) The inorganic content of deinking sludge contains calcium, aluminum, and iron oxides, which are valuable substances in cement and cement-based products. Kaolin increases the quality of ceramic products.(Deviatkin et al., 2015) Several studies have shown that deinking sludge can be gainfully utilized as a partial replacement of soil in manufacturing of building bricks (Khlif et al., 2022; Singh et al., 2018). In brick production, fiber-containing waste streams are for example used to increase porosity and, thereby, the heat insulating properties of the final product.(Deviatkin et al., 2015)

A recent research on the use of sludge rich in inorganic substances have focused on their use as landscaping and road construction material as well as a light gravel substitute feedstock.(ForestBioFacts, 2022c) Leppänen et al. (2020) studied biotechnologically modified fibre sludge as a dust-binding agent i.e. to reduce road dust. The efficiency of fibre sludge as a dust-binding agent is based on flocking, in which the dusty material is assembled into larger entities using chemical reactions.

Road dust is mainly composed of rock material that is rich in silicate compounds. The chemically modified fibre sludge in the study contained free hydroxyl groups which were able to form hydrogen and other chemical bonds with the hydroxyl groups of the silicate compounds. This resulted in larger clusters of chemical particles which, because of their size, did not dust as much as the untreated particles.(Leppänen et al., 2020)

High fibre content side streams are also potential filler materials in wood-based panels, such as in fiberboard, particleboard, millboard, and cement-bound boards. The short fibres fill the gaps between virgin fibres providing increased bending strength to the boards. However, high inorganic content (especially clay) lowers the mechanical properties of the final product. Thereby, in clay-containing side streams the clay should be decreased or removed with pre-treatment.(Deviatkin et al., 2015)

2.6.5 Filler and pigment recovery

An alternative way to utilize side streams containing fillers and coating substances is to recover these inorganic components and recycle them back into the process as a source of coating pigment or filler. Fibre clay and deinking sludge contain calcium carbonate and kaolin, which can be recovered from the ash. Carbonates and kaolin are the main filler substances used in the paper industry and cover more than 90% of the fillers and coating substances. Deinking sludge is also a source of inorganic pigments, which are commonly used for coloration.(Tofani et al., 2021)

CalciTech Synthetic Minerals Ltd have patented a process were calcium derivates are extracted from paper sludge ashes. The calcium derivatives are solubilized using a proprietary chemical agent and separated from the impurities. Afterwards, calcium derivates react with carbon dioxide to form calcium carbonate.(Higgs, 2014) However, with this method, the generated calcium carbonate requires to be re-synthesized by the addition of water and carbon anhydride to calcium oxide before being useful as a filler in the pulp and paper industry (Tofani et al., 2021).

Tofani et al. (2021) suggested an alternative filler and pigment recovery process, where filler substances (i.e., $CaCO_3$ and kaolin) are recovered from deinking sludge ash. The alternative approach consists of controlled incineration of the waste stream at 575 °C followed by bleaching of the remaining ash. By incinerating the side stream at 575 °C, the organic matter in the sludge (short fibres and ink from organic sources), which can also be absorbed by inorganic materials, can be removed without decomposition of the fillers. The bleaching process aims to remove colored metal oxide, such as iron oxides, which may still be present after incineration. As a result, recycled fillers with preserved molecular structure and sufficient brightness for i.e., newspaper production can be obtained. The addition of these fillers to paper sheets increased the brightness and opacity of the paper compared to paper sheets made without any fillers.(Tofani et al., 2021) This offers a potential to utilize deinking sludge as a source of filler substances in the pulp and paper industry.

3 Research material and methods

3.1 Structure and objectives

The scope of the experimental part of this thesis was outlined to cover a selection of chemical and physical composition analyses of four different side streams from pulp, board and tissue paper mills. The studied side streams include knot reject, fibre sludge, fibre clay and deinking sludge. The compositions are strongly influenced by the origin of the side streams and the process conditions in the mill concerned. The analyses were mainly performed in the laboratories of Aalto University. All the analyses were also purchased from an external laboratory service provider, in order to evaluate if these types of samples can be simply analysed without knowing their background.

The fibre-rich side streams were analysed for the properties that affect their valorisation possibilities. A chemical composition analysis was carried out to quantitatively determine the carbohydrate, lignin and ash content and composition of the studied fibre-rich side streams. The amount of extractives and sodium hydroxide (NaOH) as well as the dry matter content (DMC) of the studied side streams were determined. Total organic carbon (TOC), elemental and metal analyses were only purchased from an external laboratory service provider to obtain a more detailed picture of the organic and inorganic compositions of the studied samples.

Physical composition analyses were performed to collect information on the particle size distribution and fibre characteristics of the studied side streams. The fibre characteristics were analysed using both a Valmet fiber image analyser and a microscope. The fibre image analyser results were purchased from the external laboratory service provider. A visual abstract on the performed analyses is presented in Figure 5.

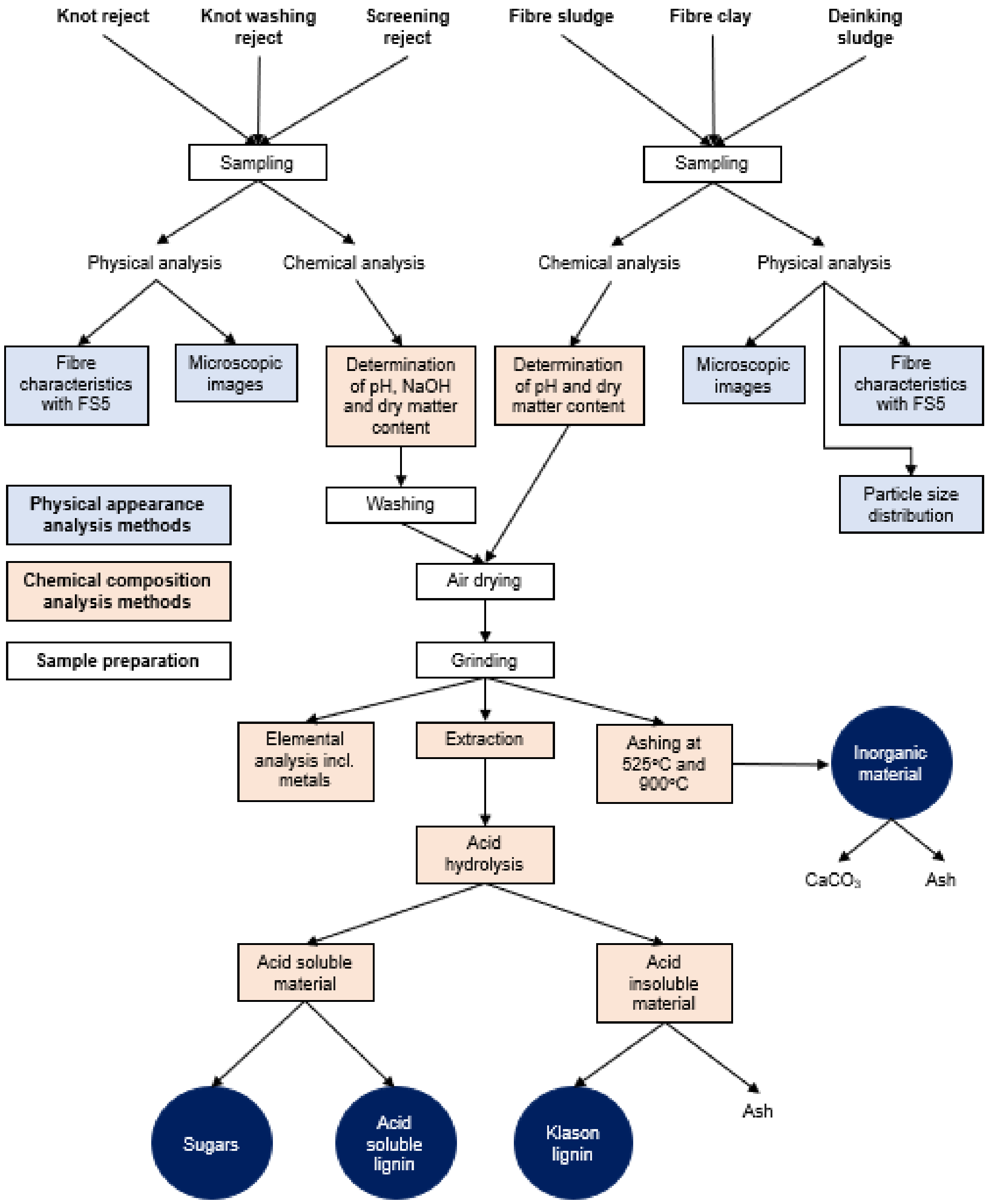


Figure 5. A visual abstract of the sample preparation methods before analyses and the chemical and physical analyses carried out.

3.2 Materials

Samples of different fibre-rich side streams were collected from Metsä Group's pulp, board, and tissue paper mills. Two knot reject samples were obtained from two different pulp mills, which produce bleached sulphate pulp from softwood and hardwood. The first knot reject sample was taken from a storage pile outside the mill. The second knot reject sample was taken directly from the process, as in this mill the side stream is recycled back into the digester. This knot reject sample consisted of the reject material from coarse screening (knot washing reject) and fine screening (screening reject), which, when combined, are known as knot reject. The knot washing reject and screening reject samples were analysed separately as the mixing ratio of these fractions in the knot reject was not known and their physical appearance was very different from each other. The fibre sludge sample was collected from the wastewater treatment plant of a pulp mill. The fibre clay sample was received from the wastewater treatment plant of a board mill. The deinking sludge sample was provided by a tissue paper mill, which uses pulp and recycled paper as feedstock. A general appearance of the selected side streams is presented in Figure 6.

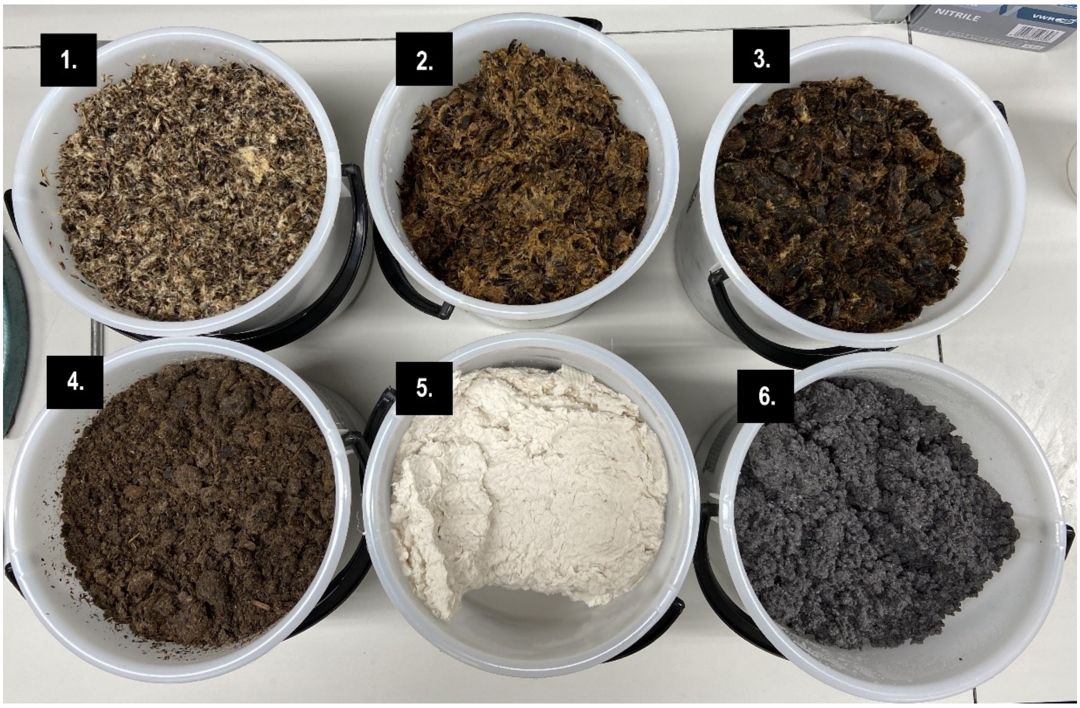


Figure 6. The analyzed samples of fibre-rich side streams included 1) knot reject, 2) screening reject, 3) knot washing reject, 4) fibre sludge, 5) fibre clay, and 6) deinking sludge.

95-97 % analytical grade sulfuric acid used for NaOH content determination and hydrolysis as well as 1 M analytical grade sodium hydroxide solution used for NaOH content determination were purchased from Merck Millipore, Germany. 100 % analytical grade acetone used for extractive analyses was purchased from VWR Chemicals, France. High-purity (>99%) sugars for sugar recovery standards (SRS) were purchased from Sigma-Aldrich, China (D(+)xylose and L(+)rhamnose), Sigma-Aldrich, Italy (D(+)galactose), Sigma-Aldrich, USA (D(+)glucose), AppliChem, Germany (D(+)arabinose), and Honeywell Fluka (D(+)mannose).

3.3 Sample preparation and treatments

The samples were stored in closed five-liter plastic buckets in a refrigerator (+4°C) until analysis. A conscious decision was made not to add preservatives to the samples. The alkaline fractions were washed before drying and milling. The washing of alkaline samples, i.e., knot reject, knot washing reject and screening reject, was done in order to remove NaOH and water-soluble phenolic compounds from the samples. Two liter of each side stream was left to soak for at least 24h in hot tap water, after which the samples were washed with hot tap and distilled water. Washes were performed using 10 liters of water at a time and the leaching of NaOH was verified by measuring the pH and conductivity of the used wash water. The wash was estimated to be adequate when the pH and electrical conductivity was close to that of distilled water (pH below 9 and conductivity below 3.0 μS/cm).

Figure 7. Example of the drying set-up. The samples were air dried in separate plastic containers in a fume hood.

The samples were prepared for chemical compositional analysis according to NREL/TP-510-42620 standard. All samples were allowed to dry on a tabletop or in a fume hood (Figure 7) until the moisture content of the samples was less than 10%. The dried fractions were ground in a Wiley mill (M02) with mesh size of 1.9 mm (Figure 8).

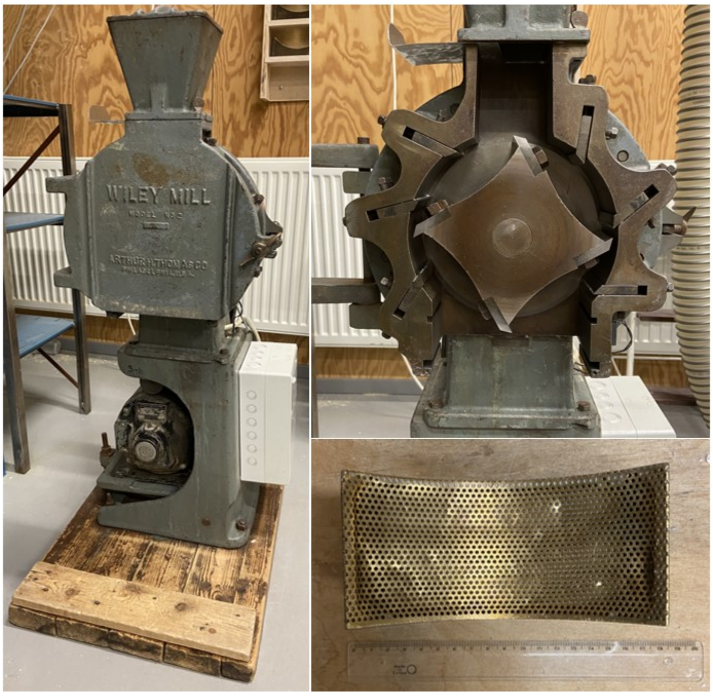


Figure 8. The side stream samples were ground in a Wiley mill to the length of 1,9 mm.

3.4 Chemical composition analysis methods

3.4.1 Sodium hydroxide and dry matter content

The dry matter content of unwashed alkaline samples consists of solids and alkali (assumed to be only NaOH in this work). As the alkali needed to be washed away, the sodium hydroxide (NaOH) and solids content of knot reject, knot washing reject, and screening reject was determined by back titration from unwashed wet samples. This method determines the NaOH content by neutralizing it to a salt, which is then easy to wash away, leaving the solids for gravimetrical determination. In the method, the reject samples were first allowed to stand in excess sulfuric acid (0.5M H_2SO_4) for 24-48 hours, after which the NaOH content was determined by back titration with sodium hydroxide (1M NaOH). The knot washing reject sample was shredded into smaller pieces before acidification to enhance the removal of NaOH from the compact structure. The neutralized solids were washed three times with 200ml hot distilled water and recovered by filtering the samples with a Büchner funnel. The washed solids were placed in an oven at (105 ± 5) °C for 48 hours after which the dry matter content (DMC) of the reject samples was determined gravimetrically.

The DMC of the studied fibre sluge, fibre clay, and deinking sludge was determined according to European standard SFS-EN 12880. The same method was applied for milled samples to determine the sample DMC for analysis.

3.4.2 Inorganic and organic matter content

The total inorganic matter (ash content) of the studied side streams was determined according to ISO 1762:2019. The samples were incinerated at 525 °C for 5 hours after which the ash content of the side streams was gravimetrically determined. The amount of organic matter was calculated by subtracting the amount of inorganic matter from the oven dry weight of the samples.

In samples containing fillers and pigments such as calcium carbonate ($CaCO_3$), clay and talc, there is practically no decomposition of these substances by ashing at 525°C. In order to determine the $CaCO_3$, silicate and mineral content of the side streams, a second ash content was determined by incinerating the samples at 900°C for 1 hour (ISO 2144:1997). The amount of $CaCO_3$ and silicates was calculated from the total ash content (determined at 525 °C) considering the ash content at 900°C and the loss on ignition (LOI) values of $CaCO_3$ and silicate at 900°C. The LOI of $CaCO_3$ at 900°C is 44% and the LOI of silicate at 900°C is 12%. The $CaCO_3$ and silicate content was determined with equations 1 and 2.

$$Xt_{525°C} = X_{cc} + X_{sil} \tag{1}$$

Where $Xt_{525°C}$ = Total mass fraction of filler substances at 525°C
X_{cc} = $CaCO_3$ fraction of the filler
X_{sil} = Silicate fraction of the filler

$$Xt_{900°C} = X_{cc}(1 - LOI_{cc}) + X_{sil}(1 - LOI_{sil}) \quad (2)$$

Where $Xt_{900°C}$ = Total mass fraction of filler substances at 900°C
LOI_{cc} = Loss on ignition (%) of $CaCO_3$ at 900°C
LOI_{sil} = Loss on ignition (%) of silicate at 900°C

For comparison, the content of calcium carbonate in the samples was also determined with two different approaches based on the results of the elemental analysis. In the first approach, the content of Ca2+ ions were used to calculate the amount of $CaCO_3$ contained in the side streams, assuming that $CaCO_3$ is the only source for Ca. The second approach assumed that all the carbonate (CO_3) in the samples was calcium carbonate.

3.4.3 Amount of extractives

The amount of extractives in the side streams was determined according to SCAN-CM 49:03. Air dried and milled samples were extracted with acetone in a soxhlet extraction apparatus. The samples were not acidified before extraction. Fibre sludge, fibre clay and deinking sludge were extracted for 4 hours and 45 minutes, whereas knot reject, knot washing reject and screening reject for 6 hours, as the standard requires a longer minimum extraction time for samples containing wood chips. The extraction cycles were adjusted to 4 or 5 times per hour. The extraction residues were transferred to aluminum dishes and the acetone was allowed to evaporate overnight. The weight of the residue was measured as the gravimetric extractive content.

3.4.4 Carbohydrate, acid soluble lignin and acid insoluble material content

The carbohydrate, acid soluble lignin and acid insoluble material composition was determined according to the standard procedure NREL/TP-510-42618. Carbohydrates were hydrolyzed into monomeric sugars in two step hydrolysis procedure with sulfuric acid. Monomeric sugars, acid soluble lignin and calcium carbonate are soluble in the sulfuric acid solution, while acid insoluble lignin (Kraft lignin), kaolin, talc and other ash components remain in solid form in the solution. The samples were placed into open Duran bottles for the first part of hydrolysis (Figure 9). Using the bottles in this step is an upgrade to the used standard. This prevents material losses, as the sample does not need to be moved from a test tube to the bottle for the second part of the hydrolysis, which takes place in closed bottles in an autoclave.

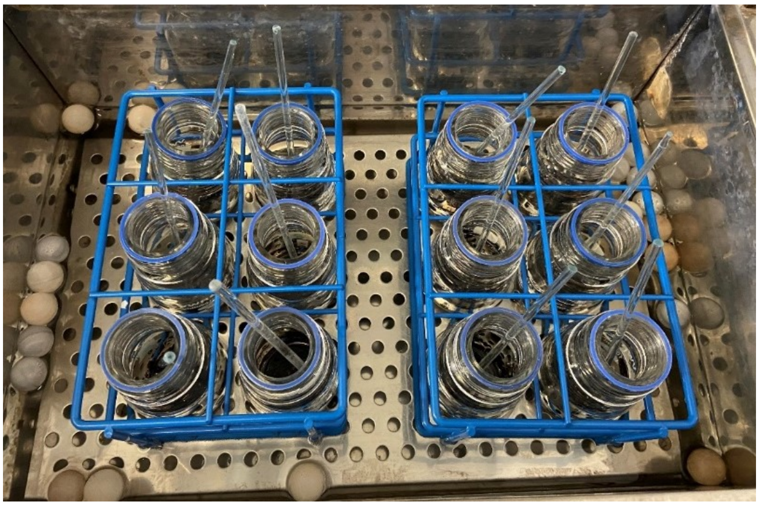


Figure 9. The samples were hydrolyzed in open Duran bottles in the first step of hydrolysis to avoid any loss of the material.

After hydrolysis, the acid hydrolysis solution was filtrated through the filtering crucibles (pore size 3) and the filtrate was collected for carbohydrate composition and acid soluble lignin analysis. The remaining solid residue was rinsed with milli-q water and the residue was dried at 105 °C for 18 hours. The oven-dried residue was considered as the total acid insoluble material also containing the ash. A set of sugar recovery standards (SRS) was prepared according to the standard to correct for losses due to destruction of sugars during dilute acid hydrolysis. SRS include D(+)glucose, D(+)xylose, D(+)galactose, D(+)arabinose, and D(+)mannose, and L(+)rhamnose. The carbohydrate content was determined from the hydrolysis filtrate by using high-performance liquid chromatography (HPLC). The samples were analyzed with Dionex ICS-5000 apparatus (column carboPac PA20).

The acid soluble lignin (ASL) was measured from the hydrolysis liquid by UV-Vis spectrophotometer (Shimadzu UV-2550). The absorbance of each sample was measured at wavelength 205 nm and using absorptivity constant of 128 $dm^3\ g^{-1}\ cm^{-1}$. The absorbance range was 0.7-1.0. Milli-Q water was used to dilute the samples and as a blank sample. The chosen wavelength was based on TAPPI UM 250.

Janson method was used to calculate the content of different polysaccharides in the samples. The method utilizes known facts of the structure of polysaccharides to express the monosaccharide content obtained from sugar analysis as polysaccharides (Janson 1970). The calculations were based on the results of performed chemical composition analyses and know Janson constants. The Janson constants for full chemical pine kraft pulp were used. Based on the Janson method, the proportion of uronic acid in xylan is 4.6 % and the molar ratio of mannan and glucomannan is 4.1. Fibre clay and deinking sludge were estimated to contain 1% lignin in the carbohydrate composition analysis.

3.4.5 Total organic matter, elemental composition and metal analysis

The total organic matter content (TOC), elemental composition and heavy metal content analyses of the studied side streams were purchased from an external laboratory service provider. The determination of carbon (C), hydrogen (H) and nitrogen (N) content in the side streams was based on ASTM D5373-21. The determination of the carbonate content in the samples was based on SCAN-N 32:98. The total organic matter content (TOC) of the samples, which also indicates the total organic carbon (C) content, was calculated by subtracting the carbon contained in the carbonate from the total carbon.

A more comprehensive elemental composition analysis was performed on the fibre sludge, the fibre clay and the deinking sludge samples, covering both ICP-OES (Inductively coupled plasma optical emission spectroscopy) and ICP-MS (Inductively coupled plasma mass spectrometry) analyses. The knot reject, the knot washing reject and the screening reject were only subjected to ICP-OES analysis. The concentrations of Ca, Fe, K, Mg, Na, S, and Si were determined by ICP-OES analysis, and the concentrations of As, B, Ba, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sb, Sr, Ti, V and Zn by the ICP-MS analysis. The ICP-OES analysis was based on ISO 17812:07 and the ICP-MS analysis on SFS EN 17294-2.

ICP analysis requires samples to be in soluble form. As a pretreatment, samples are often dissolved in acid. However, samples with high ash content contain typically substances that affect the solubility of the samples. The knot reject, the knot washing reject and the screening reject were dissolved into nitric acid, whereas a fuming nitric acid method was applied to the fibre sludge, the fibre clay, and the deinking sludge. This alternative pre-treatment method was chosen for the sludge samples when it was found that they were not fully soluble in nitric acid, nor in a combination of three acids (HCl, HNO_3 HF).

3.5 Physical appearance analysis methods

3.5.1 Physical properties and fines content

The physical appearance analyses were performed on unmilled, unwashed, and wet samples. Microscope images were taken of the samples with the Olympus SZX10 microscope to optically observe different surface structures of the samples. The microscope was also used to study the inorganic substances among the fibres in the sludge samples. Different magnifications (from 1x to 8x) were used. Samples were examined both against and without a black plate. The gamma contrast of the microscope images was adjusted to better highlight the desired features. Knot washing reject was not studied under microscope.

Analyses to determine fibre properties were purchased from an external laboratory service provider. The fibre characteristics, i.e., fibre length and width distribution, and the fines content (fraction of fibre particles that are shorter than 0.2 mm) were studied with Valmet fiber image analyzer (Valmet FS5) according to manufacturer's instructions. The average fibre length was defined according to ISO 16065-2:2014.

3.5.2 Particle size distribution

The particle size distribution of fibre sludge, fibre clay and deinking sludge was determined with Malvern Mastersizer 2000 according to manufacturer's instructions. The device measures different particle sizes and their distribution within a sample with laser diffraction in a size range of 0,02 µm – 2000 µm, yielding the distribution as vol%. The refractive index for cellulose (1.5) was applied. Water was used as dispersant. The measurements were performed in duplicated. The particle size distribution of knot reject, knot washing reject, and screening reject were not defined.

4 Results and discussion

Chemical composition and physical appearance of the selected fibre-rich side streams were analyzed to obtain more information on their organic and inorganic content as well as physical properties. The chemical composition analyses were performed on dried and ground samples. Reject samples were washed before drying (Appendix A). The physical properties of the samples were studied ‘as is’ without any sample pre-treatment. The results were compared both with literature and with results obtained from the external laboratory service provider. Based on the results, potential valorisation pathways were discussed.

4.1 Chemical composition of fibre-rich side streams

The chemical composition of the studied pulp, tissue paper and board mill side streams consist of organic and inorganic components and moisture. The dry matter and sodium hydroxide (NaOH) content, pH, elemental composition (C, H and N), carbonate and total organic carbon (TOC) content of the studied side streams is presented in Table 1.

Table 1. DMC, pH and NaOH content of the fibre-rich side streams obtained from the mill. The elemental composition (C, H and N), total carbonate and total organic carbon (TOC) contents of the side streams were determined from dry and ground samples. Reject samples were washed before composition analysis.

Raw material	DMC (%)	pH	NaOH content (%)	C (%)	H (%)	N (%)	Carbonate (%)	TOC (%)
Knot reject	30.5	9.5	0.1	48.7	5.9	0.5	0.3	48.7
Knot washing reject	28.4	10.3	0.7	51.8	6.0	0.2	0.3	51.8
Screening reject	13.1	11.0	0.5	46.8	6.0	0.1	0.4	46.7
Fibre sludge	30.9	8.9	-	42.7	4.5	0.7	6.4	41.4
Fibre clay	16.6	8.1	-	33.1	3.9	0.2	8.0	31.4
Deinking sludge	44.2	8.0	-	30.6	3.3	<0.1	11.1	28.4

The dry matter content of the side streams was relatively low (13.1 – 44.2%), which indicates that the incineration of these side streams for energy production is not economically viable, but also affects transportation costs. Therefore, prior any utilization or incineration, the DMC of these materials needs to be increased. The slight alkalinity of the side streams is largely due to different chemicals, fillers and coating substances used in the process. The carbonate content in the reject samples was very low, while the carbonate contents in the fibre sludge, the fibre clay and the deinking sludge, were 6.4%, 8.0% and 11.1% (Table 1). Most of the carbonate in these side streams presumably originates from the calcium carbonate used in the mills. As seen from Table 1, the TOC content was higher in the reject side streams compared to those in the sludge side streams. This is probably due to the lower mineral content in the reject samples, which is usually reflected in higher TOC content.

The proportion of organic and inorganic material in the studied fibre-rich side streams is presented in Figure 10. The organic matter consists of carbohydrates, lignin and organic extracted substances. The inorganic matter consists of minerals and residues from chemicals used in production, metallic substances as well as fillers, pigments, coatings, or residues from various additives and the ash from the wood.

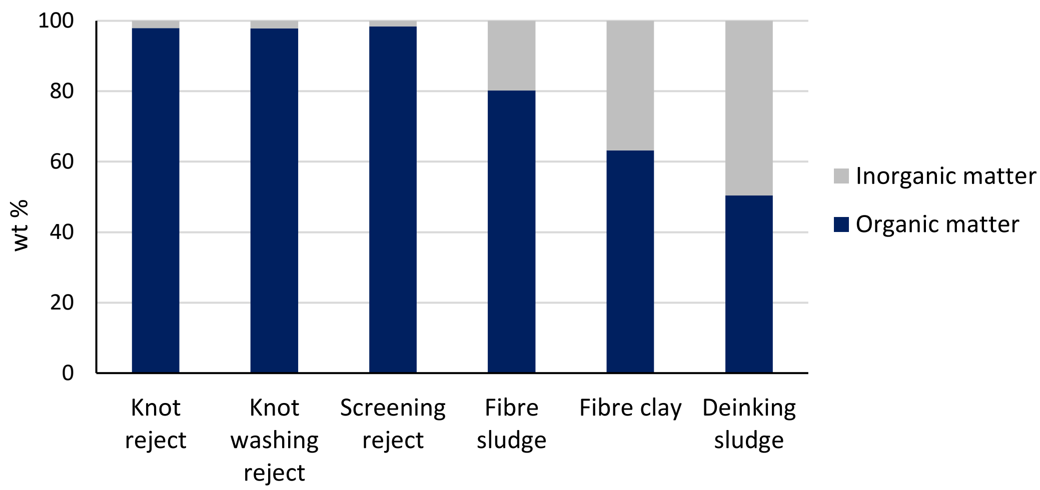


Figure 10. Proportion of organic and inorganic matter (% of dry matter) in knot reject, knot washing reject, screening reject, fibre sludge, fibre clay and deinking sludge based on ash analysis at 525°C.

The studied reject side streams consist mostly of wood and fibrous material, as can be noticed from their high organic matter content (98%). In the sludge side streams, inorganic substances make up a large proportion of their composition. Especially in the deinking sludge and the fibre clay, the amount of inorganic matter is notably higher than in other studied side streams. The amount of inorganic matter is about 49% in the deinking sludge and 37% in the fibre clay. Most of the inorganic material in sludge side streams originates from the chemicals, coating materials and fillers used in the mills. High ash content is a significant factor affecting among other things the hydrolysability and processability (e.g., filtration) of the side streams. In this thesis, the high ash samples were not deashed before chemical composition analysis in order to examine how the ash influences the analysis.

The chemical composition results of the studied side streams are summarized in Figure 11. More detailed results of the chemical compositions can be found in Appendix B and Appendix C. The sugars were expressed as polysaccharides, i.e., cellulose, arabinoxylan and galactoglucomannan.

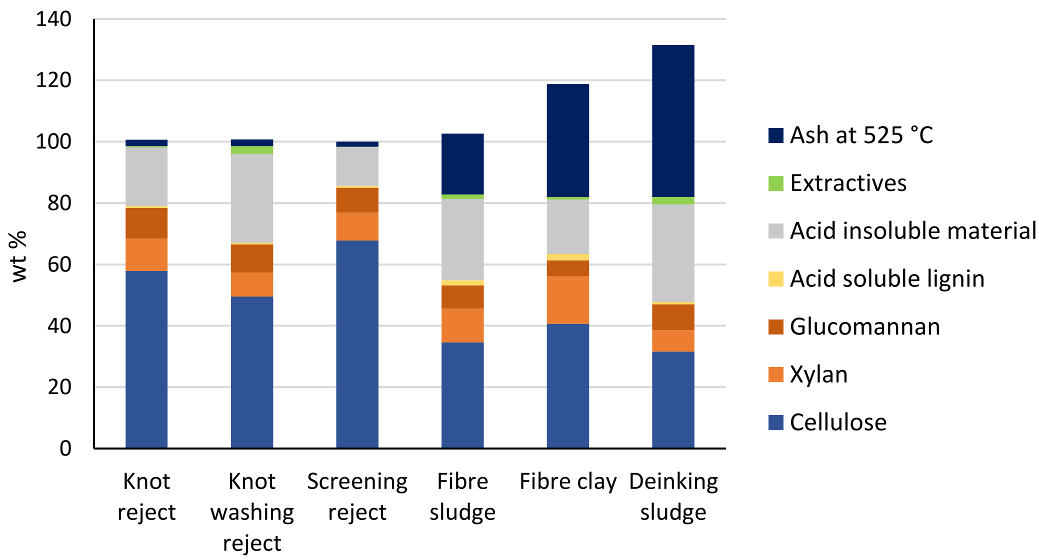


Figure 11. Overview of the chemical composition (% of dry matter) analysis results of knot reject, knot washing reject, screening reject, fibre sludge, fibre clay and deinking sludge.

The carbohydrate composition in side streams depends largely on the type of wood used in the process and may vary greatly between different mills. The chemical composition results show that reject side streams contain more carbohydrates than the sludge side streams. In the reject samples the carbohydrate content was up to 85% while in the sludge samples the amount of carbohydrates was at most 61% according to the analysis. However, the effect of the high ash content has assumably influenced these results and is discussed later.

From Figure 11 it can be seen that the total share of substances in the fibre sludge, the fibre clay and the deinking sludge exceeds 100%. This is because these samples contain substances that are included both in the ash content and in acid insoluble matter content. Acid insoluble substances such as kaolin and talc show up as Klason lignin in the lignin composition analysis, while $CaCO_3$ dissolves into acid. The amount of ash has not been considered in the acid insoluble material determination, because there is no certainty how much of the ash has been dissolved in the hydrolysis solution or if some of the carbohydrates have not been hydrolyzed as a result. The effect of ash on chemical composition analysis of sludge samples is discussed in more detail in chapter 4.1.2. All the studied side streams contained acetone soluble material, i.e., extractives. In this thesis, the extracted material was only examined quantitatively.

The amount of acid soluble lignin in the studied side streams was measured 12-16 hours after acid hydrolysis, which was not according to the procedure described in NREL/TP-510-42618 standard. After a specific time, lignin may start to precipitate in the hydrolysis liquid and, thereby, affect the results. The samples were found to have a slightly higher acid soluble lignin content when compared to the results obtained by the external laboratory service provider (Appendix D).

4.1.1 Conclusions on chemical composition of reject side streams

Knot reject, knot washing reject and screening reject have similar chemical compositions (Figure 12). The composition of the studied reject side streams corresponds well to the stage at which the material was obtained from the process. Knot washing reject consist mainly of uncooked wood knots. As discussed in chapter 2.2.2, knots may origin from over-thick chips that have ended up in the digester or from denser parts of branches. Thus, the composition of knot washing reject resembles more softwood wood chips than softwood kraft pulp. Screening reject is obtained from a later screening stage, where the coarsiest uncooked wood fractions have already been screened from the pulp. This side stream contains sticks, low-quality fibre bundles and possibly small amounts of sand that has ended up in the digester. Thereby, the composition of screening reject is roughly between softwood chips and softwood pulp. Knot reject is a mixture of knot washing reject and screening reject. The ratio of these fractions in knot reject depends largely on the mill and its screening system in place.

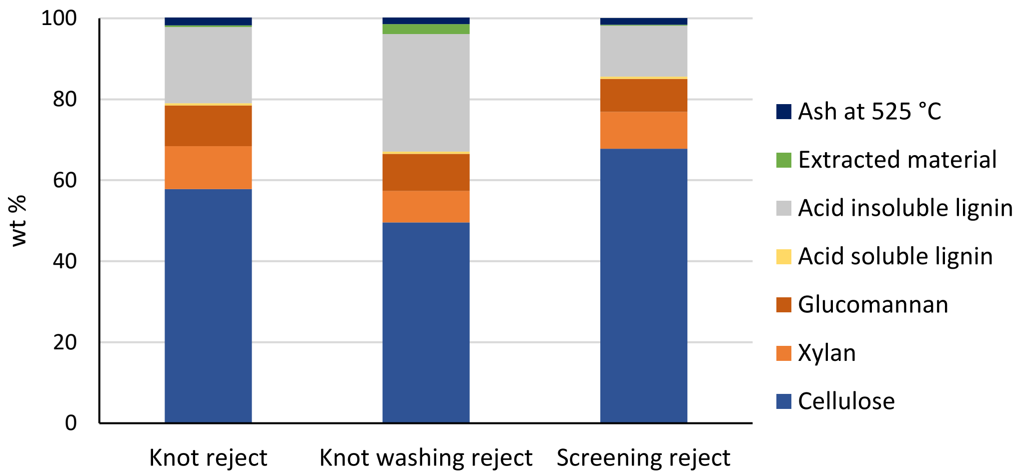


Figure 12. Composition (% of dry matter) of the knot reject, the knot washing reject and the screening reject.

The studied reject side streams have a high carbohydrate content (66.5-85.0%) and low ash content (1.7-2.2%). The ash is composed of wood silicates and other mineral substances and does not contain calcium carbonate (detailed values in Appendix B). In addition, all the studied reject samples contain lignin (13.2-29.6%) and minor amounts of extractives (0.2-2.4%). The main differences between reject samples are in cellulose and acid insoluble lignin content. From the studied reject samples, screening reject is the most fibrous side stream, which corresponds to high cellulose (67.8%) content. The high cellulose content of the screening reject is promising for cellulose-based applications. The cellulose content of the knot washing reject is comparable to that of softwood chips. In chemical pulping, hemicelluloses are degraded when the complex structure of hemicelluloses is broken down by cooking chemicals. This is also reflected in the lower hemicellulose content of the reject side streams compared to softwood.(Gullichsen and Fogelholm, 2000) The slight differences in the hemicellulose contents between the reject samples is probably due to the fact that the samples are not from the same mill and thereby the used wood raw material is different. Additionally, in the screening reject more hemicelluloses have most likely been removed during pulping as the material has become more fibrous.

The highest amount of extractives was determined in the knot washing reject in which the extract solution was visually observed to be yellowish. The amount of extractives in the knot washing reject is higher than in unbleached softwood kraft pulp (0.1%), but lower than in pine wood chips (4.3%) (SCAN-CM 49:03), which can be explained by the fact that this fraction is not yet completely fractioned during chemical pulping. In the knot reject and the screening reject the extractives have most likely dissolved to some extend during cooking, which is reflected in a low extractive content of these side streams. The amount of acid insoluble material in the reject side streams is between 12.6% and 29.0% (Appendix B).

Knot reject, knot washing reject and screening reject do not contain coating materials or fillers and so the acid insoluble material in these side streams presumably represents Klason lignin. This is also supported by the fact that the amount of acid insoluble material in the reject side streams is similar to the amount of Klason lignin in softwood (19-30%) and softwood kraft pulp before bleaching (3-19%) (Tappi 222 om-02). Lignin composition analyses revealed that the acid soluble lignin content is 0.6% both in the knot reject and the knot washing reject and 0.5% in the screening reject. These values are slightly higher than the values obtained by the external laboratory service provider (Appendix D). The results obtained by the external analysis laboratory are very close to the acid soluble lignin content of softwood which varies between 0.2% and 0.5% (Tappi 222 om-02). Thereby, it is assumed that the results obtained in this thesis have been influenced by the fact that the acid soluble lignin content was not measured within 6 hours of hydrolysis.

According to the elemental analysis results in Table 2, the reject side streams contain high amounts of calcium (Ca), natrium (Na), and sulfur (S). Ca is an abundant mineral in wood and used in the pulping and bleaching process of a pulp mill. The sodium and sulfur concentrations in the reject side streams are reasonable since Na and S based chemicals are used in the chemical pulping process. Magnesium based chemicals are used in the oxygen delignification process of the mills considered in this thesis, which explain the Mg contents in these side streams. Other elements origin most likely from wood and used chemicals. The low iron and silicon concentrations in the reject side streams indicate that these side streams do not contain Fe and Si based filler and coating substances, which are often found in sludge side streams.

Table 2. The content of main inorganic elements in the knot reject, the knot washing reject and the screening reject based on ICP-OES analysis. All concentrations expressed as mg/kg (d.w.)

Component	Unit	Knot reject	Knot washing reject	Screening reject
Calcium (Ca)	mg/kg	2880	3020	3920
Iron (Fe)	mg/kg	29.6	<10	14.3
Potassium (K)	mg/kg	325	300	57.3
Magnesium (Mg)	mg/kg	389	403	616
Manganese (Mn)	mg/kg	145	113	88.9
Sodium (Na)	mg/kg	4160	4800	1310
Sulfur (S)	mg/kg	3300	6460	2310
Silicon (Si)	mg/kg	178	24.2	107

4.1.2 Conclusions on chemical composition of sludge side streams

According to the results presented in Figure 13, the fibre sludge, the fibre clay and the deinking sludge contain carbohydrates, high amounts of ash, extractives, acid insoluble material and acid soluble lignin. Ash substances, i.e., kaolin and talc, are included both in the total amount of ash determined at 525 °C as well as in acid insoluble material content.

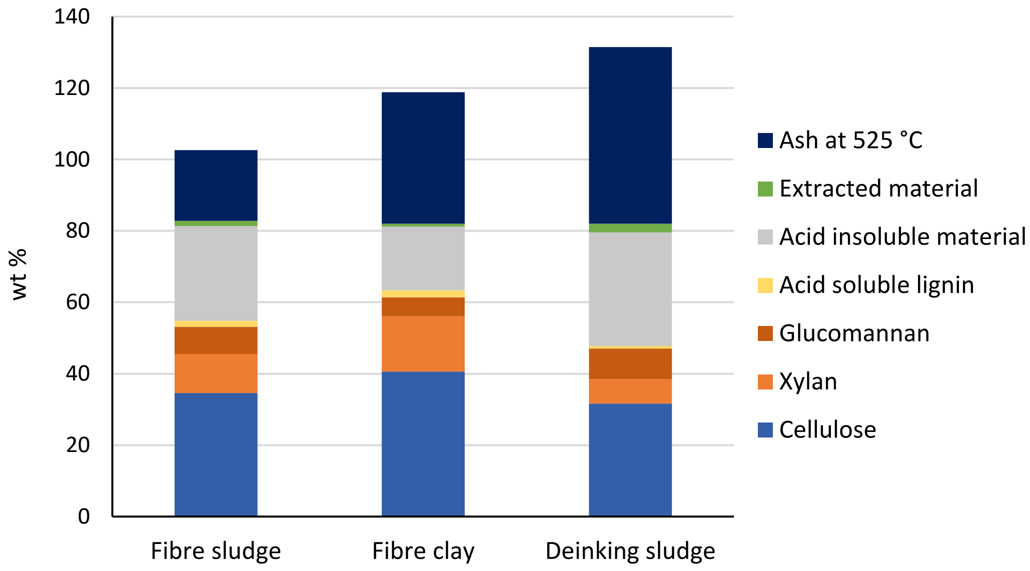


Figure 13. Composition (% of dry matter) of the fibre sludge, the fibre clay and the deinking sludge. The total amount of ash determined at 525 °C contains substances which are also included in the acid insoluble material.

The composition of sludge side streams is strongly influenced by the feedstock, processes and operating conditions used in the mills as well as the applied wastewater treatment technology. The cellulose content (34.6%) in the fibre sludge is close to that reported in other studies (Dunkat et al. 2020; Migneault et al. 2015) However, the total amount of hemicelluloses (17.6%) in the fibre sludge was more than what Dunkan et al. (2020) determined. Chemical composition analysis indicated that the fibre clay contains 40.6% cellulose and 20.8% hemicelluloses. Similarly, the deinking sludge was estimated to consist of 31.6% cellulose and 15.4% hemicelluloses. The carbohydrate content in the fibre clay and the deinking sludge was lower than in another study (Steffen et al. 2018).

The amount of acetone soluble extractives in the fibre sludge, the fibre clay, and the deinking sludge was 1.4%, 0.8% and 2.4% (Appendix B). The high acetone soluble material content in the deinking sludge was visually observed as a yellow extract solution. This fraction most probably contains some printing inks and adhesives, which can be expected to be soluble in acetone. The extractives content of the deinking sludge might also be even higher, because the determination of acetone-soluble extractives according to SCAN-CM 49:03 has not been evaluated for samples containing recycled fibres. Thereby, it is not certainly known if some of the extractives in deinking sludge have not been extracted.

The total ash content determined at 525°C in the fibre sludge, the fibre clay and the deinking sludge was 19.8%, 36.8% and 49.6% (Appendix B). Based on the carbonate (Appendix D) and elemental analysis results (Table 3), the fibre sludge contains calcium carbonate that origins most likely from the lime kiln of a pulp mill. Main components of the ash in the fibre clay and the deinking sludge were determined as $CaCO_3$ and kaolin. The inorganic substances in these side streams origin mostly from paper and board coating and filling materials. The ash content in the fibre sludge, the fibre clay and the deinking sludge was similar to the ash content of other sludge side streams originating from pulp, paper and board mills (Dunkat et al. 2020; Geng et al. 2007; Immonen et al. 2017; Steffen et al. 2018).

The carbohydrate compositions analysis according to NREL/TP-510-42618 is not recommended for samples with an ash content of more than 10%. $CaCO_3$ dissolves into acid and might have interference with appropriate acid concentrations during hydrolysis and catalyzed side reactions. As the samples were not deashed before analysis, it is not known with certainty how much the ash components have influenced the results. It is possible that some of the carbohydrates were not hydrolysed into sugars, because the ash might have neutralized some of the acid or protect the pulp from acid physically. This would result in lower carbohydrate content and in a higher acid insoluble fraction. According to Gurram et al (2015), a chemical deashing of sludge side streams before hydrolysis can increase the total sugar content even by 20%.

The acid insoluble material content was 26.5% in the fibre sludge, 13.3% in the fibre clay and 24.1% in the deinking sludge (Appendix B). Fibre sludge does not contain kaolin so the acid insoluble material in this side stream probably represents mostly Klason lignin. The amount of acid insoluble material in the fibre sludge is also close to that obtained in another study (Kemppainen et al., 2012), where the acid insoluble material was estimated to be Klason lignin. Based on the results obtained by the external analysis laboratory (Appendix D), also the amount of acid soluble lignin in the fibre sludge is close to that of another pulp mill fibre sludge (Kemppainen et al., 2012). As the chemical composition analysis results of the fibre sludge are in line with other studies, it is possible that the low $CaCO_3$ content of the fibre sludge did not interfere with the hydrolysis of carbohydrates.

In this work, the acid insoluble material in the fibre clay and the deinking sludge was assumed to contain only about 1% Klason lignin, as the initial raw material for these side streams is bleached softwood pulp or recycled paper. The rest of the acid insoluble material in these side streams consists presumably of substances insoluble in the sulfuric acid solution (i.e., kaolin, talc, and ash) as well as unhydrolyzed carbohydrates due $CaCO_3$ neutralizing the acid, which keeps the mentioned carbohydrate yield low in the analysis. It is also possible that some of the fine mineral particles have passed the crucible to the dissolved fraction. It can be concluded that the total ash (determined in 525 ˚C) of the samples did not correlate with the acid insoluble fraction, even when the carbonates were considered to be in the soluble fraction. Based on the results obtained by the external analysis laboratory (Appendix D), the acid soluble lignin content in the fibre clay (1.6 %) would be higher than in the reject samples. It is not known if the ash substances have had an influence on the acid soluble lignin content results. To avoid potential interference from these substances, it is recommended that the acid soluble lignin content would be determined in the future from deashed samples.

In metal and elemental analysis (ICP-OES and ICP-MS), the samples were pretreated with a fuming nitric acid method to dissolved form. During pre-treatment, 18 % of the fibre clay sample and 19 % of the deinking sludge sample did not dissolve in acid. The fibre sludge was completely dissolved by the treatment. Especially, silicon in silicate compounds and talc are difficult to dissolve with the selected pretreatment method. It is assumed that some of these substances remained in an insoluble form and are therefore not reflected in the total metal concentrations of the fibre clay and deinking sludge.

Metal and elemental analyses showed that the studied sludge samples contain high amounts of calcium (Ca), magnesium (Mg), and sulfur (S) (Table 3 and Table 4). The high calcium content in the fibre clay and the deinking sludge indicates the presence of $CaCO_3$ and other calcium salt (i.e., calcium sulfate) in these side streams. Calcium is also abundant in wood and one of the main minerals used in the chemical recovery process of a pulp mill, explaining the high Ca content in the fibre sludge. Sulfur in different forms is used as a cooking chemical in the chemical pulping process and as a component in fillers and coatings. Magnesium compounds are used in the oxygen delignification process and in the production of filler and coating substances. Iron and manganese are present in wood and in the fresh process water.

Table 3. Elemental concentrations in the fibre sludge, the fibre clay and the deinking sludge based on ICP-OES analysis. All concentrations expressed as mg/kg (d.w.)

Component	Unit	Fibre sludge	Fibre clay	Deinking sludge
Calcium (Ca)	mg/kg	51600	61500	141000
Iron (Fe)	mg/kg	2640	247	887
Potassium (K)	mg/kg	676	80	166
Magnesium (Mg)	mg/kg	2990	826	1590
Manganese (Mn)	mg/kg	500	20	84
Sodium (Na)	mg/kg	3240	302	442
Sulfur (S)	mg/kg	5960	8260	3570
Silicon (Si)	mg/kg	923	1290	779

The metal concentrations (Table 3 and Table 4) indicate that deinking sludge is a potential source of pigments. The side stream contains i.e., Cu, Fe, Mg, and Zn, which are used for coating and coloration applications. No aluminium ions were detected in the ICP-OES or ICP-MS results, suggesting that compounds containing aluminium were not dissolved in the pretreatment. Thereby, it is assumed that the undissolved solids of the fibre clay and the deinking sludge contain at least kaolin, which is a silicate mineral containing aluminium oxide. This would explain the low Si content in the fibre clay and the deinking sludge.

Table 4. Total metal and elemental concentrations in the fibre sludge, the fibre clay and the deinking sludge based on ICP-MS analysis. All concentrations expressed as mg/kg (d.w.)

Component	Unit	Fibre sludge	Fibre clay	Deinking sludge
Arsenic (As)	mg/kg	0.4	<0.3	<0.3
Boron (B)	mg/kg	35.7	19.3	19.7
Barium (Ba)	mg/kg	96.3	6.80	51.5
Cadmium (Cd)	mg/kg	1.4	<0.5	<0.5
Cobalt (Co)	mg/kg	0.9	0.3	0.8
Chromium (Cr)	mg/kg	8.5	4.5	3.7
Copper (Cu)	mg/kg	6.2	2.7	93.7
Iron (Fe)	mg/kg	2660	244	796
Lithium (Li)	mg/kg	<3	<3	<3
Manganese (Mn)	mg/kg	538	21.5	84.3
Molybdenum (Mo)	mg/kg	1.2	<0.3	<0.8
Nickel (Ni)	mg/kg	4.1	3.5	<3
Lead (Pb)	mg/kg	4.5	1.3	2.4
Antimony (Sb)	mg/kg	<0.3	<0.3	<0.3
Strontium (Sr)	mg/kg	57	266	375
Titanium (Ti)	mg/kg	119	<50	<50
Vanadium (V)	mg/kg	7.9	1.2	2.4
Zinc (Zn)	mg/kg	90.6	4.0	14.5

According to results in Table 4, the total heavy metal (As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, and Zn) concentrations in the fibre sludge is <3410 mg/kg, in the fibre clay <290 mg/kg and in the deinking sludge <1050 mg/kg. However, the heavy metal concentrations may be higher in the fibre clay and the deinking sludge if some of the heavy metals were not dissolved during pre-treatment.

The $CaCO_3$ content of the sludge side streams determined by three different methods is shown in Figure 14. In method A the amount of $CaCO_3$ in the side streams was gravimetrically determined from known LOI values, whereas in method B and C the $CaCO_3$ content was calculated from the Ca (Table 3) and CO_3 (Table 1) content of the side streams. The remaining ash was assumed to consist of minerals and wood silicates.

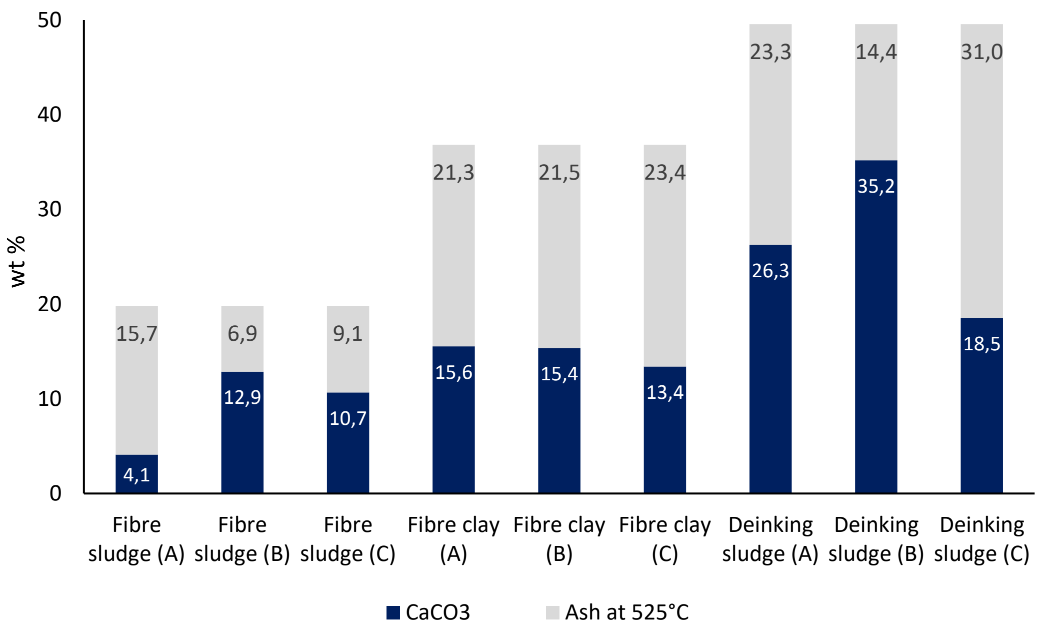


Figure 14. Total ash and $CaCO_3$ content (% of dry matter) in the sludge samples calculated by three different methods. In method A samples (A), the amount of $CaCO_3$ in the side streams is gravimetrically determined from known LOI values. In method B samples (B) the $CaCO_3$ content is determined from the Ca^{2+} ions and in method C samples (C) from the CO_3 content.

From Figure 14 it can be seen, that the $CaCO_3$ content of the sludge side streams differ depending on the chosen method. In method B, it is assumed that all the calcium ions in the samples are $CaCO_3$, while method C assumes that all the carbonates in the samples are $CaCO_3$. In reality the samples may also contain other salts, such as sodium carbonate (Na_2CO_3). The LOI method (method A) cannot distinguish between carbonate and non-carbonate minerals that may also be present in the sample and degrade in same temperatures as $CaCO_3$. As a result, the measured $CaCO_3$ content may be overestimated if other minerals are also present that can contribute to the weight loss during ignition. On the other hand, incomplete combustion of $CaCO_3$ due to the presence of other salts and additives may result in lower $CaCO_3$ contents.

Based on the elemental analysis results (Table 3 and Table 4), it can be concluded that all the sludge samples contain calcium ions or other calcium salts in addition to $CaCO_3$. Least variations in the $CaCO_3$ contents determined with the different methods was observed in the fibre clay sample. According to these results, most of the calcium and carbonate salts in the fibre clay would be calcium carbonate. The elemental analyses support the fact that the $CaCO_3$ content of fibre clay can also be determined gravimetrically with the LOI value of $CaCO_3$. With the methods based on elemental analysis (methods B and C), the $CaCO_3$ content in the fibre sludge were higher than those determined gravimetrically from LOI values. However, $CaCO_3$ is mostly used as an additive in paper and board production. Theoretically, it is possible that this side stream contains other calcium and carbonate salts, which show up as $CaCO_3$ when determined with method B and C. The results for $CaCO_3$ content in the deinking sludge are not in line with each other, even if it is assumed that all calcium would be $CaCO_3$. Thereby, a wider analysis is required if the $CaCO_3$ content in the deinking sludge is to be determined.

4.1.3 Factors that might limit the chemical composition analysis

In this thesis it was noticed that the reject samples could be analyzed quite comprehensively, while the sludge samples had some limitations. Knot reject, knot washing reject and screening reject contain only minor amounts of ash and no filler or coating materials. The reject samples required a washing step before chemical composition analysis, but otherwise the samples could be analyzed without major challenges. The high ash content in the sludge side streams posed some challenges in determining the chemical compositions of these side streams. The dissolution of $CaCO_3$

in acid or the influence of other ash components on acid concentrations may have led to a lower carbohydrate content in the sludge samples analyzed. It is recommended that in the future side streams with high ash content would be deashed before further analysis for example by washing with acid. The ash components also contributed to the determination of the metal and elemental composition. In metal and elemental analysis (ISO 17812:07; SFS EN 17294-2), biomass samples are usually dissolved in nitric acid. However, in the case of the fibre sludge, the fibre clay and the deinking sludge, it was noticed that these samples did not fully dissolve in the solvent in question.

It can be concluded that the chemical composition of the studied sludge samples with high ash content can be characterized to some extent. The amount of organic and inorganic material can be determined based on the measured ash content. A metal and elemental composition analysis can be carried out, but the pre-treatment of the side streams must consider the components contained in the ash. The amount of sugars obtained from hydrolysis can be defined, but this does not necessarily correspond to the total sugar content of the side stream. The amount of carbohydrates in the sample may be higher, if the ash components have had an influence on the hydrolysis. It is recommended that the ash is removed prior to carbohydrate analysis if accurate values are required. This would also mean that the ash needs to be removed to obtain an effective acid hydrolysis on a sugar platform application. The total lignin content of sludge side streams could not be defined by the analyses used in this thesis. As the total ash (determined in 525 ˚C) of the sludge samples did not correlate with the acid insoluble fraction, it is not known how much the acid insoluble material contained lignin. However, based on this thesis supported by the results of the literature, it is considered that the results are sufficiently indicative to allow a preliminary review on possible applications.

4.1.4 Comparison of results with externally defined results

The chemical composition analyses were also purchased from an external laboratory service provider and compared to the results obtained in this thesis. Samples of the studied side streams were washed (only applied to reject samples), air-dried and ground and sent to the external analysis laboratory for analysis. The results obtained in this thesis in terms of ash content, carbohydrate content and composition as well as extractives content are in line with the externally determined results (Appendix D). Total metal and elemental analysis were only carried out by the external laboratory service provider. However, the reliability of these results is increased by the fact that their concentrations is included into the total ash content, the total of which corresponds to the ash content determined in this thesis.

Small variations were observed in the acid insoluble material content results. The external analysis laboratory reported the acid insoluble material as Klason lignin. As explained in chapter 4.1.2, in case of fibre clay and deinking sludge, this fraction cannot be considered as Klason lignin. Thereby, it is extremely important to understand what kind of material is being analyzed if the analyses are commissioned from an external laboratory service provider. Based on the chemical composition analysis results obtained in this thesis as well as from the external laboratory service provider it can be concluded that similar results are mainly obtained for the side streams studied in this thesis, even if they are analyzed by two different operators, from which the other has the background knowledge of the samples. However, when reviewing the results obtained from an external laboratory, the limitations of the studied side streams should be known in order not to make false conclusions.

4.2 Physical appearance of fibre rich-side streams

The physical properties of the samples were studied in the form the side streams were obtained from the mills. Microscope and laboratory analysis methods were applied. The microscope was used to highlight different fine material species in the sample, while laboratory analyses were performed to get more information on the fibre and fines properties. Fibre-rich side streams are heterogenic materials that differ in their physical properties. Knot reject and screening reject contain mainly sticks, knots and fibrous material that can be distinguished by eye (Figure 15 left and middle). Knot washing reject contains mostly large pieces of wood chips that have not fibrillated during cooking (Figure 15 right). High lignin content in the reject side streams gives the materials its brown color.

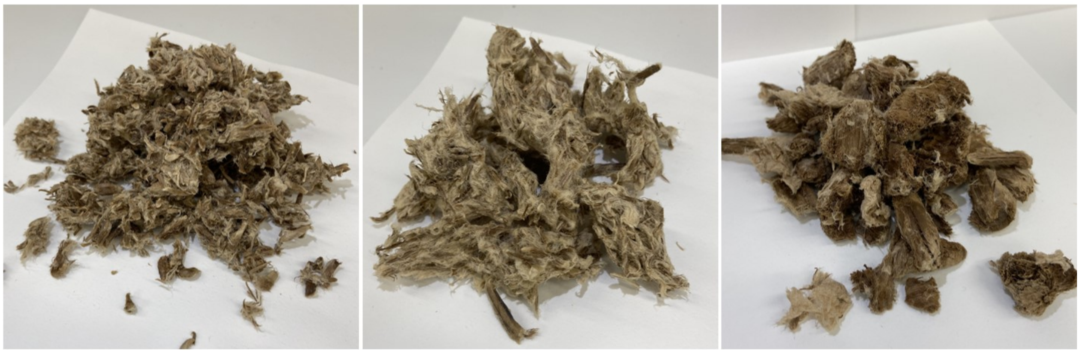


Figure 15. Samples of knot reject (left), screening reject (middle) and knot washing reject (right) studied in this thesis. The screening reject and the knot reject were obtained from the same mill.

The sludge samples studied in this thesis are presented in Figure 16. It can be seen that fibre sludge is already quite fine-grained when received from the mill, but the material contains also larger sticks and other wood-based material. The texture of fibre sludge is similar to a soil. Fibre clay is white and homogenous physically. The pigment rich wastewater in a board mill contains kaolin and gives the fibre clay its clay-like texture when dried. Deinking sludge is relatively fine matter when obtained from the mill. The printing inks in this material give the deinking sludge its appearance and gray color.

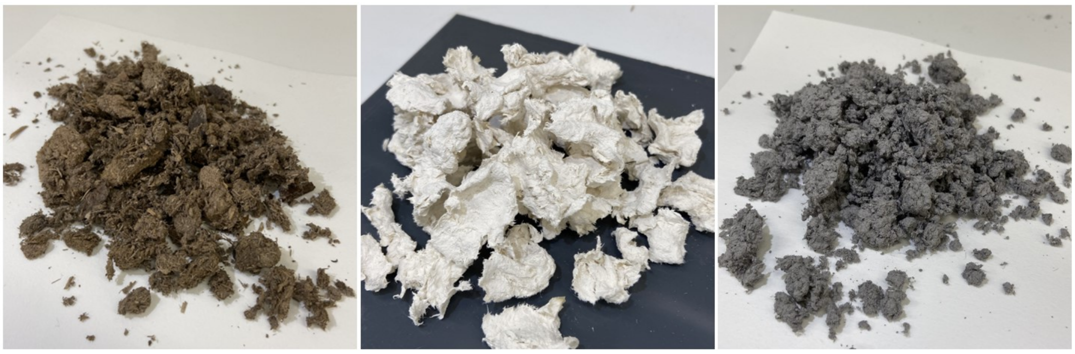


Figure 16. Samples of fibre sludge (left), fibre clay (middle) and deinking sludge (right) studied in this thesis.

4.2.1 Physical and optical properties

The physical properties of the studied side streams were observed by microscope. The only exception was the knot washing reject, which was not examined under a microscope because of its large size. From Figure 17 (left) and Figure 18 (left) it can be seen that the knot reject and the screening reject contain fibres and different sized pieces of undissolved wood. The fine matter in these side streams consists mainly of short fibres when investigated under a microscope. The fibres in the knot reject and the screening reject (Figure 17 right and Figure 18 right) are of different lengths and bend, but otherwise quite intact.

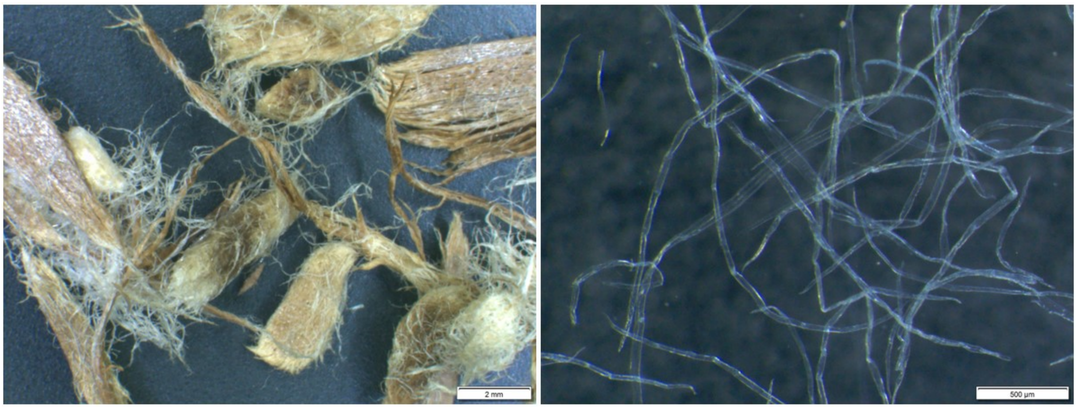


Figure 17. Microscopic images of knot reject taken with an optical microscope at 1x (left) and 5x (right) magnification.

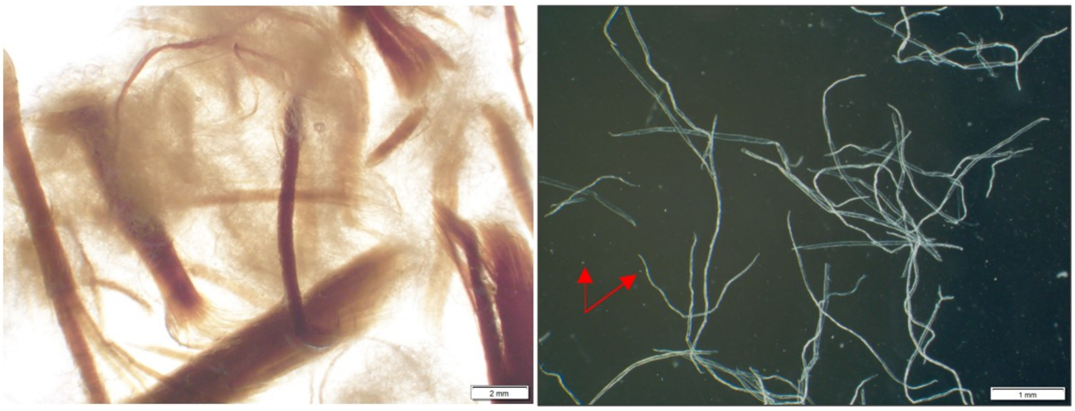


Figure 18. Microscopic images of the screening reject taken with an optical microscope at 2x (left) and 6.4x (right) magnification. The red arrows indicate the small particles observed among the fibres.

In the screening reject, some small particles can be observed among the fibres (indicated by red arrows in Figure 18 right). These particles might origin from the washing water used in the mill and contribute to the high particle content in the side stream (Table 5). The hypothesis is based on the fact that no similar fine particles were seen in the microscopic images of the knot reject even though the knot reject contains this same side stream material.

From Figure 19 it can be seen that the fibre sludge is heterogenic both in its physical composition and particle size distribution. The material includes fibres, fibre bundles, other undissolved pieces of wood of different sizes and inorganic substances. The particles (marked with a red circle in Figure 19 left) are likely aggregated $CaCO_3$ particles. The black particles in the sample might be lignin originated.

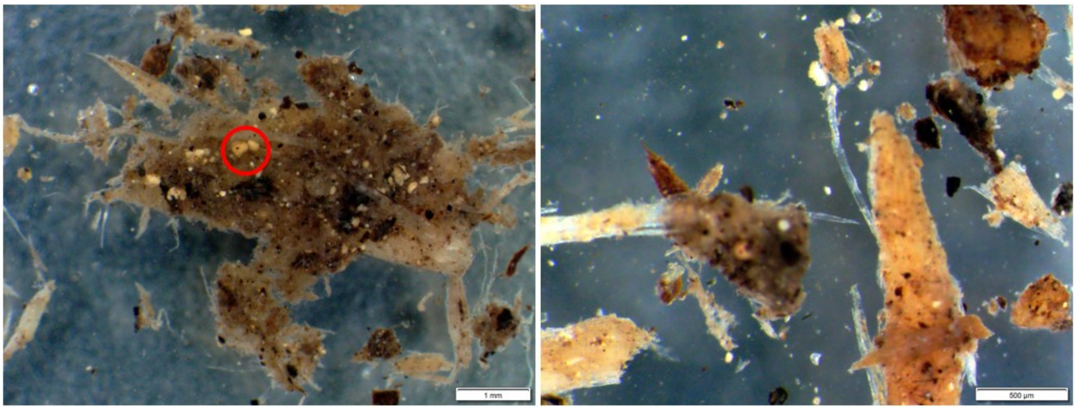


Figure 19. Microscopic images of fibre sludge taken with an optical microscope at 2x (left) and 5x (right) magnification. Examples of the particles assumed to be aggregated $CaCO_3$ particles are marked with a red circle.

Fibre clay contains fibres, decomposed matter (presumed to be organic) as well as coating and filler substances (Figure 20). The inorganic particles (examples marked with red circles in Figure 20 left) are probably aggregated $CaCO_3$ or kaolin. These particles have a diameter of up to 300 µm, which confirms that the particles are aggregated. The inorganic particles and decomposed organic matter among the fibres can be a challenge, for example in filtration. The small particles originating from the degraded organic material or the inorganic substances among the material most likely form a layer on the filter medium and / or block the filter pores and thus decrease filter capacity.

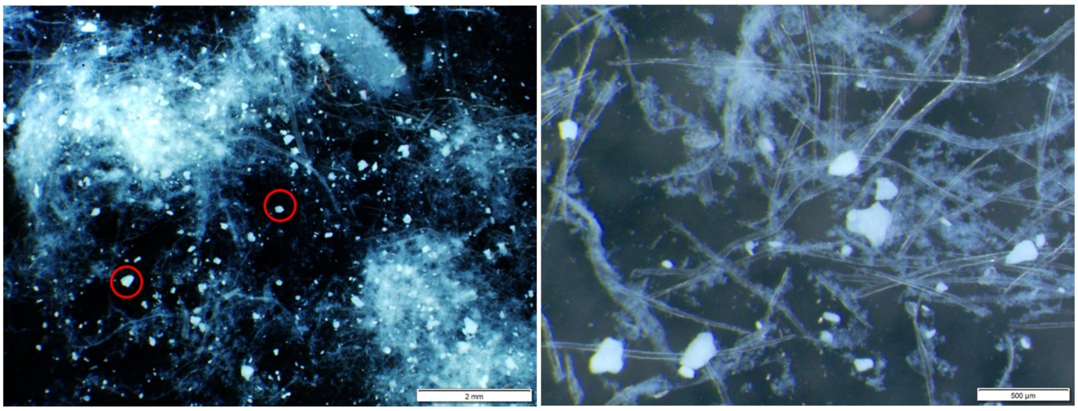


Figure 20. Microscopic images of fibre clay taken with an optical microscope at 6x (left) and 6.3x (right) magnification. High-density particles have been highlighted by exaggerating the gamma contrast. Examples of the inorganic particles, which are assumed to be aggregated $CaCO_3$ or kaolin particles, are marked with red circles.

In Figure 21, the physical appearance of deinking sludge is presented. Under a microscope, fibres of different lengths, decomposed matter and inorganic substances can be observed. Different filler substances and printing inks can be seen as colorful and black dots on the organic matter (Figure 21 right). $CaCO_3$ particles are not clearly visible although the chemical compositional analysis indicated that their concentration is higher in the deinking sludge than in the other studied sludge samples. This may be because the $CaCO_3$ are in a finer form or mixed with other substances in such a way that they were not clearly distinguished with the microscope.

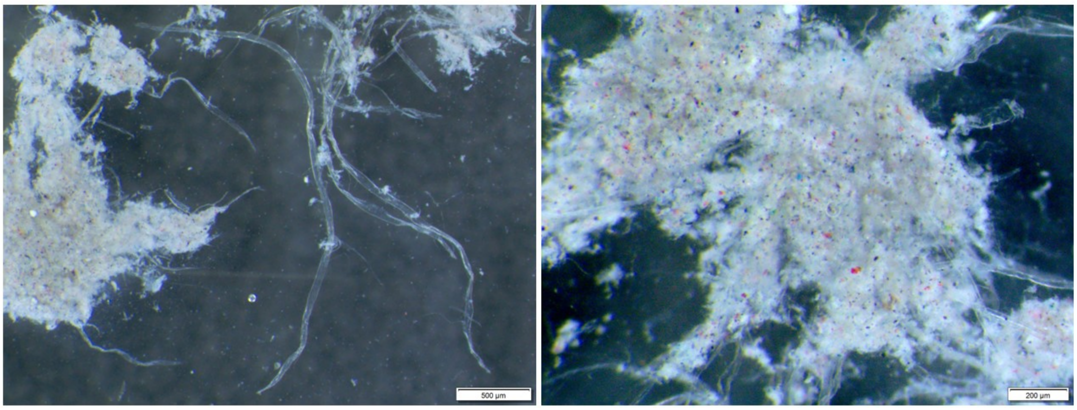


Figure 21. Microscopic images of deinking sludge taken with an optical microscope at 4x(left) and 8x(right) magnification. The colorful and black dots on the organic matter are presumed to be filler substances and printing inks.

4.2.2 Fibre characteristics and fines content

The fiber image analyzer (Valmet FS5) is intended for the examination of samples containing mainly fibres, such as pulp. Thereby, all parameters are not suitable for analyzing side streams that have a very heterogeneous composition. For example, the degree of fibrillation does not give an accurate picture of samples with no clear fibre structure. Therefore, the most important characteristics considered in this thesis were considered to be the number of particles and fibres measured, average fibre length and width, and the amount of fines (type A and B). These values are presented in Table 5. A type of fines are flake-like fines that are shorter than 0.2 mm, while B type of fines are lamella-shaped fines with length over 0.2 mm and width less than 10 μm. The full analysis reports of the fiber image analyzer are presented in Appendix E.

Table 5. The fibre and fines properties of the studied side streams measured with Valmet FS5. Content of the A type fines is expressed as percentage of the projection area of measured particles and B type of fines as percentage of length distribution.

Raw material	Particles count (n)	Fibres count (n)	Average fibre length (mm)	Average fibre width (μm)	Fines A content (%)	Fines B content (%)
Knot reject	509616	16665	1.44	26.26	33.26	0.33
Knot washing reject	483499	20962	1.66	36.79	24.01	0.19
Screening reject	1031420	11478	2.30	28.38	28.01	0.46
Fibre sludge	500953	22497	1.02	26.38	73.07	1.68
Fibre clay	69094	4733	1.05	22.07	32.58	1.36
Deinking sludge	269708	16738	0.75	24.46	82.60	12.90

The fibres in the reject side streams are on average longer than in the sludge side streams (Table 5). This is assumably because the reject samples have not been chemically and mechanically treated as much as the sludge samples. In the microscopic images of the knot reject (Figure 17) and the screening reject (Figure 18), it was also seen that the fibres are quite intact within these side streams. Based on the length to width distribution of the knot reject and the screening reject (Appendix

E), there is a lot of material that is narrow in width and long in length. Almost 40% of the fibres in the screening reject are 2.00-3.20 mm long and nearly 20% are over 3.20 mm long, which is promising for pulp-based applications. The knot washing reject contains both wide and long material much more evenly distributed than other reject side streams (Appendix E). Though it should be noted that the sample is not fully represented in the analysis as the big undissolved wood pieces cannot be analyzed as such.

The average fibre length in the deinking sludge was significantly lower than in the other analyzed sludge samples, i.e., in the fibre sludge and the fibre clay. This observation is in line with the literature (Gurram et al. 2015; Steffen et al. 2018). The short fibre length is probably because the recycled fibres in the deinking sludge have already been subjected to an extensive mechanical and chemical processing. Based on the length to width distribution of the fibre sludge and the deinking sludge (Appendix E), these materials have high amounts of short substances (fibre length < 0.2mm) with a width less than 30 µm. These particles represent most likely the pigments and fines within these side streams. The amount of flake-like fines (Type A) is significantly higher in the fibre sludge and the deinking sludge than in the fibre clay. It was observed in the microscope images (Chp. 4.2.1) that the inorganics in the fibre clay sample are aggregated. This would explain the low amount of fines and particles in this side stream. In terms of volume, the fibre clay seems to have a lot of particles, but the number of particles themselves is lower than in the other studied side streams (Table 5). This is also in line with the assumption that the pigments in the fibre clay have aggregated into larger particles.

Two features of the screening reject results stood out: The number of counted particles in the screening reject is significantly higher than in any other studied side streams, including the sludges. This indicates that the sample contains small particles when obtained from the mill, but these particles have most likely been removed from the sample during washing before chemical composition analysis. As mentioned in chapter 4.2.1, the particles may origin from the brown stock washing liquid of the pulp mill or be sand particles or other impurities that have ended up in the side stream. From the microscopic images (Figure 18), it was seen that the screening reject contains mainly fibrous material. It is possible, that the fiber image analyzer has counted short fibres as particles and not as fibres. Based on the chemical composition analysis results (Appendix B), the screening reject would contain more than twice as much cellulose as the deinking sludge. However, according to the fiber image analyzer results (Table 5), the material counted as fibres would be higher in the deinking sludge than in the screening reject. This supports the statement that the analysis of these samples is not entirely straightforward, and that the fiber image analyzer can only provide indicative results if analyzing samples with heterogeneous compositions.

4.2.3 Particle size distribution in sludge side streams

The particle size distribution of the fibre sludge, the fibre clay and the deinking sludge is bimodal, having two peaks in each distribution (Figure 22). The first peak is around 50-100 µm and the second near 1000 µm. The larger peak represents probably the fibres in the side streams, while the smaller peak presents most likely the fines and pigments in the sample. The average fibre length results of the sludge side streams (Table 5) support the possibility that the peak near 1000 µm would represent the fibres within these samples.

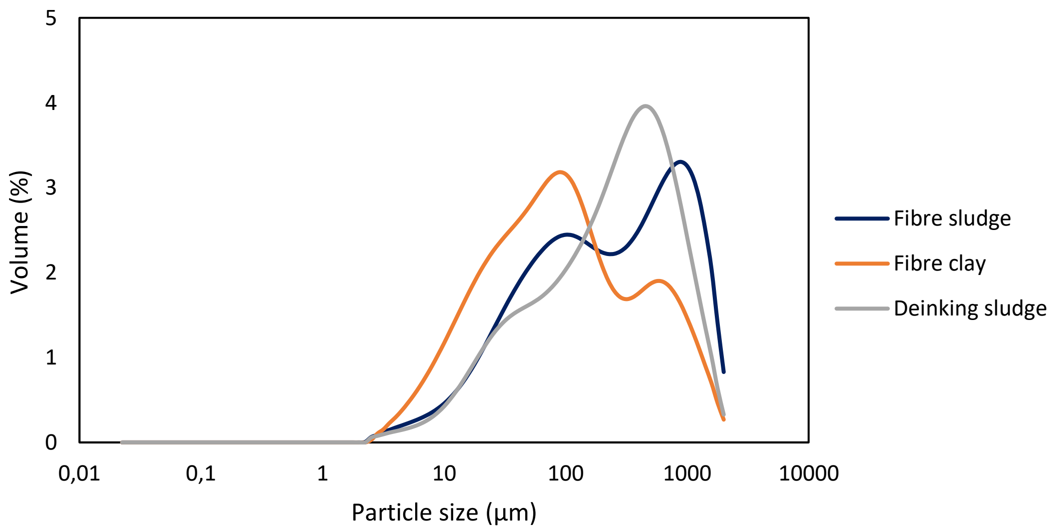


Figure 22. Particle size distribution of fibre sludge, fibre clay and deinking sludge.

Based on the particle size distribution results, the particle size of pigments and fines is quite high. In general, the particle size of unused coating pigments is no more than a few micrometers (kaolin 0.3-5 μm, $CaCO_3$ 0.7-2 μm and talc 0.3-5 μm) (ForestBioFacts, 2023b). From Table 6 it can be noticed that the samples contain less than 10% of very fine material with a particle size of less than 30 μm. However, based on the ash composition analysis, it is estimated that the $CaCO_3$ content in the fibre clay is about 16% and in the deinking sludge about 26%. Based on these results, it can be assumed that the pigments in the studied sludge side streams are aggregated into bigger particles. The microscopic images of the fibre sludge and the fibre clay (Figure 19 and Figure 20) support this assumption as large inorganic particles were noticed among the fibres. The formation of aggregates is assumably due to flocculation of fillers, which causes the filler particles to clump together. This can be caused by several factors, including changes in pH, ionic strength, and the presence of other chemicals or additives.

Table 6. Particle size distribution in sludge side streams. D(0.5) is the median particle size, while d(0.1) and d(0.9) mean that 10% of the total particles are smaller or larger than the value presented.

Raw material	**d(0.1) (μm)**	**d(0.5) (μm)**	**d(0.9) (μm)**
Fibre sludge	24.7	211.5	1108.8
Fibre clay	13.1	83.6	689.1
Deinking sludge	26.0	243.5	873.3

Based on Figure 22, it can be assumed that the deinking sludge would contain the highest amount of material with a particle size of about 900 μm, while the fibre clay would contain the least. If this material represents fibres, then the results are not in line with the ash analysis and fibre image analyzer results. Based on the ash analysis results (Appendix B), the amount of organic material is the lowest in the deinking sludge. The inorganic substances in the deinking sludge make up almost 50% of the composition of the material, while the inorganic matter is about 37% in the fibre clay and about 20% in the fibre sludge. Based on the fiber image analyzer results (Appendix E), the material in the deinking sludge would be shorter and narrower on average than in the fibre clay and the fibre sludge. It is possible that the pigments in the deinking sludge are attached to the fibres and degraded organic matter and, when viewed in volume, it appears that there would be more material in this side stream with a particle size of about 900 µm than in reality. It is also possible that the aggregates in the fibre clay and the fibre sludge make it look like there is considerably more inorganic material in these side streams when viewed in volume than what there actually is.

It must be noted, that in the particle size distribution analysis, it is assumed that the particles in the samples have a spherical particle geometry, which is not suitable for measuring fibre content. For more reliable results, fibres should be screened from the inorganic substances and the particle size distribution of the pigments and fines determined separately.

4.2.4 Physical features that might affect processability

Reject and sludge side streams have a high moisture content when obtained from the mills. The side streams are very heterogeneous and, depending on the intermediate storage, may also contain stones and other impurities. Transporting fibre-rich side streams in winter can be challenging, as the high moisture content can cause these materials to freeze and get stuck on the transport pallet.

All sludge samples were very dusty when air-dried and ground. The studied fibre sludge sample was already quite fine grained when received from the mill. The side stream dried relatively quickly in room temperature to dry matter content of 92.5% and did not pose any physical difficulties in terms of grinding. Fibre clay is easily adhered onto surfaces and turns hard when it dries. Fibre clay is difficult to screen, which is considered problematic. During intermediate storage, stones and other soil material may be mixed with fibre clay. This type of problems can prevent utilizing the side stream, for example, in incineration or as soil enrichment material. From the microscope images (Figure 20), it can be seen that fibre clay contains particles of very variable size. Different particle sizes might pose challenges, if the material is for example going to be screened or dissolved. In the deinking sludge, the particles are already fairly well separated, and the sample would not necessarily even require grinding before analysis. However, based on the particle size distribution measurements, it can be assumed that in deinking sludge the pigments are attached to the fibres. It is recommended that in further processing, the pigments would be removed from the fibrous material and analyzed separately.

Knot reject and screening reject were found to have similar physical characteristics. The material does not stick to surfaces and dries quickly. The main problems were experienced in the heterogeneity and grindability of the samples. In addition to sticks, the samples contain fibrous material that sticks firmly to the larger wood material. This made screening difficult and prevented the particle size analysis. The composition of these samples also caused grinding problems. The materials easily drifted into the walls of the mill, causing the mill to jam. It was estimated that this was due to the light weight of the dried knot reject and the screening reject samples, which prevented the samples from falling to the bottom of the mill during grinding.

4.3 Evaluation of potential application possibilities

The evaluation of potential application possibilities of the studied side streams was based on the chemical composition results, physical appearance and on literature. As discussed, pulp, tissue paper and board mill side streams are interesting feedstocks in various applications due to their non-food competing status, high availability, and low cost. Additionally, as fibre-rich side streams are renewable feedstock, their wider use could reduce dependence on fossil resources in some applications.

4.3.1 Utilization in sugar platform

The reject side streams are desirable sources of fermentable compounds, because of their high carbohydrate content and low ash content. In this thesis, the highest carbohydrate content and the lowest ash content was determined for the screening reject. Based on the chemical composition analysis results, the knot reject and the screening reject are interesting feedstocks for sugar platform. The metal and elemental analyses indicated that these materials do not contain coating or filler substances, which would negatively influence acid hydrolysis. Although the carbonate analysis of the reject side streams showed a fairly straightforward hydrolysis of carbohydrates into sugars, it is not certain how these side streams would perform in industrial acid hydrolysis and what kind of sugar yields would be obtained. The reject side streams contain also high amount of lignin, which is left over in acid hydrolysis. Thereby, the suitability of reject samples in acid hydrolysis requires further investigation before the profitability can be assessed.

As discussed in chapter 2.6.1, in the production of sugar platform products, e.g., bioethanol, enzymatic hydrolysis is mostly favored over acid hydrolysis. However, based on the literature, the strong structure of knot reject makes it difficult to be accessed by enzymes regardless that the side stream has been chemically treated in the digester during pulping (Wang et al., 2012). The production of sugar platform products from knot reject with enzymatic hydrolysis would probably require high dosages of enzymes. The high cost of enzymes combined with the expected amount needed for hydrolysis would probably reduce the profitability of using knot reject in sugar platform. In addition, it is not known if the high lignin content in knot reject interferences with enzymatic hydrolysis and fermentation processes. Given the low production volume of knot reject and the possible challenges in utilizing the side stream in sugar platform, it is presumably more cost-effective to recycle the knot reject back into the digester and use it in pulp production.

The use of fibre sludge as a feedstock in sugar platform would be of interest due to its relatively high sugar content (47%), manageable ash content (20%) and high availability. The value of this side stream would increase considerably if it could be used as a raw material in the sugar platform instead of being incinerated. In the chemical composition analyses it was found out that high ash content in the side streams negatively affects the hydrolysis of the analysis. However, as discussed in chapter 4.1.2, it is possible that the moderate ash content, especially $CaCO_3$ content, of the fibre sludge did not necessarily interfere with the acid hydrolysis of carbohydrates. This assumption was supported by the fact that the composition results of the fibre sludge were in line with literature. However, further research is still required to know if the ash components in fibre sludge would affect sugar yields and whether the use of fibre sludge as a raw material in sugar platform would be profitable.

Based on this thesis, the fibre clay and the deinking sludge showed higher potential in other applications than in sugar platform products. The high amounts of inorganic substances in the fibre clay and the deinking sludge would most likely interfere in acid hydrolysis and potentially lower the sugar yields. As discussed in chapter 2.6.1, ash components have also shown to negatively affect the enzyme activity during enzymatic hydrolysis and to buffer pH. Based on the metal analyses, these side streams also contain contaminants such as heavy metals and chemicals used in the process, which can affect the efficiency of hydrolysis and fermentation. Thereby, fibre clay and deinking sludge would probably require additional treatment steps where the ash of these side streams would be removed before hydrolysis. Using large amounts of chemicals for the pre-treatment of side streams with high ash content would be both expensive and environmentally undesirable. If high ash containing side streams would be used in sugar platform, it would be important to investigate the effect of ash on sugar yields and examine pH change to introduce efficient and economical enzymatic or acidic hydrolysis of these side stream.

4.3.2 Utilization in agriculture, composite and construction materials

From the studied fibre-rich side streams, fibre sludge was considered as the most potential side stream for agricultural uses. According to the metal analysis results (Table 4), the total heavy metal concentrations (As, Cd, Cr, Ni, Pb, Cu and Zn) in the fibre sludge were lower than the Finnish heavy metal limit values for fertilizer products, which were reported in the study of Pöykiö et al. (2018). The high TOC value (41%) in the fibre sludge indicates that this residue could act as a potential source of carbon (C) if it would be used as a fertilizer. The fibres in this side stream could potentially improve soil structure and, thereby, reduce erosion. According to the elemental analysis results (Table 3), the total Ca (51600 mg/kg), Na (3240 mg/kg), S (5960 mg/kg) and Zn (91 mg/kg) concentrations in the fibre sludge were clearly higher than those reported in the study of Pöykiö et al. (2018) for the mineral soil of Finland. However, the use of fibre sludge as a fertilizer in Finland would not increase the mineral soil concentrations of Mg, K, Cu, because the concentrations of these nutrients in this residue were lower than those in the mineral soil.

The high average fibre length of the knot reject and the screening reject combined with their quite intact fibre condition (Figure 17 and Figure 18) indicate that these side streams could be hypothetically suitable for applications where strength, durability and flexibility are crucial properties. The fibres within these side streams could potentially be used in the production of coatings and films or as load bearing components in other composite materials. The dissolution of knot reject for film production could potentially be easier than with the sludge side streams, due to the lower ash content. The high lignin content in the knot reject could potentially improve the mechanical properties, hydrophobicity, and UV-shielding of the composite films. The long fibres in the screening reject could also potentially be utilized as supporting materials in the textile industry. For example, in the viscose process, the long fibres could potentially be utilized for filtration. However, this would require that the fibres can be dissolved and do not end up in the final product.

The high mineral content of the fibre clay and the deinking sludge could be useful in biocomposites and in construction material. In construction materials, the mineral content within these side streams could provide hardness and low biodegradability for the product. As presented in chapter 2.6.4, there are already existing applications where deinking sludge has been utilized gainfully as a building material. Fibre clay and deinking sludge could also potentially act as reinforcing filler materials in thermoplastic composites, as these side streams contain short fibres and similar additives and fillers that are commonly used in plastics for extrusion products to give stiffness and improved processing properties for the product. Due to the current status of these side streams, the raw material costs would be low. The studied fibre clay is in terms of chemical composition similar to the fibre clay investigated by Immonen et.al (2017), which would support its potential usability in various injection moulded and extruded products. One the other hand, the high moisture content of fibre clay could limit its utilization in biocomposites as industrial scale drying method for fibre clay require further development. The formation of aggregates in the fibre clay, which was indicated in the physical appearance analysis results, also requires consideration if this material would be used in biocompoistes. The utilization of this side stream in composites would probably require the use of dispersants, additional pH adjustment, or optimization of mixing conditions.

4.3.3 Utilization of fillers and pigments

Based on the chemical composition analysis results, deinking sludge and fibre clay are interesting sources of fillers and pigments that could potentially be exploited, e.g., in different paper grades or recovered and recycled back into the process as a filler makeup source. The principal components in the inorganic material of the fibre clay and the deinking sludge consist of fillers or coating agents, such as calcium carbonate and kaolin, but also of other chemicals, such as talc, calcium sulphate and titanium oxide. The filler substances could potentially act as a partial replacement of fresh fillers in different paper grades, such as in newspapers. Deinking sludge is also a source of other inorganic pigments, which could potentially be used for coating and coloration. The pigments in the deinking sludge could potentially improve performance and mechanical properties for example in mineral/MFC composites. The utilization of the pigments and fillers found in deinking sludge would have a relevant impact in the paper recycling industry and add value for this side stream.

5 Conclusions

In this master's thesis, selected fibre-rich side streams from Metsä Group's pulp, board and tissue paper mills were characterized to outline their suitability as raw material sources for side products. The chemical compositions and physical appearances of knot reject, fibre sludge, fibre clay and deinking sludge were studied. These types of fibre-rich side streams are interesting materials as they are typically considered as waste and most often end up being incinerated. The main challenges for their utilization range from their complex compositions to the logistics and market demand for their utilization.

The hypothesis of this thesis was that the studied fibre-rich side streams contain components, that could be utilized as raw materials for value-added products. The chemical composition analyses indicated that the reject side streams contain 67-85% carbohydrates, 13-30% lignin, 0.2-2.4% extractives and 1.7-2.2% ash. The studied sludge side streams contain about 47-61% carbohydrates, 0.8-2.4% extractives and 20-50% inorganic substances. The lignin content within the sludge side streams could not be reliably analyzed and the problem was highlighted with fibre clay and deinking sludge. The main inorganic substances of the fibre clay and the deinking sludge were estimated to consist of calcium carbonate and kaolin.

As a result of this thesis, it can be concluded that fibre-rich side streams contain valuable components that have the potential to be utilized in various applications. Based on this thesis and previous research on the subject, it is estimated that the most promising uses of the studied side streams would be to utilize fibre sludge as a feedstock in sugar platform or in agriculture and use fibre clay as a reinforcement material in composites. In case of deinking sludge, it is believed that more value would be obtained from the fillers and pigments than from the organic part. The filler substances could potentially act as a partial replacement of fresh fillers in different paper grades and the pigments could potentially be used for coatings and coloration. Despite the high carbohydrate content and low ash content of knot reject, which makes the side stream an attractive feedstock for sugar platform, it is believed that it is more profitable to recycle the knot reject back into the digester and use it for pulp production. However, more research and development are still required on the processing of fibre-rich side streams into by-products in economical way.

This thesis also discussed the analytical challenges and solution suggestions. The results from the chemical composition analyses indicated that the high ash content and especially the high $CaCO_3$ content in the fibre clay and the deinking sludge hampered the carbohydrate and lignin analysis. Based on this thesis, there is no certainty how much of the ash in the sludge side streams has been dissolved in the hydrolysis solution, during the carbohydrate analysis, or if some of the carbohydrates have not been hydrolyzed because of the high ash content. This hinderance can be overcome by combining the ash analysis with the knowledge that there is no more than minor lignin content in these samples, leading to the understanding that the non-ash material is carbohydrates. The results of the analyses obtained in this thesis were well in line with external laboratory service results, making it fully possible to utilize paid services if the above understanding is kept in mind, if ash removal is not desired.

For future work, the impact of ash in carbohydrate content analysis should be further investigated, comparing carbohydrate analysis from the samples to ones that have gone through an ash removal. It is also recommended to assess the profitability especially if the high ash side streams are to be used as raw materials on sugar platform. In the future, it would be useful to perform similar chemical composition analyses on pulp, which is produced from the same raw material and originates from the same mill (if possible) and use it as a reference. The variations in the compositions of the studied side streams according to the season and possible process changes would be worth investigating if their suitability for different applications is to be further explored.

To conclude, fibre-rich side streams have potential as feedstock for a variety of new applications. The use of these side streams in value-added products would help to reduce waste and promote sustainability within the industry. Overall, there is growing interest in developing new technologies and processes for recovering and utilizing these materials in a resource-efficient way.

References

Ahmad, A., Banat, F. and Taher, H. (2020). A review on the lactic acid fermentation from low-cost renewable materials: Recent developments and challenges. *Environmental Technology & Innovation*, 20. https://doi.org/10.1016/j.eti.2020.101138

Alkasrawi, M., Al-Othman, A., Tawalbeh, M., Doncan, S., Gurram, R., Singsaas, E., Almomani, F. and Al-Asheh, S. (2021). A novel technique of paper mill sludge conversion to bioethanol toward sustainable energy production: Effect of fiber recovery on the saccharification hydrolysis and fermentation. *Energy*, 223. https://doi.org/10.1016/j.energy.2021.120018

Amândio, M. S. T., Pereira, J. M., Rocha, J. M. S., Serafim, L. S. and Xavier, A. M. R. B. (2022). Getting Value from Pulp and Paper Industry Wastes: On the Way to Sustainability and Circular Economy. *Energies.*, *15*(11). https://doi.org/10.3390/en15114105

Anonymous. (2022). Internal interviews with Metsä Group experts.

Bajpai, P. (2014). Recycling and Deinking of Recovered Paper. Refining of Recycled Fibres. pp.181-197. https://doi.org/10.1016/B978-0-12-416998-2.00010-6

Brown, D.M., Pawlak, J. and Grunden, A.M. (2021). Bacterial valorization of pulp and paper industry process streams and waste. *Applied Microbiology and Biotechnology.*, 105(4), pp. 1345–1363. https://doi.org/10.1007/s00253-021-11107-2

Branco, R., Serafim, L. and Xavier, A. (2019). Second Generation Bioethanol Production: On the Use of Pulp and Paper Industry Wastes as Feedstock. *Fermentation.*, *5*(1). https://doi.org/10.3390/fermentation5010004

Cavka, A., Guo, X., Tang, S.-J., Winestrand, S., Jönsson, L. J. and Hong, F. (2013). Production of bacterial cellulose and enzyme from waste fiber sludge. *Biotechnology for Biofuels.*, 6(1). https://doi.org/10.1186/1754-6834-6-25

De Azevedo, A.R.G., Alexandre, J., Marvila, M.T., Xavier, G. de C., Monteiro, S.N. and Pedroti, L.G. (2020). Technological and environmental comparative of the processing of primary sludge waste from paper industry for mortar. *Journal of Cleaner Production.*, 249. https://doi.org/10.1016/j.jclepro.2019.119336

Deviatkin, I., Kujala, A. and Horttanainen, M. (2015). Deinking Sludge Utilization Possibilities: Technical, Economic and Environmental Assessments. LUT Scientific and Expertise Publications. Available: https://urn.fi/URN:NBN:fi-fe201505269106

Directive 2008/98/EC. Directive (EU) 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain directives. *Official Journal of the European Union* (OJ). L 312/3. Available: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32008L0098

Dimic-Misic, K., Salo, T., Paltakari, J. and Gane, P. (2014). Comparing the rheological properties of novel nanofibrillar cellulose-formulated pigment coating colours with those using traditional thickener. *Nordic Pulp & Paper Research Journal*, *29*(2), 253-270. https://doi.org/10.3183/npprj-2014-29-02-p253-270

Donkor, K. O., Gottumukkala, L. D., Diedericks, D. and Görgens, J. F. (2021). An advanced approach towards sustainable paper industries through simultaneous recovery of energy and trapped water from paper sludge. *Journal of Environmental Chemical Engineering*, 9(4). https://doi.org/10.1016/j.jece.2021.105471

Duncan, S. M., Alkasrawi, M., Gurram, R., Almomani, F., Wiberley-Bradford, A. E. and Singsaas, E. (2020). Paper Mill Sludge as a Source of Sugars for Use in the Production of Bioethanol and Isoprene. *Energies.*, 13(18). https://doi.org/10.3390/en13184662

Du, H., Parit, M., Wu, M., Che, X., Wang, Y., Zhang, M., Wang, R., Zhang, X., Jiang, Z. and Li, B. (2020). Sustainable valorization of paper mill sludge into cellulose nanofibrils and cellulose nanopaper. *Journal of Hazardous Materials*, 400, https://doi.org/10.1016/j.jhazmat.2020.123106.

Elloumi, A., Makhlouf, M., Elleuchi, A. and Bradai, C. (2016). Deinking Sludge: A New Biofiller for HDPE Composites. *Polymer-Plastics Technology and Engineering*, 55(10), pp. 1012–1020. https://doi.org/10.1080/03602559.2015.1132432

ForestBioFacts. (2022a). Wood can be turned into a variety of products. [Accessed 15 December 2022]. Available: https://forestbiofacts.com/introduction-to-forest-based-bioeconomy/versatile-products-out-of-wood/

ForestBioFacts. (2022b). Kraft pulping. [Accessed 27 December 2022]. Available: https://forestbiofacts.com/pulping-and-biorefining/kraft-pulping/

ForestBioFacts. (2022c). Other waste management methods. [Accessed 28 December 2022]. Available: https://forestbiofacts.com/pulping-and-biorefining/kraft-pulping/

ForestBioFacts. (2023a). Deinking. [Accessed 27 February 2023]. Available: https://forestbiofacts.com/recycled-fibre/additives/deinking/

ForestBioFacts. (2023b). Coating pigments – general. [Accessed 27 February 2023]. Available: https://forestbiofacts.com/natural-fibre-products/production-of-paper-and-board/pigment-coating/coating-materials/coating-pigments-general/

Geng. X., Zhang, S.Y. and Deng, J. (2007). Characteristics of paper mill sludge and its utilization for the manufacture of medium density fiberboard. *Wood and Fiber Science: Journal of the Society of Wood Science and Technology.*, *39*(2), pp. 345–351.

Gigante, V., Cinelli, P., Sandroni, M., D'ambrosio, R., Lazzeri, A. and Seggiani, M. (2021). On the Use of Paper Sludge as Filler in Biocomposites for Injection Moulding. *Materials.*, *14*(10). https://doi.org/10.3390/ma14102688

Gottumukkala, L.D., Haigh, K., Collard, F.-X., van Rensburg, E. and Görgens, J. (2016). Opportunities and prospects of biorefinery-based valorisation of pulp and paper sludge. *Bioresource Technology, 215*, pp. 37-49. http://dx.doi.org/10.1016/j.biortech.2016.04.015

Gullichsen, J. and Fogelholm, C-J. (2000). Chemical Pulping. Papermaking science and technology. ISBN 952-5216-06-3.

Gurram, R.N., Al-Shannag, M., Lecher, N.J., Duncan, S.M., Singsaas, E.L. and Al-kasrawi, M. (2015). Bioconversion of paper mill sludge to bioethanol in the presence of accelerants or hydrogen peroxide pretreatment. *Bioresource Technology,* 192, pp. 529–539, http://dx.doi.org/10.1016/j.biortech.2015.06.010

Haddar, M., Elloumi, A., Koubaa, A., Bradai, C., Migneault, S. and Elhalouani, F. (2017). Effect of High Content of Deinking Paper Sludge (DPS) on the Reinforcement of HDPE. *Journal of Polymers and the Environment,* 25, pp.617-627. https://doi.org/10.1007/s10924-016-0837-9

Haddar, M., Elloumi, A., Koubaa, A., Bradai, C., Migneault, S. and Elhalouani, F. (2018). Synergetic effect of Posidonia oceanica fibres and deinking paper sludge on the thermo-mechanical properties of high density polyethylene composites. *Industrial Crops and Products.*, 121, pp. 26–35. https://doi.org/10.1016/j.indcrop.2018.04.075

Haile, A., Gelebo, G.G., Tesfaye, T., Mengie, W., Mebrate, M.A., Abuhay, A. and Limeneh, D.Y. (2021). Pulp and paper mill wastes: utilizations and prospects for high value-added biomaterials. *Bioresources and Bioprocessing.*, 8(1). https://doi.org/10.1186/s40643-021-00385-3

Hassan, K., Villa, A., Kuittinen, S., Jänis, J. and Pappinen, A. (2018). An assessment of side-stream generation from Finnish forest industry. *Journal of Material*

Cycles and Waste Management, 21, pp. 265-280. https://doi.org/10.1007/s10163-018-0787-5

Higgs, R.P. Production and/or recovery of products from waste sludge. US pat. 8,658,119 B2,25 Feb 2014

Immonen, K., Wikström, L., Torvinen, K., Furu, L-E. and Saari, T. (2017). Fibre clay to polypropylene and polylactide (PLA) based composites. Available: https://cris.vtt.fi/en/publications/biocomposites-from-side-streams-of-paper-and-board-industry-fibre

ISO 1762:2015. (2015). Paper, board and pulps — Determination of residue (ash) on ignition at 525 degrees C. International Organization for Standardization.

Janson, J. (1970). Calculation of the polysaccharide composition of wood and pulp. Paperi ja Puu, vol.52:5, pp.323-9.

Kemppainen, K., Ranta, L., Sipilä, E., Östman, A., Vehmaanperä, J., Puranen, T., Langfelder, K., Hannula, J., Kallioinen, A., Siika-aho, M., Sipilä, K. and von Weymarn, N. (2012). Ethanol and biogas production from waste fibre and fibre sludge – The FibreEtOH concept. *Biomass and Bioenergy*, 46, pp. 60–69. https://doi.org/10.1016/j.biombioe.2012.03.027

Kang, L., Wang, W. and Lee, Y. Y. (2010). Bioconversion of Kraft Paper Mill Sludges to Ethanol by SSF and SSCF. *Applied Biochemistry and Biotechnology: ABAB.*, 161(1-8), pp. 53–66. https://doi.org/10.1007/s12010-009-8893-4

Khlif, M., Makni, H., Kharrat, F. and Bradai, C. (2022). Influence of the Incorporation of Deinking Sludge on the Physical and Mechanical Properties of Clay Bricks. *Journal of Materials in Civil Engineering*, 34(9). https://doi.org/10.1061/(ASCE)MT.1943-5533.0004378

Kuokkanen, M.J., Mäentausta, O.K. and Kuokkanen, T.J. (2018). Eco- and Material-Efficient Utilization Applications of Biotechnologically Modified Fiber Sludge. *Bioresources.*, 13(1), pp. 1457–1474. https://doi.org/10.15376/biores.13.1.1457-1474

Krigstin, S. G. (2008). Determination of the mineral constituents of recycled paper mill sludge. *Tappi Journal.*, 7(6), pp. 9–14.

Leão, A. L., Cherian, B. M., de Souza, S. F., Sain, M., Narine, S., Caldeira, M. S. and Toledo, M. A. S. (2012). Use of Primary Sludge from Pulp and Paper Mills for Nanocomposites. *Molecular Crystals and Liquid Crystals.*, 556(1), pp. 254–263. https://doi.org/10.1080/15421406.2012.635974

Lehr, M., Miltner, M. and Friedl, A. (2021). Removal of wood extractives as pulp (pre-)treatment: a technological review. *SN Applied Sciences*, 3(886), https://doi.org/10.1007/s42452-021-04873-1

Leppänen, T., Mustonen, E., Saarela, H., Kuokkanen, M. and Tervonen, P. (2020). Productization of Industrial Side Streams into By-Products – Case: Fiber Sludge from Pulp and Paper Industry, *Journal of open innovation : technology, market, and complexity, 6*(4), pp. 185–15, https://doi.org/10.3390/joitmc6040185

Lohiniva, E., Mäkinen, T. and Sipilä, K. (2001). Lietteiden käsittely: Uudet ja käytössä olevat tekniikat. VTT Technical Research Centre of Finland. VTT Tiedotteita - Meddelanden - Research Notes No. 2081. https://publications.vtt.fi/pdf/tiedotteet/2001/T2081.pdf

Ma, Y. (2018). Fibre spinning from various low refined, recycled lignocelluloses using ionic liquid. Doctoral thesis, Espoo, Finland. Available: http://urn.fi/URN:ISBN:978-952-60-8170-0

Matilainen, M., Pisto, S., Rinnepelto, P. and Kinnunen, N. (2013). Metsäteollisuuden ravinteet - Metsäteollisuuden sivuvirtojen hyödyntäminen lannoitevalmisteina. Apila Group Oy Ab.

Metsäteollisuus ry. (2023). Tilastot. [Accessed 5 January 2023]. Available: https://www.metsateollisuus.fi/tilastot

Migneault, S., Koubaa, A. and Perré, P. (2014). Effect of Fiber Origin, Proportion, and Chemical Composition on the Mechanical and Physical Properties of Wood-Plastic Composites. *Journal of Wood Chemistry and Technology*, 34(4), pp. 241–261. https://doi.org/10.1080/02773813.2013.869604

Murariu, M. and Dubois, P. (2016). PLA composites: From production to properties. *Advanced Drug Delivery Reviews*, 107, pp. 17–46. https://doi.org/10.1016/j.addr.2016.04.003.

Molin, U. and Teder, A. (2002). Importance of cellulose/hemicellulose-ratio for pulp strength. *Nordic Pulp & Paper Research Journal.*, 17(1), pp. 14–19a. https://doi.org/10.3183/npprj-2002-17-01-p014-019

Mäkinen, L., Ämmälä, A., Körkkö, M. and Niinimäki, J. (2013). The effects of recovering fibre and fine materials on sludge dewatering properties at a deinked pulp mill. *Resources, Conservation, and Recycling*, *73*, pp. 11–16. https://doi.org/10.1016/j.resconrec.2013.01.011

MW-Kehitys Oy. KUMARA - Kuitusaven mahdollisuudet raaka-aineena uusiotuotteisiin -hanke. [Accessed 16 January 2023]. Available:

https://www.manttavilppula.fi/elinkeinoelama/kehittamishankkeet-1/paattyneet-hankkeet/kumara-kuitusaven-mahdollisuudet/

Nazari, B. and Bousfield, D. (2016). Cellulose nanofibers influence on properties and processing of paperboard coatings. *Nordic Pulp & Paper Research Journal*, *31*(3), pp. 511-520. https://doi-org.libproxy.aalto.fi/10.3183/npprj-2016-31-03-p511-520

Nurmesniemi, H., Pöykiö, R. and Keiski, R. L. (2007). A case study of waste management at the Northern Finnish pulp and paper mill complex of Stora Enso Veitsiluoto Mills. *Waste Management,* 27(12), pp. 1939–1948. https://doi.org/10.1016/j.wasman.2006.07.017

Park, H., Cruz, D., Tiller, P., Johnson, D.K., Mittal, A., Jameel, H., Venditti, R. and Park, S. (2022). Effect of ash in paper sludge on enzymatic hydrolysis. *Biomass and bioenergy*, 165, https://doi.org/10.1016/j.biombioe.2022.106567

Prasetyo, J., Zhu, J., Kato, T. and Park, E. Y. (2011). Efficient production of cellulase in the culture of Acremonium cellulolyticus using untreated waste paper sludge. *Biotechnology Progress.*, 27(1), pp. 104–110. https://doi.org/10.1002/btpr.534 ‘

Presas, T., and Mensink, M. (2011). 2050 Roadmap to a low-carbon bio-economy. Confederation of European Paper Industries.

Pöykiö, R., Watkins, G. and Dahl, O. (2018). Characterization of primary and secondary wastewater treatment sludge from a pulp and board mill complex to evaluate the feasibility of utilization as a soil amendment agent and a fertilizer product. *Journal of Bioresources and Bioproducts*, 3(3), pp. 88-95. https://doi.org/10.21967/jbb.v3i3.174

Rasa, K., Pennanen, T., Peltoniemi, K., Velmala, S., Fritze, H., Kaseva, J., Joona, J. and Uusitalo, R. (2021). Pulp and paper mill sludges decrease soil erodibility. *Journal of Environmental Quality JEQ.*, 50(1), pp. 172–184. https://doi.org/10.1002/jeq2.20170

Rosa, T. S., Trianoski, R., Michaud, F., Yamashita, F. and Iwakiri, S. (2021). Sludge Fiber Waste and Kraft Lignin Powder as Fillers in Polylactic Acid Biocomposites: Physical, Mechanical, and Thermal Properties. *Polymers.*, 13(5), pp. 672–14. https://doi.org/10.3390/polym13050672

Saari, O., Nenonen, M., Oasmaa, K. and Lönnqvist, S. (1998). Kuitusaven tuotteistamisen raportti. Finncao L8

Saha, N., Saba, A., Saha, P., McGaughy, K., Franqui-Villanueva, D., Orts, W., Hart-Cooper, W. and Reza, M. (2019). Hydrothermal Carbonization of Various Paper Mill

Sludges: An Observation of Solid Fuel Properties. *Energies.*, 12(5). https://doi.org/10.3390/en12050858

Salo, T., Dimic-Misic, K., Gane, P. and Paltakari, J. (2015). Application of pigmented coating colours containing MFC/NFC: Coating properties and link to rheology. *Nordic Pulp & Paper Research Journal.*, *30*(1), pp. 165–178. https://doi.org/10.3183/npprj-2015-30-01-p165-178

SCAN-CM 49:03. (2003). Content of acetone-soluble matter. Scandinavian pulp, paper and board testing committee.

Singh, S. K., Kulkarni, S., Kumar, V. and Vashistha, P. (2018). Sustainable utilization of deinking paper mill sludge for the manufacture of building bricks. *Journal of Cleaner Production.*, 204, pp. 321–333. https://doi.org/10.1016/j.jclepro.2018.09.028

Singh, S., Sithole, B., Lekha, P., Permaul, K., & Govinden, R. (2021). Optimization of cultivation medium and cyclic fed-batch fermentation strategy for enhanced polyhydroxyalkanoate production by Bacillus thuringiensis using a glucose-rich hydrolyzate. *Bioresources and Bioprocessing.*, 8(1). https://doi.org/10.1186/s40643-021-00361-x

Sebastião, D., Gonçalves, M. S., Marques, S., Fonseca, C., Gírio, F., Oliveira, A. C. and Matos, C. T. (2016). Life cycle assessment of advanced bioethanol production from pulp and paper sludge. *Bioresource Technology*, *208*, pp. 100–109. https://doi.org/10.1016/j.biortech.2016.02.049

Skuse, D., Phipps, J. and Larspon, T. (2021). Co-ground mineral/microfibrillated cellulose composite materials: Recycled fibers, engineered minerals, and new product forms. *Tappi Journal.*, *20*(1), pp. 49–58. https://doi.org/10.32964/TJ20.1.49

Steffen, F., Janzon, R. and Saake, B. (2018). Enzymatic treatment of deinking sludge – effect on fibre and drainage properties. *Environmental Technology*, 39(21), pp. 2810–2821. https://doi.org/10.1080/09593330.2017.1365948

Syamsudin. and Rizaluddin, A.T. (2021). Review on renewable energy sources based on thermal conversion in the pulp and paper industry. *Center for Pulp and Paper*, 3(1).

Taylor, R., Nattrass, L., Alberts, G., Robson, P., Chudziak, C., Bauen, A., Libelli, I. M., Lotti, G., Prussi, M., Nistri, R., Chiaramonti, D., lópez-Contreras, A. M., Bos, H. L., Eggink, G., Springer, J., Bakker, R. and van Ree, R. (2015). From the Sugar Platform to biofuels and biochemicals: Final report for the European Commission Directorate-General Energy. *E4tech/Re-CORD/Wageningen UR*. https://ec.europa.eu/energy/content/sugar-platform-biofuels-and-biochemicals_en

Tappi 222 om-02. (2006). Acid-insoluble lignin in wood and pulp

Tawalbeh, M., Rajangam, A. S., Salameh, T., Al-Othman, A. and Alkasrawi, M. (2021). Characterization of paper mill sludge as a renewable feedstock for sustainable hydrogen and biofuels production. *International journal of hydrogen energy*, 46(6), pp.4761-4775. https://doi.org/10.1016/j.ijhydene.2020.02.166.

Thompson, G., Swain, J., Kay, M. and Forster, C.F. (2001). The treatment of pulp and paper mill eÇuent: a review. *Bioresource technology*, 77(3), pp. 275–286. https://doi.org/10.1016/s0960-8524(00)00060-2

Tofani, G., de Nys, J., Cornet, I. and Tavernier, S. (2021). Alternative Filler Recovery from Paper Waste Stream. *Waste and Biomass Valorization.*, *12*(1), 503–514. https://doi.org/10.1007/s12649-020-01011-7

Tourunen, O. (2016). Kuitusaven hyödyntäminen leijupetikattilassa. Thesis.

Vandi, L-J., Chan, C., Werker, A., Richardson, D., Laycock, B. and Pratt, S. (2018). Wood-PHA Composites: Mapping Opportunities. *Polymers.*, 10(7). https://doi.org/10.3390/polym10070751

Vilarinho, I.S., Gameiro, T., Capela, M.N., Carvalheiras, J., Caetano, A.P.F., Novo, C., Novais, R.M., Seabra, M.P. and Labrincha, J.A. (2022). Review of recycling alternatives for paper pulp waste. *Frontiers in Materials*, 9. https://doi.org/10.3389/fmats.2022.1006861

Virolainen, P. (2017). Metsäteollisuudessa syntyvien biohajoavien jätteiden hyötykäyttötilanne ja -mahdollisuudet. Kaakkois-Suomen Elinkeino-, liikenne- ja ympäristökeskus. ISSN 2242-2854

Vodovnik, M., Vrabec , K., Hellwig, P., Benndorf, D., Sežun, M., Gregori, A., Gottumukkala, L. D., Anderson, R. C. and Reichl, U. (2018). Valorisation of deinking sludge as a substrate for lignocellulolytic enzymes production by Pleurotus ostreatus. *Journal of Cleaner Production.*, *197*, pp. 253–263. https://doi.org/10.1016/j.jclepro.2018.06.163

Wang, L., Wang, J. G., Littlewood, J. and Cheng, H. B. (2014). Co-production of biorefinery products from kraft paper sludge and agricultural residues: opportunities and challenges. *Green Chemistry*, *16*(3), pp. 1527–1533.
https://doi.org/10.1039/c3gc41984c

Wang, W., Kang, L. and Lee, Y. Y. (2010). Production of Cellulase from Kraft Paper Mill Sludge by Trichoderma Reesei Rut C-30. *Applied Biochemistry and Biotechnology : ABAB.*, 161(1-8), pp. 382–394. https://doi.org/10.1007/s12010-009-8863-x

Wikström, L., Hakala, J., Saarivuori, E., Forsström, U. and Keränen, J. (2018). Utilization of side streams from paper industry as fillers in polypropylene composites. *Polymer Composites*, 39(11), pp. 4000–4009. https://doi.org/10.1002/pc.24449

Williams, A. (2017). The Production of Bioethanol and Biogas from Paper Sludge. Masters' thesis. Stellenbosch University. Available: https://scholar.sun.ac.za

Willför, S., Hemming, J., Reunanen, M. and Holmbom, B. (2003). Phenolic and Lipophilic Extractives in Scots Pine Knots and Stemwood. *Holzforschung*, 57(4), pp. 359-372. https://doi-org.libproxy.aalto.fi/10.1515/HF.2003.054

Yu, T., Li, Y. and Ren, J. (2009). Preparation and properties of short natural fiber reinforced poly(lactic acid) composites. Transactions of Nonferrous Metals Society of China, 19(3), pp. 651–655. https://doi.org/10.1016/S1003-6326(10)60126-4

Zambare, V.P. and Christopher, L.P. (2020). Integrated biorefinery approach to utilization of pulp and paper mill sludge for value-added products. *Journal of Cleaner Production,* 274, https://doi.org/10.1016/j.jclepro.2020.122791

Appendix A. pH and NaOH content of fibre-rich side streams

Side stream	pH	γ (μS/cm)	Washing required	Washing cycle	pH after washing	γ after washing (μS/cm)	NaOH (%)
Knot reject	9.50	325	Yes	5	8.97	4.92	0.05
Knot washing reject	10.29	529	Yes	12	8.80	3.30	0.67
Screening reject	10.99	385	Yes	10	8.80	4.40	0.51
Fibre sludge	8.86	-	No	-	-	-	-
Fibre clay	8.11	-	No	-	-	-	-
Deinking sludge	8.04	-	No	-	-	-	-

Appendix B. Chemical composition analysis results

Analysis	Unit	Knot reject	Knot washing reject	Screening reject	Fibre sludge	Fibre clay	Deinking sludge
DMC	%	30.49	28.38	13.12	30.94 ± 0.11	16.63 ± 1.83	44.18 ± 0.18
Acetone soluble extractives	%	0.42	2.43	0.20	1.45	0.84	2.37
Cellulose	%	57.84 ± 0.10	49.57 ± 0.51	67.80 ± 0.00	34.63 ± 0.60	40.62 ± 0.02	31.64 ± 0.11
Arabinoxylan	%	10.58 ± 0.04	7.75 ± 0.02	9.11 ± 0.04	10.93 ± 0.26	15.47 ± 0.04	6.91 ± 0.02
Galactoglucomannan	%	10.04 ± 0.08	9.20 ± 0.04	8.12 ± 0.20	7.59 ± 0.02	5.26 ± 0.03	8.54 ± 0.09
Acid soluble lignin	%	0.55 ± 0.00	0.55 ± 0.02	0.54 ± 0.00	1.72 ± 0.01	2.02 ± 0.02	0.69 ± 0.01
Acid insoluble material	%	19.15 ± 0.30	29.04 ± 0.52	12.62 ± 0.52	26.51 ± 0.35	17.78 ± 0.42	31.81 ± 0.67
Ash at 525 °C	%	2.04 ± 0.14	2.16 ± 0.01	1.66 ± 0.07	19.81 ± 0.29	36.81 ± 0.22	49.55 ± 0.15
Ash at 900 °C	%	1.79 ± 0.10	1.89 ± 0.12	1.57 ± 0.01	16.12 ± 0.56	27.42 ± 0.26	35.20 ± 0.02
Calcium carbonate determined from LOI values	%	0	0.05	0	4.12	15.55	26.27
Minerals and wood silicates	%	2.04	2.11	1.98	15.70	21.26	23.28

Appendix C. Carbohydrate composition analysis results

Monosaccharide	Unit	Knot reject	Knot washing reject	Screening reject	Fibre sludge	Fibre clay	Deinking sludge
Glucose	%	59.08 ± 0.81	51.09 ± 1.88	70.07 ± 0.35	31.74 ± 0.60	27.33 ± 0.23	19.85 ± 1.30
Xylose	%	8.94 ± 0.11	6.79 ± 0.20	8.05 ± 0.07	8.35 ± 0.16	9.64 ± 0.11	3.51 ± 0.20
Mannose	%	7.10 ± 0.02	6.51 ± 0.13	6.05 ± 0.17	4.45 ± 0.03	2.42 ± 0.01	3.34 ± 0.19
Galactose	%	1.12 ± 0.05	1.09 ± 0.04	0.69 ± 0.01	1.19 ± 0.04	0.46 ± 0.00	0.98 ± 0.04
Arabinose	%	1.29 ± 0.02	0.75 ± 0.02	0.95 ± 0.01	1.09 ± 0.05	0.29 ± 0.01	0.55 ± 0.04
Rhamnose	%	0	0	0	0.27 ± 0.01	0.18 ± 0.00	0.09 ± 0.01
Total monosaccharides	%	76.53 ± 1.01	66.24 ± 2.28	85.80 ± 0.59	47.09 ± 0.38	40.32 ± 0.36	28.31 ± 1.77

Appendix D. Chemical composition analysis results (externally determined)

Analysis	Unit	Knot reject	Knot washing reject	Screening reject	Fibre sludge	Fibre clay	Deinking sludge
DMC of air-dried samples	%	94.9	95.0	95.4	93.2	91.6	96.8
Ash at 525 °C	%	2.2	2.2	1.6	21.6	35.2	49.3
Acetone soluble extractives	%	0.41	2.67	0.15	1.59	0.90	2.58
Monosaccharides	mg/100mg	77.4	63.6	84.4	46.2	38.5	26.3
Arabinose	mg/100mg	1.2	0.7	0.9	1.0	<0.3	0.6
Galactose	mg/100mg	1.1	1.1	0.6	1.1	0.5	1.0
Glucose	mg/100mg	59.8	49.5	69.7	32.3	26.7	18.6
Xylose	mg/100mg	8.2	6.0	7.4	7.4	9.1	3.0
Mannose	mg/100mg	7.0	6.3	5.8	4.3	2.3	3.1
Acid soluble lignin	%	0.3	0.5	0.3	1.5	1.6	0.2
Acid insoluble material	%	17.8	30.6	11.4	27.6	19.7	30.6
Carbonate	%	0.337	0.273	0.415	6.40	8.03	11.1
C	%	48.73	51.8	46.82	42.67	33.05	30.58
H	%	5.88	6.03	5.95	4.54	3.93	3.25
N	%	0.46	0.19	0.11	0.68	0.15	<0.1
TOC	%	48.66	51.75	46.74	41.39	31.44	28.36

Appendix E. Fibre image analyzer results (externally determined)

Analysis	Unit	Knot reject	Knot washing reject	Screening reject	Fibre sludge	Fibre clay	Deinking sludge
Sample statistics							
Particle count	n	509616	483499	1031420	500953	69094,00	269708,33
Fibre count	n	16665	20962	11478	22497	4733,00	16738,33
Fibre length (length-weighted)	mm	1,44	1,66	2,3	1,02	1,05	0,75
Fibre length results							
Lc(n)	mm	0,34	0,35	0,64	0,13	0,28	0,11
Lc(l)	mm	1,20	1,32	2,11	0,47	0,85	0,29
Lc(w)	mm	1,98	2,02	2,79	1,51	1,47	1,18
Lc(n) ISO	mm	0,91	0,95	1,52	0,52	0,72	0,41
Lc(l) ISO	mm	1,44	1,66	2,30	1,02	1,05	0,75
Lc(w) ISO	mm	2,01	2,06	2,78	1,72	1,51	1,52
Other results							
Fibre width	µm	26,26	36,79	28,38	26,38	22,07	24,46
Curl	%	5,29	3,15	11,08	9,96	5,37	13,06
Kink	(1/m)	1209,50	693,00	1796,80	2893,00	1224,35	3197,83
Kink / 1000	1/1000 fibres	1104,80	656,80	2731,60	1493,00	886,05	1299,63
Fines A	%	33,26	24,01	28,01	73,07	32,58	82,60
Fines B	%	0,33	0,19	0,46	1,68	1,36	12,90
Fines	%	97,26	92,60	98,11	98,98	94,19	99,05
Fibrillation (%)		1,06	1,23	1,06	1,23	1,16	1,75

Valmet Summary

Sample identification

Sample name	Knot reject

Sample statictics

Particle count	509616 n
Fiber count	16665 n

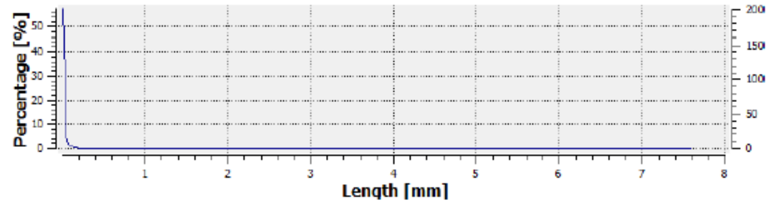
Fiber length results

Lc(n)	0.341 mm
Lc(l)	1.196 mm
Lc(w)	1.975 mm
Lc(n) ISO	0.914 mm
Lc(l) ISO	1.440 mm
Lc(w) ISO	2.006 mm

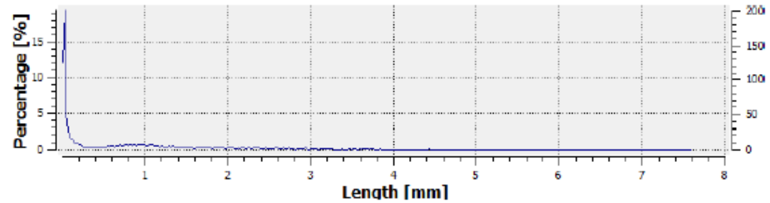
Other results

Fiber width	26.26 µm
Curl	5.29 %
Fines A	33.26 %
Fines B	0.33 %
Fibrillation	1.06 %

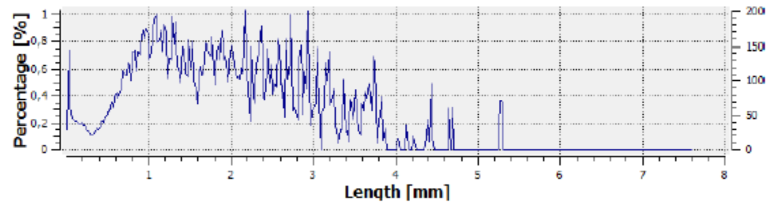
Arithmetic distribution



Length weighted distribution



Weight weighted distribution



Valmet Summary

Sample identification

Sample name	Knot reject

Sample statictics

FA image count	4095 n
Particle count	509616 n
Fiber count	16665 n

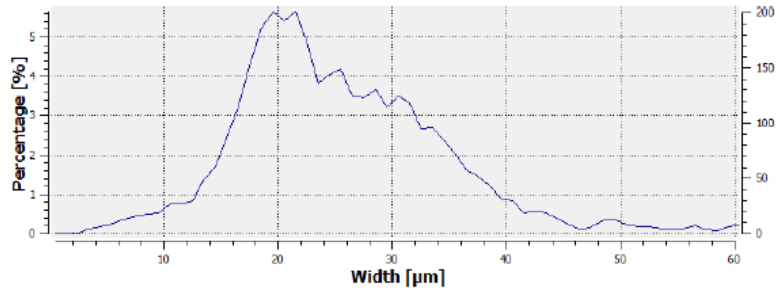
Other results

Fiber width	26.26 µm
Curl	5.29 %
Gravimetric coarseness	mg/m
Kink	1209.5 1/m
Kink / 1000	1104.8 1/1000 fibers
Fines A	33.26 %
Fines B	0.33 %
Fines %	97.26 %

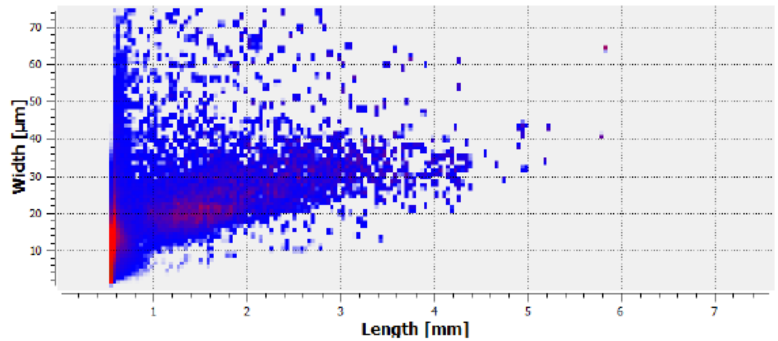
Fiber fractions

	Length	Width	Mass	Fibrillation
0.00 - 0.20 mm	25.6 %	16.5 µm	12.3 %	
0.20 - 0.60 mm	10.4 %	21.4 µm	8.3 %	1.30 %
0.60 - 1.20 mm	26.5 %	23.2 µm	23.7 %	1.25 %
1.20 - 2.00 mm	19.3 %	28.2 µm	24.9 %	1.05 %
2.00 - 3.20 mm	14.4 %	32.7 µm	24.0 %	0.94 %
3.20 - 7.61 mm	3.8 %	34.3 µm	6.9 %	0.88 %

Fiber width distribution



Length/width distribution



Valmet Summary

Sample identification

Sample name	Knot washing reject

Other results

Fiber width	36.79 µm
Curl	3.15 %
Fines A	24.01 %
Fines B	0.19 %
Fibrillation	1.23 %

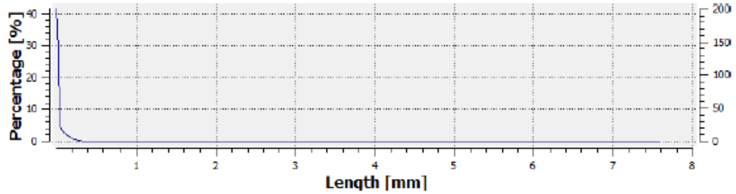
Sample statictics

Particle count	483499 n
Fiber count	20962 n

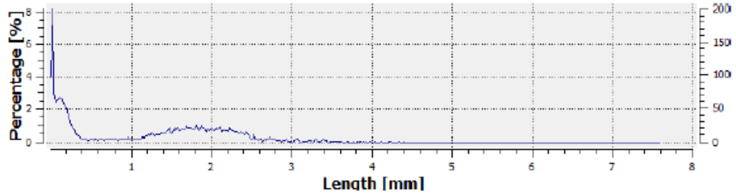
Fiber length results

Lc(n)	0.351 mm
Lc(l)	1.322 mm
Lc(w)	2.022 mm
Lc(n) ISO	0.947 mm
Lc(l) ISO	1.656 mm
Lc(w) ISO	2.061 mm

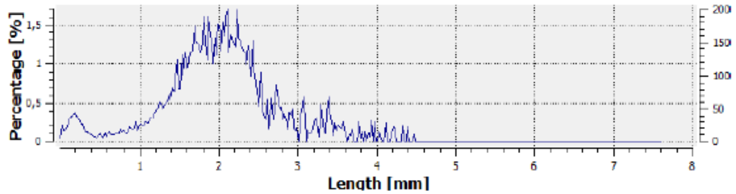
Arithmetic distribution



Length weighted distribution



Weight weighted distribution



Valmet Summary

Sample identification

Sample name	Knot washing reject

Other results

Fiber width	36.79 µm
Curl	3.15 %
Gravimetric coarseness	mg/m
Kink	693.0 1/m
Kink / 1000	656.8 1/1000 fibers
Fines A	24.01 %
Fines B	0.19 %
Fines %	92.60 %

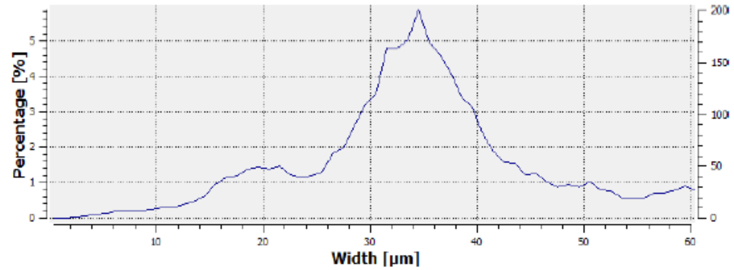
Sample statictics

FA image count	4080 n
Particle count	483499 n
Fiber count	20962 n

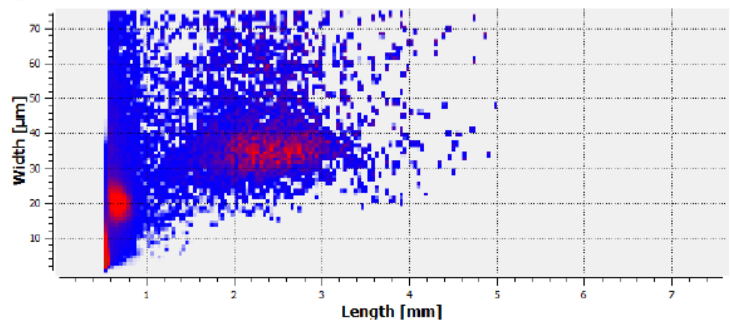
Fiber fractions

	Length	Width	Mass	Fibrillation
0.00 - 0.20 mm	22.8 %	21.5 µm	9.8 %	
0.20 - 0.60 mm	11.3 %	25.0 µm	6.8 %	1.17 %
0.60 - 1.20 mm	7.7 %	36.5 µm	8.9 %	1.36 %
1.20 - 2.00 mm	31.2 %	38.3 µm	37.6 %	1.32 %
2.00 - 3.20 mm	24.0 %	40.2 µm	31.7 %	1.28 %
3.20 - 7.61 mm	2.9 %	46.2 µm	5.3 %	1.17 %

Fiber width distribution



Length/width distribution



Valmet Summary

Sample identification

Sample name	Screening reject

Sample statictics

Particle count	1031420 n
Fiber count	11478 n

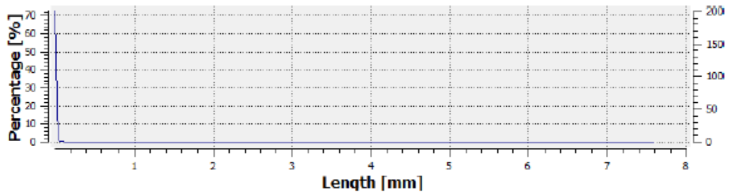
Fiber length results

Lc(n)	0.644 mm
Lc(l)	2.112 mm
Lc(w)	2.785 mm
Lc(n) ISO	1.520 mm
Lc(l) ISO	2.302 mm
Lc(w) ISO	2.782 mm

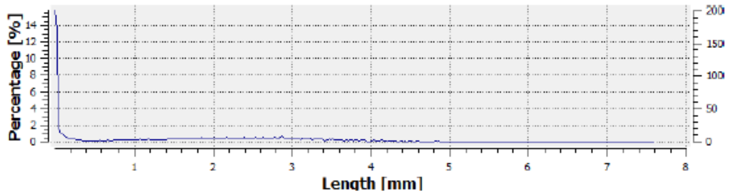
Other results

Fiber width	28.38 µm
Curl	11.08 %
Fines A	28.01 %
Fines B	0.46 %
Fibrillation	1.06 %

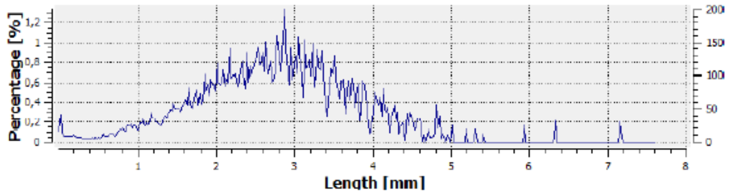
Arithmetic distribution



Length weighted distribution



Weight weighted distribution



Valmet Summary

Sample identification

Sample name	Screening reject

Sample statictics

FA image count	4057 n
Particle count	1031420 n
Fiber count	11478 n

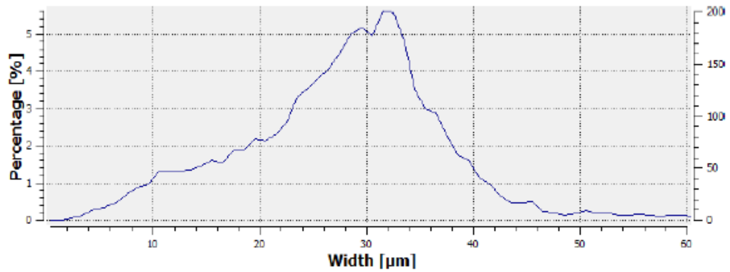
Fiber fractions

	Length	Width	Mass	Fibrillation
0.00 - 0.20 mm	9.8 %	16.3 µm	3.6 %	
0.20 - 0.60 mm	4.2 %	22.0 µm	2.9 %	1.33 %
0.60 - 1.20 mm	9.3 %	25.0 µm	7.7 %	1.40 %
1.20 - 2.00 mm	19.7 %	27.6 µm	18.9 %	1.20 %
2.00 - 3.20 mm	38.3 %	30.0 µm	42.5 %	1.09 %
3.20 - 7.61 mm	18.7 %	32.3 µm	24.5 %	0.99 %

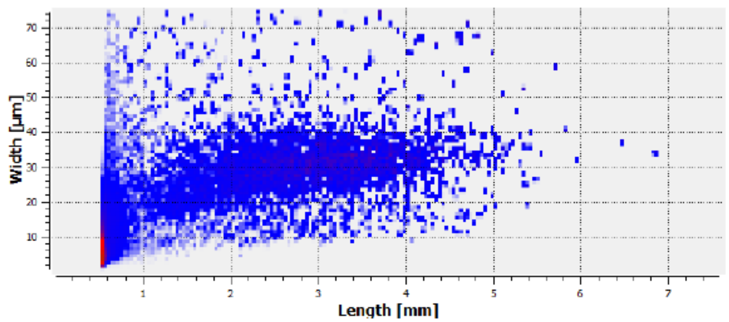
Other results

Fiber width	28.38 µm
Curl	11.08 %
Gravimetric coarseness	mg/m
Kink	1796.8 1/m
Kink / 1000	2731.6 1/1000 fibers
Fines A	28.01 %
Fines B	0.46 %
Fines %	98.11 %

Fiber width distribution



Length/width distribution



Valmet Summary

Sample identification

Sample name	Fibre sludge

Sample statictics

Particle count	500953 n
Fiber count	22497 n

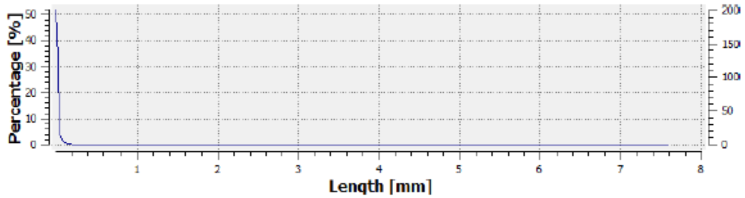
Fiber length results

Lc(n)	0.129 mm
Lc(l)	0.468 mm
Lc(w)	1.513 mm
Lc(n) ISO	0.516 mm
Lc(l) ISO	1.024 mm
Lc(w) ISO	1.718 mm

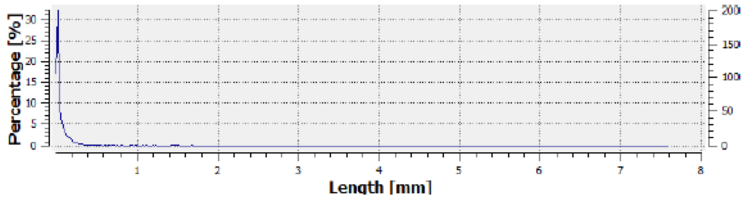
Other results

Fiber width	26.38 µm
Curl	9.96 %
Fines A	73.07 %
Fines B	1.68 %
Fibrillation	1.23 %

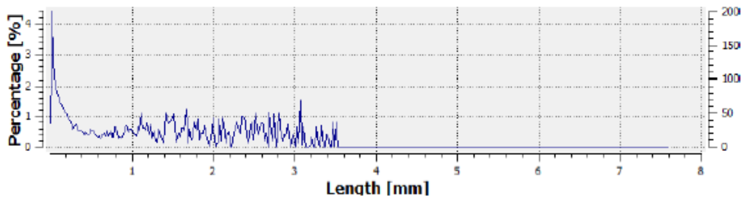
Arithmetic distribution



Length weighted distribution



Weight weighted distribution



Valmet Summary

Sample identification

Sample name	Fibre sludge

Sample statictics

FA image count	4105 n
Particle count	500953 n
Fiber count	22497 n

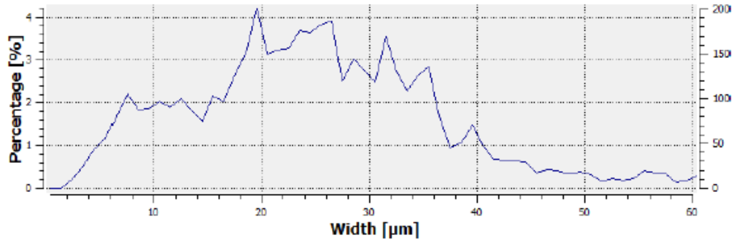
Other results

Fiber width	26.38 µm
Curl	9.96 %
Gravimetric coarseness	mg/m
Kink	2893.0 1/m
Kink / 1000	1493.0 1/1000 fibers
Fines A	73.07 %
Fines B	1.68 %
Fines %	98.98 %

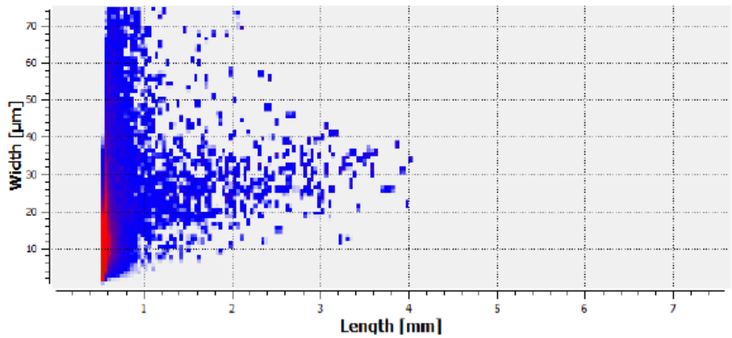
Fiber fractions

	Length	Width	Mass	Fibrillation
0.00 - 0.20 mm	68.6 %	18.4 µm	50.5 %	
0.20 - 0.60 mm	13.0 %	27.6 µm	21.4 %	1.58 %
0.60 - 1.20 mm	7.1 %	27.1 µm	10.2 %	1.39 %
1.20 - 2.00 mm	5.8 %	28.7 µm	9.0 %	1.15 %
2.00 - 3.20 mm	5.0 %	30.5 µm	8.1 %	1.02 %
3.20 - 7.61 mm	0.5 %	30.0 µm	0.8 %	0.92 %

Fiber width distribution



Length/width distribution



Valmet Summary

Sample identification

Sample name	Fibre clay

Sample statictics

Particle count	70966 n
Fiber count	4829 n

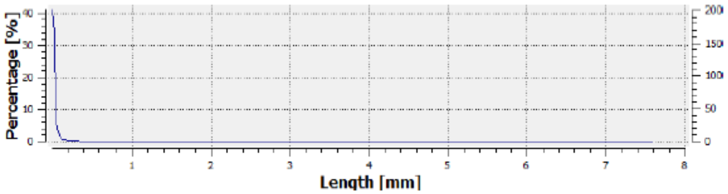
Fiber length results

Lc(n)	0.279 mm
Lc(l)	0.836 mm
Lc(w)	1.467 mm
Lc(n) ISO	0.717 mm
Lc(l) ISO	1.036 mm
Lc(w) ISO	1.503 mm

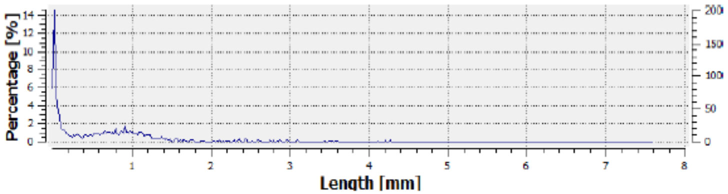
Other results

Fiber width	21.99 µm
Curl	5.46 %
Fines A	33.42 %
Fines B	1.60 %
Fibrillation	1.18 %

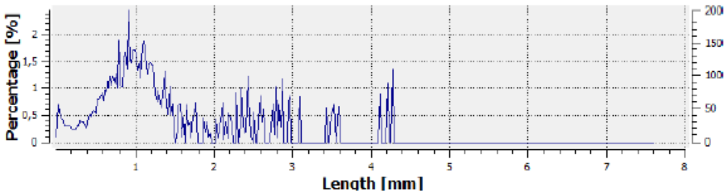
Arithmetic distribution



Length weighted distribution



Weight weighted distribution



Valmet Summary

Sample identification

Sample name	Fibre clay

Sample statictics

FA image count	2037 n
Particle count	70966 n
Fiber count	4829 n

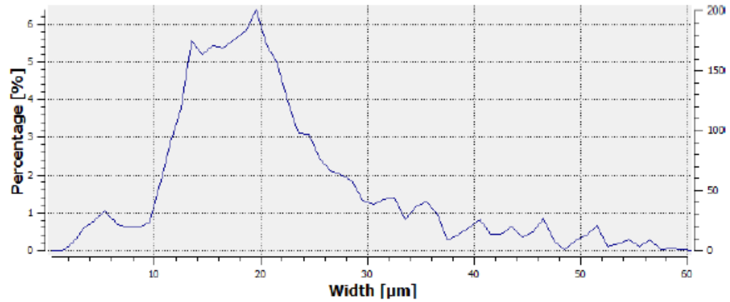
Fiber fractions

	Length	Width	Mass	Fibrillation
0.00 - 0.20 mm	23.8 %	18.1 µm	18.5 %	
0.20 - 0.60 mm	17.2 %	20.0 µm	14.7 %	1.36 %
0.60 - 1.20 mm	39.7 %	20.2 µm	32.4 %	1.22 %
1.20 - 2.00 mm	11.6 %	26.3 µm	16.8 %	1.06 %
2.00 - 3.20 mm	6.2 %	34.2 µm	14.1 %	1.26 %
3.20 - 7.61 mm	1.5 %	35.8 µm	3.6 %	1.08 %

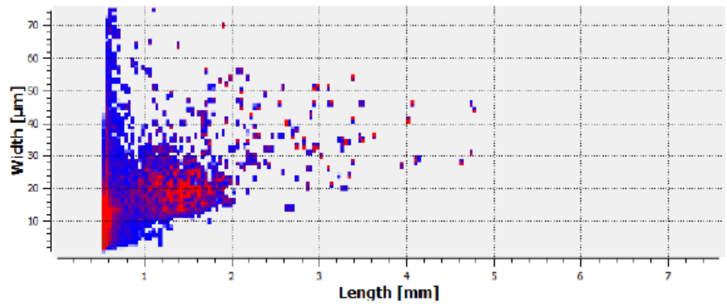
Other results

Fiber width	21.99 µm
Curl	5.46 %
Gravimetric coarseness	mg/m
Kink	1226.3 1/m
Kink / 1000	878.9 1/1000 fibers
Fines A	33.42 %
Fines B	1.60 %
Fines %	94.25 %

Fiber width distribution



Length/width distribution



Valmet Summary

Sample identification

Sample name	Deinking sludge

Sample statictics

Particle count	268790 n
Fiber count	16159 n

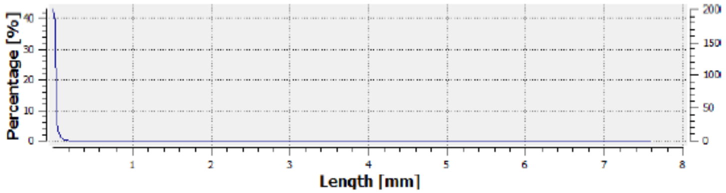
Fiber length results

Lc(n)	0.110 mm
Lc(l)	0.286 mm
Lc(w)	1.193 mm
Lc(n) ISO	0.409 mm
Lc(l) ISO	0.742 mm
Lc(w) ISO	1.539 mm

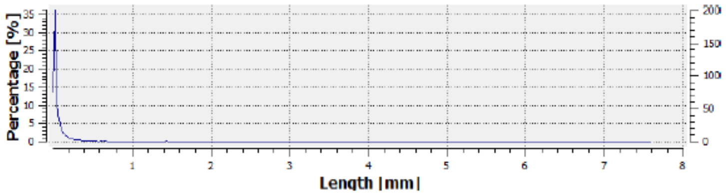
Other results

Fiber width	24.62 µm
Curl	12.94 %
Fines A	82.65 %
Fines B	12.72 %
Fibrillation	1.78 %

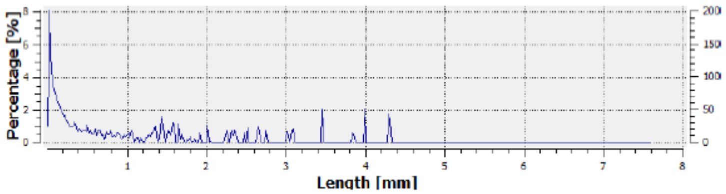
Arithmetic distribution



Length weighted distribution



Weight weighted distribution



Valmet Summary

Sample identification

Sample name	Deinking sludge

Sample statictics

FA image count	2064 n
Particle count	268790 n
Fiber count	16159 n

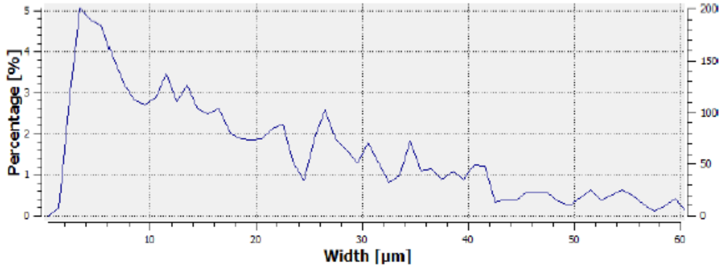
Fiber fractions

	Length	Width	Mass	Fibrillation
0.00 - 0.20 mm	81.1 %	20.0 µm	68.4 %	
0.20 - 0.60 mm	10.8 %	28.8 µm	18.8 %	1.88 %
0.60 - 1.20 mm	3.8 %	24.9 µm	4.6 %	1.60 %
1.20 - 2.00 mm	2.6 %	32.9 µm	5.1 %	1.41 %
2.00 - 3.20 mm	1.2 %	32.9 µm	2.2 %	1.34 %
3.20 - 7.61 mm	0.6 %	31.1 µm	0.8 %	1.82 %

Other results

Fiber width	24.62 µm
Curl	12.94 %
Gravimetric coarseness	mg/m
Kink	3288.4 1/m
Kink / 1000	1347.2 1/1000 fibers
Fines A	82.65 %
Fines B	12.72 %
Fines %	99.07 %

Fiber width distribution



Length/width distribution