OPTIMIZATION OF WASTEWATER TREATMENT PLANT AFTER MODIFICATION OF THE PULPING PROCESS AT OULU MILL

Lappeenranta–Lahti University of Technology LUT

Master's thesis in Sustainable science and solutions program

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ABSTRACT

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Keywords: Pulp mill, wastewater, hydrogen sulphide, redox, ORP, ferric sulphate, odour, primary clarifier, aeration tank, activated sludge plant, effluent treatment

In this thesis, possibilities for optimizing the operation of Stora Enso's Oulu pulp mill's wastewater treatment plant were investigated. The target of this thesis is to reduce the costs of energy and chemical consumption in the wastewater treatment plant. Odour problems caused by hydrogen sulphide were also researched.

The work includes three different test phases. In the first test phase, a target value was set for oxygen concentration in the aeration tank and the automation control was taken into use. Before starting the test phase, oxygen concentration was unnecessarily high. The test phase was successful because a lower oxygen concentration and energy savings were achieved.

At the pulp mill's wastewater treatment plant, ferric sulphate is used to control odour problems caused by hydrogen sulphide. In the second test phase, the goal was to investigate the possibility of using redox potential as a parameter for adjusting ferric sulphate. During the test phase input of ferric sulphate was first adjusted to lower and then to higher values. Samples were taken daily from which changes in the redox value and sulphate concentration were analysed. The results shows that redox potential can be used for adjusting ferric sulphate, because redox potential reacts quickly when adjusting ferric sulphate. The normalization of the sulphate concentration back to the normal value needed a longer reaction time than the normalization of redox potential.

In the third test phase, the quality of the wastewater flows from different fractions is analysed and the largest sources of sulphate were found. Sulphate is one of the most important factors for the generation of hydrogen sulphide, in addition to suitable conditions. The biggest sources of sulphate were found from the circulation overflow water of the pulp drying process, the wastewater from the continuous cooking process, and in the wastewater from the recovery process.

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Tässä diplomityössä tutkittiin optimointi mahdollisuuksia Stora Enson Oulun sellutehtaan jätevedenpuhdistamon toiminnassa. Tavoitteena oli vähentää kemikaali ja energia kustannuksia jätevedenpuhdistamolla. Samalla ratkottiin rikkivedyn aiheuttamia hajuongelmia.

Työ sisältää kolme eri koepistettä. Ensimmäisessä koepisteessä ilmastuksen happipitoisuudelle asetettiin tavoite arvo sekä otettiin automaatiosäätö käyttöön. Ennen koepisteen aloittamista happipitoisuus oli tarpeettoman korkea. Koepiste onnistui. sillä alempi happipitoisuus ja energian säästö saavutettiin.

Sellutehtaan jätevedenpuhdistamolla käytetään ferrisulfaattia rikkivedyn aiheuttamien hajuongelmien hallintaan. Koepiste 2:ssa tavoitteena oli tutkia redox-potentiaalin käyttömahdollisuutta ferrisulfaatin säätö parametrinä. Koepisteen aikana säädettiin ferri sulfaatin syöttöä ensin pienempiin ja sitten suurempiin arvoihin. Päivittäin otettiin näytteitä, joista tutkittiin redox-arvon ja sulfaatin konsentraation muutoksia. Tuloksena voidaan sanoa, että redox-potentiaali toimisi hyvin ferrisulfaatin säätöön, sillä redox potentiaali reagoi nopeasti ferrisulfaatin syöttöä säädettäessä. Sulfaattipitoisuuden palautuminen takaisin normaaliin arvoon, tarvitsee kuitenkin pidemmän reagointi ajan kuin redox.

Kolmannessa koepisteessä analysointiin jätevedenpuhdistamolle kulkeutuvien jätevesien laatuja eri jakeista ja löydettiin suurimmat sulfaatin lähteet. Sulfaatti on rikkivedyn syntymiselle yksi tärkeimmistä tekijöistä, sopivien olosuhteiden lisäksi. Suurin sulfaatin lähde löytyi kuivatuksen nollaveden ylikaadosta, keittämön alueen jätevesistä sekä lipeäpuolen jätevesistä.

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Finally, I'm going to thank myself as well. The topic was not easy and it required a lot of independent work. However, in the end, I got the job done and I can now be proud of myself. I did it!

Oulu 13.6.2023

Anna Lassila

ABBREVIATIONS

AAS	Atomic absorption spectrometer
ADt	Per produced tonne of air-dry pulp
AOX	Adsorbable organic halides
BAT	Best available technique
BOD	Biological oxygen demand
COD	Chemical oxygen demand
DO	Dissolved oxygen
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EOX	Electrocatalytic oxidation
F/M	Food and microorganism ratio
IC	Ion chromatography
N	Nitrogen
ORP	Oxidation-reduction potential
P	phosphorous
Redox	Reduction-oxidation
SRT	Solid retention time
SVI	Sludge volume index
TOC	Total organic carbon
TSS	Total suspended solids
VFA	Volatile fatty acids
VOCs	Volatile organic compounds
WW	Wastewater

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Abstract

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Abbreviations determination

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1. Introduction

Sustainable development is one driving force in industries' actions. Decisions are made by thinking about environmental, economic, and social aspects. The goal is to make industrial processes as sustainable as possible. (Springer 2000, 3-4) The pulp and board industry is one of the most energy consuming industry fields in the world. For one ton of produced paper, the pulp and paper industry consumes 250-300 m^3 of water. (Chaundhry & Paliwal 2018) Because of changing environmental regulations, the pulp and paper industry must be able to reduce its environmental impact on air, water, and land. Industries have to adapt to new restrictions and monitor carefully produced waste and effluents. (Asghar et al. 2007) Besides decreasing environmental impact, nowadays it is also important to search for ways to reduce energy consumption because of increased electricity and heating energy prices (Hiilamo 2022). Like every other industry today, Stora Enso's Oulu Mill is constantly reducing its environmental impact on water, air, and land. The pulping process has recently been changed to produce an unbleached sulphate pulp instead of a bleached sulphate pulp. With this change, the amount and the quality of wastewater have also changed. The purpose of this study is to research methods for optimizing the operation of the wastewater treatment plant after modification of the pulping process and at the same time find solutions for its ongoing odour problem.

The production of unbleached sulphate pulp produces 20-60 m^3/metric ton of wastewater, and the production of bleached sulphate pulp produces 60-100 m^3/metric ton of wastewater. (Dahl et al. 2008, 89) Wastewater from the unbleached pulp process does not have any AOX (adsorbable organic halides) -compounds and the amount of phosphorous and COD is only half of wastewater from bleached pulp. (Cabrera 2017) According to Cabera (2017) wastewater from the bleaching process contains more compounds of lignin than wastewater from the unbleached pulp process. The most common odour producer in wastewater treatment plants is hydrogen sulphide (H_2S) (WEF 2004, 134) and it is also considered as a indicator of odours in wastewater (Pulkkinen 2014, 1). Hydrogen sulphide also causes corrosion of concrete in wastewater treatment systems. (Krom et al. 2001, 1) Desulfovibrio-bacteria cause a biological reaction in which sulphate (SO_4^{-2}) will be become reduced, and hydrogen sulphide is produced under anaerobic conditions. (Pulkkinen 2014, 5; WEF 2004,

134) ORP (oxidation-reduction potential) can be used to assess whether the conditions in wastewater are suitable for the generation of hydrogen sulphide. ORP describes wastewater's ability for oxidation or reduction. ORP values for hydrogen production are between -50 mV to –250 mV. (Pulkkinen 2014, 7; Higgins 2013) Ferric salts can be used to prevent odours caused by hydrogen sulphide (Boon et al. 2007, 2-5). Ferric sulphate prevents the redox value from decreasing to the conditions necessary for the generation of hydrogen sulphide. Commonly, ferric sulphate is used to precipitate and remove phosphorus and solids from wastewater. For odour control, the use of ferric sulphate is less common. (Kaseva 2013, 14-17)

This thesis includes a theory part and a practical part. The theory part includes descriptions about the general kraft pulping process, products, and the content of effluents. There is also a description of relevant legislation and regulations, information about wastewater treatment in the pulp and board industry in general, and a description of Oulu mill's processes. The practical part includes the creation of a model of a wastewater treatment plant by Wedge, measurement plan description, results, and discussion of test phases' results. The modelling process chart of wastewater treatment plant in Wedge is used for analysing parameters during test phases. The targets for optimization will provide tools to improve energy efficiency of the aerobic tank, optimize the feed of ferric sulphate and find the biggest sulphate sources from upstream flows. Used measurement methods include Wedge-software for monitoring different parameters and laboratory analyses. The goal of the test phases is to find solutions and reasons for odour problems caused by hydrogen sulphide in the primary clarifier.

2. Wastewaters from the pulping process

This chapter consists of three parts: a general model of the pulping process, typical products from pulping processes, and the produced wastewaters. An example of pulp and paper process with effluents is presented in figure 1.

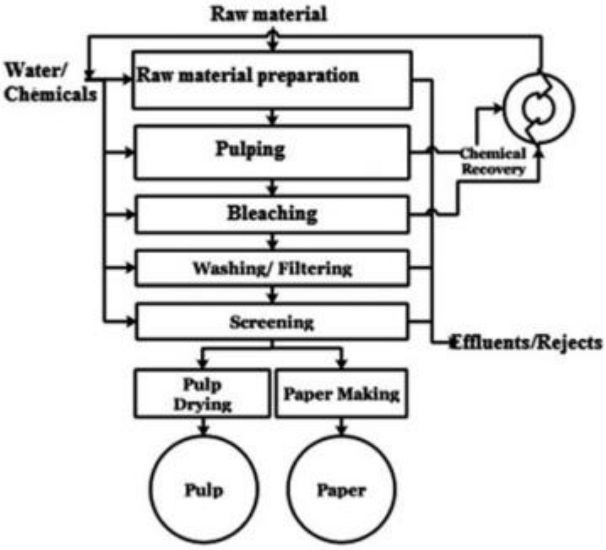


Figure 1. A process chart of the pulp and paper making process. (Bajpai 2017, 56)

2.1 General model of the pulping process

One of the most common sulphate pulping process methods is presented in this chapter. The process steps are wood handling, cooking, washing, screening, oxygen delignification, bleaching, and drying. In figure 2 the distribution between different chemical pulping methods is presented.

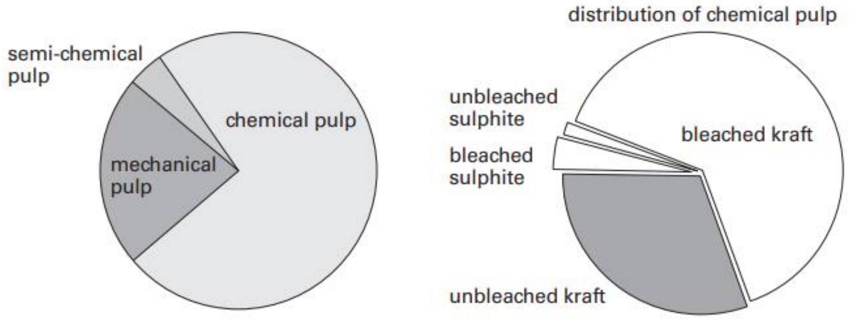


Figure 2. Distribution between different pulping methods. (Gunnar 2009, 9)

It can be seen from figure 2 that chemical pulping is the most popular method for producing pulp and most mills use a bleaching process to produce white and bright paper. However, the share of unbleached kraft pulp is more than a quarter of the total amount. Kraft pulping is the most used method of chemical pulping.

2.1.1 Wood handling

Wood is transported to the mill by train, truck, or waterways. To avoid the decay of the wood, it has to be used as fast and fresh as possible. This is the reason why wood storage is relatively small in the field. (Bajpai 2015, 14; KnowPulp 2022) After transportation, logs are cut into standard length before entering to the process (Gunnar et al. 2009, 13). The process steps of wood handling are:

1. **De-icing:** In winter logs are frozen so a de-icing process is needed before debarking. This process is usually located on the infeed conveyor of the debarking drum. (KnowPulp 2022)

2. **Debarking:** The goal is to remove as much as possible of the outer layer of the wood (bark) with minimum wood losses (Dutt et al 2021, 33). Debarking is performed in a drum, usually by using water. If there is still some bark left after debarking, it will be seen later in the finished paper as darker impurities. (KnowPulp 2022)

3. **Washing and collection of stones:** After debarking, the logs will be washed in a conveyor under water showers while all stone are collected by stones removal rollers. (KnowPulp 2022)

4. **Chipper infeed line:** The chipper infeed line contains a metal detector which stops the process when recognising metal contaminants in logs. (Gunnar et al. 2009, 13)

5. **Chipper:** Logs are cut into as homogenous chips as possible. This way chips have a large surface area to help cooking chemicals to work better. (Dutt et al. 2021, 33-34) The chipper has a huge effect on the resulting pulp's quality. (Bajpai 2015, 14-15)
6. **Screening**: Screening helps to separate too little or too large pieces from the chip flow. (Bajpai 2015, 14-15)

The by-products, bark and sawdust, are treated by drying and chipping them into smaller pieces (Bajpai 2015 14-15). After treating all by-products, they will be transported to the power plant. In the power plant the by-products are burned to produce energy for the mill's usage. (Gunnar at al. 2009, 22) The bark and sawdust can be collected together or transported separately to the power plant (KnowPulp 2022).

2.1.2 Cooking

The cooking process takes place in the digester where all chips are fed (Fogelholm et al. 1999, 39). The main purpose of the cooking process is to separate lignin from the chips by using chemicals and heat to release wood fibres (Gunnar et al. 2009, 4). The other purpose of the cooking process is to keep cellulose containing fibres as long, unbroken, and as strong as possible (KnowPulp 2022). Together with lignin, cooking also removes wood extractives and approximately half of the wood fibres will be dissolved due to pulping chemicals (Gunnar et al. 2009, 4). In the sulphate cooking process white liquor is used for dissolving lignin from wood fibres. White liquor contains a sodium hydroxide (NaOH) and a sodium sulphide (Na_2S). (Bajpai 2015, 16) The temperature in the sulphate pulping process is normally between 150-170 °C (Dutt et al. 2021, 35; KnowPulp 2022).

There will be some lignin left in the pulping mass because the lignin removing process in cooking is not perfect. This leftover lignin is described with a kappa number. The kappa number for bleached pulp is typically between 15-30 and for unbleached pulp it can be between 40-100. The lignin will cause a brown colour in the pulp which can be modified by the bleaching process. (Biermann 1996, 86-87)

Two examples of cooking processes are batch cooking and continuous cooking. In batch method, pulp is processed through each phase individually before moving to the next digester in the cooking process. The digester facility contains many digesters. In the continuous process, chips and chemicals are continuously fed into the top of the digester and mass is removed from the bottom. Different phases of the continuous process happen in different zones of the digester. (KnowPulp 2022)

2.1.3 Oxygen delignification

Oxygen delignification is considered an environmental and economical investment. This process occurs after the cooking process and its purpose is to remove residual lignin from the pulp. Oxygen delignification uses oxygen and alkali to reduce lignin and it can include one or two stages. This process lowers the kappa number with a more gentle and selective process than bleaching. (Biermann 1996, 133) The oxygen delignification process oxidizes lignin with oxygen into a form which is possible to dissolve into alkali (Genco et al. 2012, 9-10). Because the pH is between 9,5-10,5 and the temperature is approximately 100°C degrees, the process environment is alkaline (Bennett 2017, 33). It removes the colour of lignin compounds and impurities from the pulp (KnowPulp 2022).

2.1.4 Washing and screening

Pulp always contains some contaminants, like dissolved minerals and the organic substances of black liquor from pulp fibres, which can cause problems in the quality of production runnability and damages equipment. These contaminants can be removed by washing and screening. Impurities or contaminants can be divided into wood impurities and non-wood impurities. (Brown et al. 2017, 5)

The washing process occurs after the cooking process and between each bleaching stage. The washing of the brown mass after cooking will recover the dissolved organic and inorganic materials. (Bajpai 2015, 16-21) Washing between bleaching stages will reduce carryover of harmful substances to the next phase. It is also possible to change the pulp's pH, temperature, or consistency so it will adjust better to the next step. Washing makes it possible to recover residual liquor. (Sixta 2008, 511) When the pulp is washed between bleaching phases, it will reduce bleaching chemical need and number of impurities in bleaching effluents. (Bajpai 2015, 16-21)

A major part of wood and non-wood impurities are removed during the screening process in a screen room. The main purpose of this process stage is to minimize impurities going through the process. A good screening process will reduce costs of chemicals in later processes because there are not as many impurities disturbing the white and bright colour of the paper. Separation is performed by dividing impurities by different sizes or weights of particles. (Bajpai 2015, 16-23) Mechanic screening is used when particles are separated by different sizes or shapes. Gravimetric or centrifugal screening is used when separating particles by different weights. Both methods are used because screening is performed in different stages and both are needed for separating all kind of impurities from the pulp. (Sixta 2008, 561-562)

2.1.5 Bleaching

The main purpose of the bleaching process is to increase the brightness and cleanliness of pulp. All particles of pulp are either brightened or removed to achieve a clean white colour. The main cause for the brown colour of pulp is residual lignin which must be treated or removed. Bleaching is carried out in several stages because only one bleaching stage cannot achieve the target brightness without damaging pulp's strength. After every bleaching stage there is a washing process where pulp is washed before the next stage. (Bajpai 2018, 465-471)

Bleaching continues the colour modifying and delignification process of the pulp and it uses bleaching chemicals. The chemicals used in bleaching are more selective than the chemicals used in cooking, so they are more precise at removing lignin from pulp. The bleaching chemicals are presented in table 1. (Fogelholm et al. 1999, 150-151)

Table 1. Bleaching chemicals and their functions. (Fogelholm et al. 1999, 151; KnowPulp 2022)

Group number	Chemicals	Function
Group 1	Chlorine (Cl_2) Ozone (O_3) Peroxide acid (Paa, Caa)	Reaction with aromatic lignin units
Group 2	Chlorine dioxide (ClO_2) Oxygen (O_2)	Reaction with free phenolic hydroxyl groups
Group 3	Hypochlorite (H) Hydrogen peroxide (H_2O_2)	Reaction only with certain functional groups

2.1.6 Drying

In unintegrated mills, it is necessary to have drying, baling, and storage facilities for pulp to enable easier transport to different locations. The pulp is also dried in integrated mills in situations when some of the pulp is sold directly to the customers. (KnowPulp 2022) The moisture content of pulp is approximately 10 % and density of the bales is between 600-800 kg/m^3 (Fogelholm et al. 1999, 225-226). The quality of dried pulp is different than not dried pulp. When pulp is dried, hornification phenomena accurse, this means weaker fibre swelling on wetting, smaller water retention capacity, and smaller water adsorption of fibres. (KnowPulp 2022)

The drying process is divided into sections. The first section is the wire and press section (wet end) and there are four different types of processes: drum machine, fourdrinier machine, pick-up machine, and double-wire machine (Fogelholm et al. 1999, 667-669). In the first section pulp is dried by using thermal energy from outside. Dewatering is performed so that the dry solids content of the pulp is 90 % after the wire and press section. After the wire and press section pulp moves to the dryer section which has two types: web drying and flash drying. (KnowPulp 2022) All drying methods produce evaporated water which can be utilized for heating process water and buildings in the mill area. The evaporated water is always removed from the drying process because it contains a lot of heat and moisture which cannot be utilized in the drying process. (Fogelholm et al. 1999, 229-230)

2.1.7 The chemical cycle of the pulping process

Cooking chemicals are mostly collected from the washing process and then treated and used again in the pulping process. This chemical cycle is called the recovery cycle. The collected liquor from the washing process is a weak black liquor and it contains spent cooking chemicals and dissolved organic material. (Gunnar et al. 2009, 5-6) The main targets in chemical cycle are reutilizing inorganic cooking chemicals, energy production, reducing pollution in the air and water, and regeneration of inorganic cooking chemicals (Bajpai 2018, 425).

Evaporation is the first part of the recovery cycle, during which the black liquor's solid content is increased and the liquor is dewatered (approximately 95 % of the water content is reduced). After the evaporation process the product is called strong black liquor. Na_2SO_4 - chemical is added and the mixed liquid is fed into the recovery boiler. (Gunnar et al. 2009, 5-6) The burned strong black liquor forms smelt which includes recovered inorganic cooking chemicals. The compounds Na_2S and Na_aCO_3 form smelt, (Bajpai 2018, 425) which is created in the recovery boiler by utilizing recycling water. The water will be evaporated, and it can be used in a turbine and generator to produce energy for mill. (Gunnar et al. 2009, 5-6) Green liquor is the liquor that remains after the burning process in the recovery boiler. Green liquor contains dissolved smelt and water, and it is basically black liquor without organic material. (KnowPulp 2022; Bajpai 2018, 425)

Green liquor also contains solid material which needs to be separated from the liquor. This process must be done before the white liquor preparation plant to avoid clogging and breaking process equipment and pipes. The first step is to add calcium oxide (CaO) to the green liquor and this mixture will form a slaked lime (calcium hydroxide, $Ca(OH)_2$). In the causticizing process, calcium hydroxide and sodium carbonate are used to create sodium hydroxide and a solid lime mud. White liquor can be collected from this mixture by separating the lime mud via filtration or thickening. After this treatment the white liquor is ready to be used again in the cooking process. The lime mud will be washed from the white liquor in the washing plant. The separated and washed white liquor from the lime mud is called weak whitewash and it is used in the smelt dissolver. The lime mud's calcium carbonate is burned, and it forms reburned lime (CaO) which is used again in the chemical cycle. (Gunnar et al. 2009, 298-299)

2.2 Products from pulping processes

Different types of pulps, pulping products and their properties are presented in table 2. The pulp types are divided into four categories: bleached softwood pulp and hardwood pulp, and unbleached softwood pulp and hardwood pulp.

Table 2. The different types of pulping types, papers, and cardboards from kraft pulping. (KnowPulp 2022; Metsä, Pulp end uses; Cord, D; Stora enso)

Type of pulp	Products	Properties
Bleached softwood pulp	Reinforcement pulp: 1. Magazine paper 2. Fine paper	1. Tearing resistance, tensile strength, fibre length, linear density of fibre, homogeneity 2. High brightness, cleanliness, rapid tensile strength development, good brightness performance, homogeneity
	Board chemical pulp 1. Packaging food products 2. Coating and printing 3. Folding board	High strength, high bulk: 1. Chemical and physical cleanliness 2. Optical properties, smoothness, porosity 3. High brightness, cleanliness, rapid tensile strength development, homogeneity
	Tissue papers	Softness, smoothness, dust-freeness, absorbency, high bulk, cleanliness
Bleached hardwood pulp	Fine paper chemical pulp	Cleanliness, good brightness performance, even formation, high opacity, smooth surface
	Paperboards	Brightness performance, high bulk, stiffness cleanliness
	Tissue papers	Softness, flexible fibres, sheet bulk, good liquid adsorption

Unbleached softwood pulp, high yield chemical pulp:	Kraft liner base stock (base layer)	Good tensile strength, bursting strength, tearing strength, stiffness, high Kappa number (30-100), high bulk
	Liquid packaging board (thick base layer)	Bending stiffness, high bulk, bursting strength, absorbency, cleanliness, density
	Sack paper	Kappa number 60, defibrated, air permeability, stiffness, sufficient friction, strength, good stretch, tensile strength
	Laminating paper	Kappa number 50, defibrated, absorbency, processability
Unbleached hardwood pulp	Core-board	Internal bond strength, high bulk, high caliper, stiffness
	Corrugated board	Good cross direction strength, stiffness, high bulk,

2.3 Effluents from pulping processes

The effluent from the pulping process consists of traces of wood and its changed forms, wood polymers, process chemicals and process chemical reaction products, different kinds of fillers, and auxiliary chemicals. (Dahl et al. 2008, 87) The main sources of effluents from the pulping process are wastewaters from wood handling, cooking, pulp washing, and pulp bleaching stages. The effluent from the pulping process also contains lignin which will cause the brown colour of it. (Bajpai 2017, 61-63)

The following parameters are used when describing the quality of wastewater: BOD (biological oxygen demand), COD (chemical oxygen demand), suspended solids, nutrients, AOX (adsorbable organic halides), chloro-organics, colour, and toxicity. The parameters describe:

- BOD is used for measuring biological oxygen demand and it describes biological oxygen demand for seven days.

- COD describes the amount of oxygen which is consumed in the dissolving chemical composition of the impurity.

- Nitrogen and phosphorous are the most common nutrients in wastewater. Nitrogen is typically measured using the Kjeldahl method.

- AOX describes the number of adsorbable organic halides in wastewater.

- The toxicity of water depends on the concentration of toxic compounds in the wastewater (Bajpai 2017, 61-63).

Examples of effluent load amounts from the pulping process are presented in table 3. The presented loads are effluent flow, amount of suspended solids, BOD, COD, nitrogen, and phosphorous.

Table 3. Examples of effluent loads when producing pulp from forest products. (Dahl et al. 2008, 89)

Product	**Effluent flow [m^3/metric ton]**	**Suspended solids [kg/metric ton]**	**BOD [kg/metric ton]**	**COD [kg/metric ton]**	**Nitrogen [g/metric ton]**	**Phosphorous [g/metric ton]**
Sulphate pulp, unbleached	20-60	12-15	5-10	20-30	200-400	80
Sulphate pulp, conventional bleaching	60-100	12-18	18-25	60-120	300-500	120

In table 3 it can be seen that there is difference in loads between bleached and unbleached pulps. The amount of the produced suspended solids are similar in both cases, but the biggest difference is between amount of produced BOD, COD, and phosphorous. These all are bigger amounts when producing bleached kraft pulp, which is due to the use of bleaching chemicals and more precise lignin removal from the pulp. It also has to be noticed that effluent flow’s volume is much bigger, almost double, when producing bleached pulp.

Table 4 presents the amount of TSS, BOD, AOX, COD, P, and N in the wastewater flows from different pulp mill processes. The unit m3/Adt describes produced volume per produced tonne of an air-dry pulp (British Columbia 2018).

Table 4. Loads of wastewater from different departments. (Cabrera 2016)

Department	**Flow, m3/Adt**	**TSS kg/Adt**	**BOD, kg/Adt**	**AOX, kg/Adt**	**COD, kg/Adt**	**P, g/Adt**	**N, kg/Adt**
Debarking	2,5	4	2	0	5	20	0,2
Washing and screening	0,5	3	1	0	2	1	0,015
Bleaching	31	2	10	1,2	35	47	0,075
Condensates	1	0	1	0	3	0	0
Total	35	9	14	1,2	45	68	0,290

From table 4 it can be noticed that the amount of AOX in effluent is 0 from all other departments except bleaching. In table 4, the bleaching process is the most hazardous process stage when producing pulp. In the bleaching process dangerous chemicals like chlorine, hydrogen peroxide, and ozone are used. Most pollutants are produced in the bleaching stage. (Dudhagara et al. 2021) TSS (total suspended solids) in effluent is higher from debarking, washing, and screening departments than from the bleaching stage. All other values of effluent loads are greater when considering effluent from the bleaching department. Table 5 presents effluent loads from wood debarking, pulping and pulp bleaching processes.

Table 5. Wastewater forming from different process stages in sulphate pulping production. (Dudhagara et al. 2021)

Wood debarking	Pulping	Pulp bleaching
- bark particles - suspended solids - grits - pigments - dirt - BOD	- colour - bark particles - soluble wood material - resin - acid - fatty acid - VOCs (volatile organic compounds) - (AOX)	- dissolved lignin - colour - COD - carbohydrates - AOX - EOX (Electrocatalytic oxidation) - VOCs

- COD	- BOD - COD - dissolved inorganic compounds	- chlorophenols - halogenated hydrocarbons

From table 5 it can be noticed that the pulping process generates some amount of AOX compounds. From the previous tables 3 and 4 the amount of AOX is 0, so it can be considered that the produced amount is very small and it is not taken into account. The pulping process generates the biggest amount of different kinds of impurities in wastewater.

3. Regulations and legislation for controlling wastewater treatment

This chapter describes how different regulations and legislation control industrial wastewater treatment in Finland. EU-level legislation and regulations are considered first, after that is described more carefully how industries have to follow BAT, and finally is described Finland's regulations. AFRY's 2020 guidelines for the management of industrial wastewater has presented the necessary regulations and legislations on the EU and international level for the correct functioning of industrial wastewater treatment plants (AFRY, 2020).

3.1 EU

Industrial emission directive (IED, 2010/75/EU) is one of the main pieces of industrial emissions legislation. The main purpose of this directive is to protect the environment and human health from harmful emissions in the whole EU area by utilising best available techniques (BAT). Industrial emission directive also affects to wastewater treatment because by this directive industry is responsible for monitoring emissions to water, air, and land. (75/2010) Urban wastewater treatment directive (UWWTD, 91/271/EEC) is made to protect natural water supplies against damage from industrial and urban wastewater discharge. This directive gives information about how to treat wastewater and produced sludge and how much emissions can be discharged into natural water systems. (91/271/EEC)

Water framework directive's (WFD, 2000/60/EC) purpose is to give emission limits and demand wastewater treatment before discharging wastewater into surface water, transitional water, coastal water, or groundwater. This directive will prevent damage to aquatic life and also protect it from disaster. The water framework directive leads water consumption to sustainable water use in the long-term. By this directive, all industries have to have some water services for wastewater. (2000/60/EC)

3.2 BAT (2014/687/EU)

The commission implementing decision establishing the best available techniques (BAT) for the production of pulp, paper, and board (2014/687/EU) defines the emission limits for water discharged into water systems. When unbleached kraft pulp is produced using the best available technique, the wastewater flow should be between 15-40 m3/ADt. The produced odours from wastewater treatment can be prevented by avoiding prolonged retention times or anaerobic conditions. By following BAT, uncontrolled organic matter decomposition, decay, and deposit will be avoided. For example, controlled vents and sufficient mixing in wastewater treatment systems, will help to avoid unwanted odours. The continuously monitored variables of wastewater are wastewater flow, temperature, and pH. (2014/687/EU, 12-13) The monitoring frequency for different parameters according to BAT are presented in table 6.

Table 6. Monitoring frequency for different parameters. (2014/687/EU, 15-16)

Parameter	**Monitoring frequency**
COD or TOC (total organic carbon)	Daily
BOD5 or BOD7	Weekly
TSS (Total suspended solids)	Daily
Total nitrogen	Weekly
Total phosphorous	Weekly
When using peroxide bleaching: -EDTA (Ethylenediaminetetraacetic acid) -DTPA (Diethylenetriaminepentaacetic acid)	Monthly
AOX	Once a month or once every two months
Relevant metals	Once a year

The yearly emission levels for bleached and unbleached kraft pulps are presented in table 7. The concentration of BOD is assumed to be small (under 25 mg/l d). (2014/687/EU)

Table 7. Yearly emission levels for bleached and unbleached kraft pulp. (2014/687/EU, 20)

Parameter	Bleached kraft pulp: Yearly average [kg/ADt]	Unbleached kraft pulp: Yearly average [kg/ADt]
COD	7-20	2,5-8
TSS	0,3-1,5	0,3-1,0
Total nitrogen	0,05-0,25	0,1-0,2

Total phosphorous	0,01-0,03	0,01-0,02
AOX	0-0,2	-

3.3 Finland

All industries in Finland must follow the environmental protection plan that considers how their activity may have environmental impact or produce pollution to the environment. The environmental protection plan considers emissions for land, air, and water. This plan demands the right wastewater treatment systems are used before discharging any wastewater into local water systems. The environmental protection plan states that the wastewater producer is responsible to monitor and control their own wastewater treatments. (527/2014) The meaning of environmental protection plan (527/2014) is explained in table 8:

Table 8. The purposes of the environmental action plan. (527/2014)

1.	Prevent the risk and possibility of pollution to the environment Prevent and decrease emissions and environmental damage Eliminate the impacts of pollution
2.	Support sustainable development Prevent climate change Protect healthy, ecologically sustainable, and biologically diverse environment
3.	Promote the future sustainable use of natural resources Decrease the amount and toxicity of waste Prevent any impact of waste produced
4.	Form an assessment of pollution produced from activities Consider the impact of the action on the environment
5.	Give citizens the opportunity to affect decision-making when considering the environment

The purpose of the water services act (119/2001) is to ensure clean water for households and protect public health and the environment. This act ensures clean water and a functioning sewage system for households and industries. (119/2001) The government decree on substances dangerous and harmful to the aquatic environment (1022/2006) follows the environmental protection act (86/2000). The main purpose of this decree is to protect aquatic life from harmful and dangerous substances and improve water systems quality. In the decree, the limit values for emissions have been indicated. (1022/2006)

4. Wastewater treatment in the pulp and paper industry

Wastewater treatment stages can either be divided by physical, chemical, and biological treatment methods, or by preliminary, primary, secondary, and tertiary treatments. (VanGuilder 2018, 183-186) In this thesis the wastewater treatment process is divided into preliminary, primary, secondary, and tertiary treatments. The removal of substances from different wastewater treatment stages is presented in table 9.

Table 9. Different stages of wastewater treatment and substances removed. (Sperling 2007,164)

Level	Preliminary treatment	Primary treatment	Secondary treatment	Tertiary treatment
Removal	-Coarse suspended solids	-Settleable suspended solids -Particulate BOD	-Particulate BOD -Soluble BOD	-Nutrients -Pathogenic organisms -Metals -Inorganic dissolved solids -Remaining suspended solids -Non-biodegradable compounds

The first part of the wastewater treatment process is called a preliminary treatment or a pre-treatment. The pre-treatment consists of for example, coarse screening, grit removal, neutralisation, cooling, and equalisation of effluent flow. (Dahl et al. 2008, 89) The pre-treatment removes the main parts of coarse particles from wastewater (Navaratnam 1998, 131). The primary treatment is located after pre-treatment. The primary treatment removes the main part of suspended solids. (Cabrera 2016)

The secondary treatment is also called biological treatment. The biological treatment removes dissolved and organic compounds that are not settled. The microorganisms decompose particles either in anaerobic or aerobic conditions. (VanGuilder 2018, 188)

The tertiary treatments include advanced wastewater treatment methods. The tertiary treatment removes some specific impurities that cannot be removed during preliminary, primary, or secondary treatments. Examples of tertiary treatment processes are disinfection, ultraviolet radiation, and feeding chemicals, like chlorine or ozone. (VanGuilder 2018, 198)

Sludge is typically collected from two different units in a wastewater treatment plant. The first part of sludge is collected from primary sedimentation, and it is called primary sludge. The second part of the sludge is collected from secondary sedimentation, and it is called secondary sludge. If a wastewater treatment plant has an activated sludge system, the part of the sludge is collected as secondary sludge and the rest is recycled back to the aeration tank. The tertiary treatment produces a chemical sludge that is also treated in the sludge treatment plant. (Andreottola et al. 2010, 8-9)

4.1 Preliminary treatment

The largest particles and impurities are removed from effluent before primary treatment. (Sperling 2007, 164). Bar screening is one example of this kind of process. There are two types of bar screens: coarse screening and fine screening. For collecting all material and impurities, screens are placed at specific angles and are usually cleaned by using a mechanical raking operation. The mechanical raking process can work on a timed basis or by pressure-sensing methods. (Navaratnam 1998, 128; VanGuilder 2012, 186)

The screening process does not remove all pieces of sand and stones, some are small enough to get through the screens. These smaller materials can cause problems in subsequent parts of the plant, so often they are removed by using a grit remover. Usually, the grit remover is a parabolic-shaped channel through which the effluent flows. (Water environment federation 2018, 56) This flow will cause particles sedimentation through gravity. Grit removal removes particles less than 0,2 mm but bigger than 0,15 mm in diameter. (Nesaratnam 1998, 130-131; VanGuilder 2018, 186)

4.2 Primary treatment

Primary sedimentation is one example of a primary treatment method. In this process fine particles settle down at the bottom of a sedimentation tank through gravity. (Nesaratnam 1998, 131-132, 145) Four types of settling happens in the sedimentation tank: discrete settling, flocs' settling, hindered settling, and thickening. When the sludge reaches the bottom, it starts to thicken. (Hynninen 1998, 58-59) The sedimentation at the bottom is called settled sewage and it is collected as primary sludge. Primary sedimentation removes approximately 70% of suspended solids, 65% of oil and grease, and 30% of BOD. Treated and cleaned water overflows from the weirs and flows to the next process stage in the plant. (Nesaratnam 1998, 131-132, 145; VanGuilder 2018, 187) The basic types of sedimentation tanks are a rectangular tank with horizontal flow, a circular tank with radial flow, and a hopper-bottomed tank with upward flow (Nesaratnam 1998, 132). The depth of these tanks is between 2-5 meters and retention time is between 2-6 hours (VanGuilder 2018, 187). Rectangular and circular tanks have mechanical sludge scraping system, whereas hooper-bottomed tanks have hoppers that collect sludge. (Nesaratnam 1998, 132)

Another example of a primary treatment method is a flotation clarifier, which uses air bubbles to elevate suspended solids to the surface of the flotation clarifier's tank. The suspended solids form sludge on the surface which is then removed by using a stripper. The heaviest particles will still settle down at the bottom. The sludge is removed from the bottom of the flotation clarifier tank. This process can be utilized after the biological treatment. The advantages of a flotation clarifier, when comparing primary sedimentation, are efficacy for poorly settling sludge and the fact that it does not require a large space. The disadvantages of a flotation clarifier are high energy consumption and high operating costs. (Hynninen et al. 1998, 62-63)

4.3 Secondary treatment

Secondary treatment is also called biological treatment (Nesaratnam 1998, 139). In the biological treatment, two kinds of bacteria are working, either heterotrophic or autotrophic bacteria. Heterotrophic bacteria use organic compounds as a carbon and energy source. They can live in aerobic, anoxic, or anaerobic environment. Autotrophic bacteria use inorganic carbon as a source of cell carbon. As an energy source they use ammonia, H_2S, and Fe^{2+}. (Andreottola et al. 2010, 109-110) In biological oxidation microorganisms break down carbonaceous matter using oxygen and as a result generate carbon dioxide, water, biomass, and other by-products like ammonia. (Nesaratnam 1998, 139¸ Andreottola et al. 2010, 109-110) The reaction between carbon-containing matter and microorganisms is presented in equation 1:

$$carbon\_containing + oxygen \xrightarrow{microorganisms} carbon\ dioxide + water + biomass + byproducts \qquad (1)$$

Biological treatment separates suspended solids to 30 mg/l or less and BOD to 20 mg/l or less. (Nesaratnam 1998, 139) Two examples of biological treatment processes are an activated sludge process and a biological filter.

4.3.1 Activated sludge system

The key role for achieving the best possible result when cleaning wastewater is held by microorganisms in the aeration tank and their living environment. There are two different stages in the activated sludge system: aeration stage and sludge settlement stage. (Gray 2004, 465) The system requires a tank, an aeration system, a sedimentation tank, a return activated sludge process, and a system for removing part of the activated sludge, called excess sludge. (Nesaratnam 1998, 140-141) An example of an activated sludge process scheme is presented in figure 3.

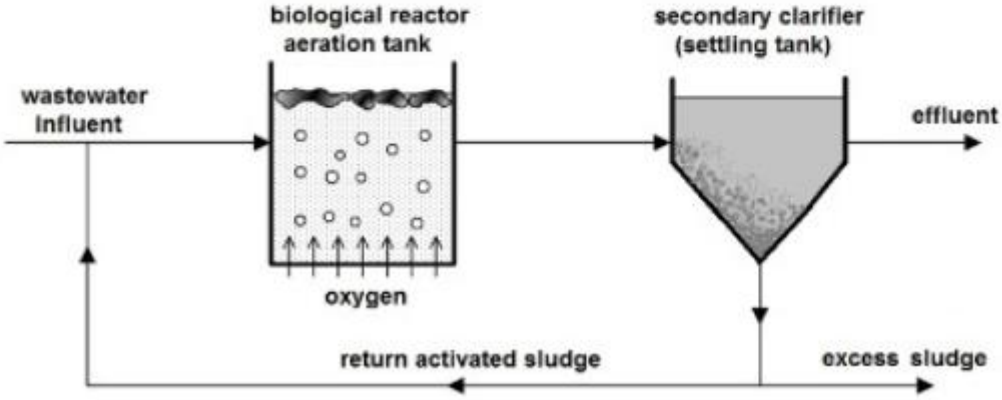


Figure 3. Process scheme of activated sludge system. (Fracz 2016)

The aeration system is needed in the aeration tank in order for biological activity to happen. There are three kind of aeration systems: surface aerators, open-ended pipes, and porous diffusers. The amount of air introduced is one of the main factors in determining microorganism's activity in the aeration tank and an efficient mixing system (Gray 2004, 467). The amount of dissolved oxygen is one of the restrictive values in the aeration tank, and it should be between 1-2 mg/l. The aeration tank also contains protozoa organisms which help, together with bacteria, to make clear and clean effluent. The protozoa have also key role in reducing the number of pathogenic bacteria. To achieve the best result, it is important to consider amounts of nutrients in the activated sludge process. (Nesaratnam 1998, 140-141)

The F/M ratio is an important parameter to consider in an activated sludge system. It describes the organic loading rate, or in other words, food and microorganism ratio. This measurement makes sure that microorganisms have enough nutrients for the decomposition of organic matter in wastewater flow. (Antonelli et al. 2003, 111-112; Nesaratnam 1998, 142-141)

The sedimentation tank after the activated sludge system has a similar function as primary sedimentation. Treated water flows over weirs and moves on to the next process step. The particles and impurities in the water settle down at the bottom of the tank where sludge is collected. A portion of the sludge is recycled back to the aeration tank, and it is mixed with the incoming wastewater flow. (Nesaratnam 1998, 145)

4.3.2 Biological filter

A biological filter is one of the options for an aerobic process in biological treatment and it is usually located after primary sedimentation (Nesaratnam 1998, 147-152). There are functional microorganisms like bacteria, fungi, algae, and protozoa in the biological filter. These microorganisms form a biological film or slime on the surface of the tank, which is called a biological filter. The microorganisms’ transportation on the surface of the tank is controlled with four main processes: diffusion, convection, sedimentation using gravity, and activity of microorganisms. (Chaundhary et al. 2003)

Commonly, the filter is circular, but it can also be rectangular. The biological filter contains a dosing system, a filter bed, underdrains for sludge removal, a sedimentation tank, and a ventilation system. The purpose of the dosing system is to spread sewage all over the surface of the filter bed. The microorganisms do not need a separate aeration system if the bed is well ventilated enough. (Nesaratnam 1998, 147-152) Microbial activity is the most important variable to monitor because it has the biggest effect on the process’ performance and efficiency. A regular and sufficient source of organic substances and nutrients is mandatory for achieving a properly working process. (Chaundhary et al. 2003)

Secondary sedimentation after the biological filter differs from normal secondary sedimentation in the activated sludge system in that does not involve a sludge recycling system. All collected sludge from secondary sedimentation is collected and returned back to the primary sedimentation tank where it will settle down at the bottom. (Nesaratnam 1998, 151) The advantages and disadvantages of an activated sludge system and a biological filter is presented in table 10.

Table 10. Advantages and disadvantages of activated sludge system and biological filter (Nesaratnam 1998, 153-155)

Advantages of activated sludge system	Advantages of biological filter system
- Better chance to control quality of discharged effluent - No need to worry about filter flies - Loss of heat is smaller - Generally, needs less space	- Uses less energy - Needs less attention - Silent - Better treatment of toxic materials - Convert ammonia to nitrate more easily and cheaply
Disadvantages of activated sludge system	**Disadvantages of biological filter system**
- Needs continuous monitoring - Consumes a lot of energy and labour - Not fast enough for treating peak loads - Noisy - Operating costs rise more when energy costs rise - More vulnerable to toxic materials - Needs high concentrations of oxygen to convert ammonia to nitrate	- Requires a lot of space - Needs a lot of heat pumping - No chance to control quality of discharging effluent

4.4 Tertiary treatment

There are different methods for removing suspended solids. One example is micro straining. This method removes particles with a diameter is bigger than 20 µm. The collected particles are fed back to the effluent inlet and an ultraviolet system is used to prevent microorganism growth in the system. (Nesaratnam 1998, 173-174; Öllös 1991) The micro straining method removes approximately 35-75 % of suspended solids and 12-50 % of BOD from the wastewater (Tebbutt 1998, 240). Another example is sand filtration, which utilizes gravity. This method requires backwashing cleaning regularly to prevent clogging. The collected particles are fed back to the wastewater inlet. (Nesaratnam 1998, 173-174; Wang et al. 2021, 322)

An example of the ammonia removal method is to use biological nitrification or denitrification. The nitrification method utilizes microorganisms to transform the ammonia to nitrite and then to nitrate. The nitrate is transformed to nitrogen gas under anaerobic conditions. (Nesaratnam 1998, 176-177; Hopcroft 2015, 131)

Chemical oxidation is a method for reducing total organic loading and changing organic material to a more biodegradable form. It can be used as a disinfection method for wastewater. The oxidizing agents used are chlorine, ozone, oxygen, and air. The process requires storage and dosage equipment. Any unused oxidizing agent can be recovered from the effluent in the aqueous or gaseous phase. (Hynninen 1998, 90; Nesaratnam 1998, 183-184; Hopcroft 2015, 131-13) The ultraviolet method is one of the processes to disinfect wastewater as a tertiary treatment. This method requires a low concentration of suspended solids and a good filtration method before use. The ultraviolet method needs only a short contact time for reaction, but it needs a lot of energy to work as intended. This method is more expensive than using chemical like chlorine. (Hopcroft 2015, 134; Tebbutt 1998, 203-209)

The phosphorous removal process is used when treated effluent is discharged into sensitive water systems. Orthophosphate is possible to precipitate using chemicals like lime, alum, ferric chloride, or ferric sulphate. Other phosphate compounds, residual organic phosphorous and polyphosphates, can be removed by adsorption reaction. The method can achieve about 30-40 % phosphorous removal. (Nesaratnam 1998, 178-179; Hopcroft 2015, 130; Sperling 2007, 168-169) Phosphorous can also be removed using a biological method. The bacteria destroy phosphorous compounds and store them in their cells. This method has two operation zones: a fermentation zone and an oxygen-rich zone. Volatile fatty acids (VFAs) are created in the first zone, and these are used as an energy source for the phosphate accumulating organisms. The phosphate accumulating organisms oxidize the VFAs in the second step which will then be returned back to the first step. (Hopcroft 2015, 131; Sperling 2007, 168-169)

4.5 Sludge treatment

Mixed sludge consists of 95-99 % water and all the collected solid matter from the water treatment processes. By using chemicals the content of the solid matter in the sludge can be increased. Tertiary treatment is a good method for improving separation of the solid matter from the water. (Nesaratnam 1998, 211-212) The characteristics of primary and secondary sludges are presented in table 11.

Table 11. Characteristics of primary and secondary sludges. (Nesaratnam 1998, 211)

	Primary sludge	**Secondary sludge**	
		Activated sludge system	**Biological filter**
Dry solids content	5 %	1 %	2 %
Density	1050 kg/m^3	1003 kg/m^3	1010 kg/m^3
Volatile solids content	60 - 80 %	50 – 70 %	50 – 70 %

From table 11 it can be seen that the concentration of dry solids is higher in primary sludge than in secondary sludge. This can be explained by the order of the treatment methods in the wastewater treatment plant. Primary sludge is collected first from the wastewater and it consists of more solid particles than wastewater later in the plant. The typical composition of sludge is presented in figure 4.

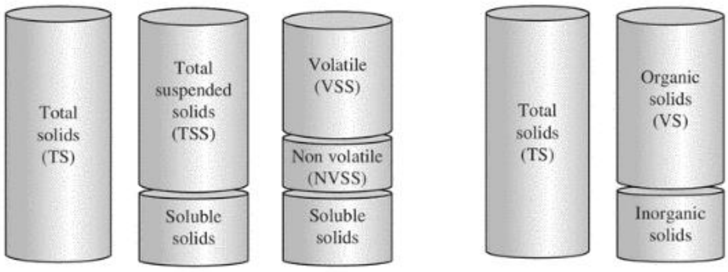


Figure 4. Composition of sludge. (Andreottola et al. 2010, 9)

Figure 4 shows that most of the sludge consists of total suspended solids or organic solids. The composition of sludge is important to recognise when considering correct treatment methods. (Andreottola et al. 2010, 9) The stages of treating sludge are thickening, stabilisation, conditioning, dewatering, disinfection, and final disposal (Nesaratnam 1998, 212-226).

4.5.1 Thickening

In thickening the sludge, the goal is to reduce the amount of water in the sludge and increase the solid content. (Nesaratnam 1998, 213-214) One of the most common methods for sludge thickening is a gravity thickening method. This method decreases the load of the sludge for the next processes and also separates the gases from wastewater (Antonelli et al. 2003, 109; Hynninen 1998, 115) The sludge content can increase from 0,3-3 % to 10 %. Sedimentation tanks are usually circular and it use gravity for settling solid particles at the bottom of the tank. (Hynninen 1998, 115) Lagoons can be used as a sludge thickening method using evaporation. The design of lagoons is easy and inexpensive. The main disadvantages are odour problems and contamination of local groundwater. (Springer 2000, 435) Lagoons for sludge water separation also require a large area. (Nesaratnam 1998, 218)

4.5.2 Stabilisation

Lime ($Ca(OH)_2$ or CaO) is usually utilized as a chemical agent in chemical stabilisation. Because of the lime, the pH of the sludge will increase to 12 and the majority of the pathogens will be destroyed. This method requires a big amount of lime (100-200 kg/tonne of dry solids) therefore it is not a popular method. (Nesaratnam 1998, 219; Tebbutt 1998, 229) The efficacy of chemical stabilization depends on the amount of chemical input and this method will increase sludge production. (Hynninen 1998, 116)

4.5.3 Conditioning

There are three commonly used chemicals in the sludge conditioning process. These three are lime, ferric chloride, and polymers. They can be used together or separately. (Springer

2000, 433; Tebbutt 1998, 225-226) By using a chemical conditioning process, the adsorbed water can be separated from the sludge by adding polymer. The use of ferric chloride and lime helps to separate water from solids but also increases sludge production. (Nesaratnam 1998, 212-213; Hynninen 1998, 115) To achieve the best possible results, it is required to have a big amount (100-200 kg/tonne dry solids) of these inorganic chemicals. The disadvantage of ferric chloride is its high corrosivity. (Springer 2000, 433) When using polymers, the amount needed is much smaller (approximately 10 kg/tonne dry solids) than inorganic chemicals. The cost of the polymers is bigger than the cost of inorganic chemicals which affects to the choice of chemical. The chemicals are mixed with sludge in the flocculation tank. (Nesaratnam 1998, 212-213; Hynninen 1998, 115)

4.5.4 Dewatering

The main target of sludge dewatering is to reduce as much water as possible. One of the most common methods is the filter press. In the filter press two circulating belts or two plates are squeezed together with the sludge going through them. In other words, the plates or belts press the water out of the sludge. (Antonelli et al. 2003, 124-125) The achieved dry solid content of the sludge cake according to this method is approximately 35 %. (Nesaratnam 1998, 214-215) This method consists of two different stages: removal of water utilizing gravity and water removal by pressing the sludge. The belt press can be controlled by changing speed, pressure, and inflow rate. (Hynninen 1998, 117)

There are three different alternatives in the centrifuges process: disc, bowl/basket, and scroll units (Springer 2000, 438; Tebbutt 1998, 228). Centrifuges can achieve 30 % dry solid content in the sludge. This method uses centrifugal forces to pile solid particles on the outer wall. All separated water from the sludge flows in the centre port. The centrifuge process works better for sludge that contains inorganic substances than for organic ones. Energy consumption of this process is high. (Nesaratnam 1998, 215-216: Hynninen 1998, 116-117; Tebbutt 1998, 228)

4.5.5 Final disposal

The produced sludge from a wastewater treatment plant can be utilized for energy production in the waste incineration process. When using sludge for incineration, the volume of the sludge will decrease as organic matter is burned. The residual is only inorganic matter. To burn sludge in a boiler, the solid content of the sludge has to be at least 20 - 40 %. After incineration, the ash is also possible to utilize, for example, as a soil improvement agent. The concentration of heavy metals, toxic compounds, and the content of organic compounds must be analysed before use. These compounds have limit values when considering soil improvement. (Hynninen 1998, 125-128: Springer 2000, 447-448: Nesaratnam 1998, 223-226)

5. Optimal conditions and challenges of effluent treatment in pulping industries with activated sludge process

This chapter describes some of the challenges faced by the activated sludge process and also describes the optimal conditions for wastewater treatment. The following challenges are described:

- how to avoid producing odours caused by hydrogen sulphide
- how to keep nutrition concentration in balance
- how to control dissolved oxygen concentration
- how to handle pH-level changes
- how to avoid bulking and foaming

5.1 Optimal conditions for effluent treatment

The optimal operation conditions for an activated sludge system are described in this chapter. The function of an activated sludge system is based on the decomposition of organic material in wastewater by microorganisms. Microorganisms need enough oxygen for this action. It has been estimated that one-kilogram consumed BOD will produce 0,4-0,7 kg of new biomass. The key factors affecting operating efficient are the amount of nutrients, temperature, pH, oxygen content, and concentration of toxic substances. (Hynninen 1998, 68-80; Nesaratnam 1998, 140)

It is beneficial to keep temperature around 35 °C because at this temperature decomposition happens 3-5 times faster than at 20 °C (Hynninen 1998, 68-80). The ratio between organic carbon and nutrients should be BOD:N:P=100:5:1 in wastewater, according to literature. (Nesaratnam 1998, 141; PSATS 2014, 10). Generally, the organic carbon to nutrient ratio in forest industry effluent is BOD: N: P = 100: 1,5: 0,225 (Hynninen 1998, 68-80). The concentration used in calculations for nitrogen is 2-2,5 mg/l and for phosphorous 0,1-0,2 mg/l. The optimal value for pH is between 7-7,5 but a range between 6,8-8 is workable when considering microorganisms. The sufficient level of dissolved oxygen concentration is between 1,5 - 2 mg/l. (Hynninen 1998, 68-80; Springer 2000, 338-339; PSATS 2014, 11; Mancuso 2021)

The factors F/M -ratio (sludge load), SRT (solid retention time), SVI (sludge volume index), and content of sludge have to be considered when designing and monitoring on activated sludge system. The F/M ratio describes the amount of produced sludge and the optimal values for it is between 0,1 - 0,5 kg (BOD)/ kg (MLVSS). (Hynninen 1998, 68-80; Springer 2000, 344; Nesaratnam 1998, 145) The SRT or age of sludge for an activated sludge system is between 5 - 15 days. The target volume of SVI is 120 mg/l. The content of the sludge is described as dry weight of solids per unit volume of sludge, and its optimal value is between 2,5 - 4 kg/m3. (Hynninen 1998, 68-80)

5.2 Odours caused by hydrogen sulphide

The most common odour source is hydrogen sulphide (H_2S) (WEF 2004, 134) and it is also considered as an indicator of odours in wastewater treatment plants. The smell of hydrogen sulphide is described as a rotten egg. (Pulkkinen 2014, 1) Hydrogen sulphide causes odour problems and can also cause concrete corrosion in the wastewater treatment systems. (Krom et al. 2001, 1) Production of hydrogen sulphide is a physio-chemical process. This process happens in both the water and air phases of sewer networks. (Boon et al. 2007, 2-5) Hydrogen sulphide production starts in wastewater biofilm when the concentration of oxygen is too low (less than 0,1 mg/l) and an anaerobic condition is achieved. Desulfovibrio-bacteria are responsible for the biological reaction where sulphate (SO_4^{-2}) becomes reduced, and hydrogen sulphide is produced under anaerobic conditions. (Pulkkinen 2014, 5; WEF 2004, 134) The reaction is represented in equation 2: (Bagheri et al. 2016, 4; Pulkkinen 2014, 5; WEF 2004, 134)

$$SO_4{}^{-2} + 2\,C + 2\,H_2O \xrightarrow{Bacteria} 2\,HCO_3{}^{-} + H_2S \qquad (2)$$

The variables that most affect the generation of hydrogen sulphide are the concentration of organic material (BOD) and nutrients, concentration of sulphate, temperature, concentration of dissolved oxygen (DO), and retention time. (WEF 2004, 135) One of the most important factors for determining the production of hydrogen sulphide is pH-level. The equilibrium of hydrogen sulphide in wastewater, when considering pH level, is presented in figure 5. (House & Weiss 2014)

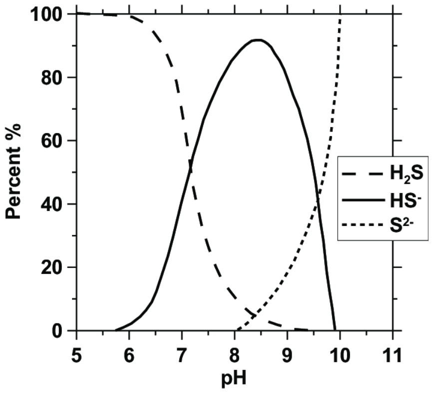
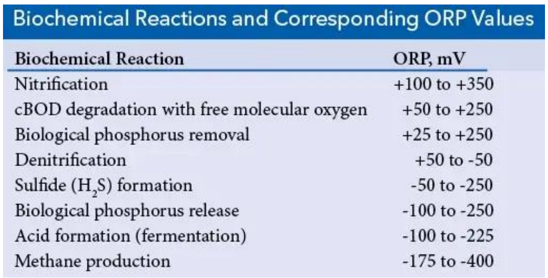


Figure 5. The relationship between pH and hydrogen sulphide production. (House & Weiss 2014, 4)

Figure 5 shows that when pH is below 7, the generation of hydrogen sulphide is at its highest point. Based on figure 5, it can be said that the best value for pH is above 8 for hydrogen sulphide emission control. Unfortunately, in a wastewater treatment plant, it is necessary to keep ph-level around 7, as previously mentioned.

Oxidation-reduction potential (ORP) describes wastewater's ability for oxidation or reduction. The unit for ORP is a millivolt (mV) and values can be negative or positive. (Higgins 2013) The bigger the ORP-value, the better conditions are for the oxidation of the compounds. Correspondingly, the smaller the value is, the better the conditions are for the reduction of the compounds. (Pulkkinen 2014, 6-7) Different ORP-value levels for different biochemical reactions are presented in figure 6. The figure shows that between +50 mV and +300 mV there is no potential for creating hydrogen sulphide. This is because nitrate will be an oxidizing agent instead of sulphide. ORP values for hydrogen production are between -50 mV and –250 mV. (Pulkkinen 2014, 7; Higgins 2013)



Biochemical Reactions and Corresponding ORP Values

Biochemical Reaction	ORP, mV
Nitrification	+100 to +350
cBOD degradation with free molecular oxygen	+50 to +250
Biological phosphorus removal	+25 to +250
Denitrification	+50 to -50
Sulfide (H_2S) formation	-50 to -250
Biological phosphorus release	-100 to -250
Acid formation (fermentation)	-100 to -225
Methane production	-175 to -400

Figure 6. Corresponding ORP values for different biochemical reactions. (Higgins 2013)

For controlling odours caused by hydrogen sulphide, there are two different strategies: odour prevention and odour compound removal. (Bagheri et al. 2016, 1) One method for decreasing hydrogen sulphide is to increase redox potential by adding thermodynamically favourable electron acceptors. These acceptors can be, for example, oxygen, nitrate, and nitrite. (Boon et al. 2007, 2-5)

Ferric salts are an example of chemical that reduces odour compounds. Hydrogen sulphide can be removed by iron salts. (Boon et al. 2007, 2-5) Iron salts are not as sensitive to temperature changes as aluminium salts and ferric salts are also better for removing natural organic matter. (Matilainen et al. 2010, 3-4) According to Boon et al. 2007 ferric salts are better for controlling dissolved sulphide than ferrous salts. The chemical formula of ferric sulphate is $Fe_2(SO_4)_3$ and the function of this chemical is based on a Fe^{3+}- ion. This chemical also reduces the amount of phosphorous in wastewater (Delgado 2017, 15, 56) by removing organic matter (Vesilaitosyhdistys 2020, 14). It can also be used in very low and high pH levels for removing colour from the water. Ferric sulphate can be in solid or liquid form. (Bratby 2016, 37) Reduction of hydrogen sulphide from wastewater using ferric sulphate is presented in equation 3: (Andrades et al. 2004,1; Pohanish 2017, 1408; Delgado 2017, 15)

$$H_2S_{(g)} + Fe_2(SO_4)_{3\,(aq)} \rightarrow S_{(s)} + 2FeSO_{4\,(aq)} + H_2SO_{4\,(aq)} \qquad (3)$$

In ferric sulphate the iron is in the form Fe^{3+} and it will be reduced to Fe^{2+}, while at the same time oxidizing hydrogen sulphide to elemental sulphur. (Boon et al. 2007, 5; Ebrahimi et al. 2002, 1; Kiilerich et al 2018) This reaction is presented in equation 4:

$$H_2S + 2Fe^{3+} \rightarrow S^0 + 2Fe^{2+} + 2H^+ \qquad (4)$$

Iron (2+) oxidizes sulphur and forms FeS as a product. (Boon et al. 2007, 5; Krom et al. 2001, 2; Kiilerich et al 2018) This reaction is presented in equation 5:

$$Fe^{2+}{}_{(aq)} + HS^- \rightarrow FeS_{(s)} + H^+ \qquad (5)$$

Cipriani, M et al. (2018) have presented the results of using the iron salt blend to control hydrogen sulphide generation in sewage treatment. According to them, an 83 % lower hydrogen sulphide level in the air was achieved by using the iron salt blend chemical. (Cipriani et al. 2018)

5.3 Nutrition balance

Generally, the organic carbon to nutrient ratio in forest industry effluent is BOD: N: P = 100: 1,5: 0,225. (Hynninen 1998, 68-80) The use of chemicals is necessary to increase the concentration of nitrogen and phosphorous in wastewater. A commonly used chemical as a nitrogen source is urea (CH_4N_2O) and as phosphorous source, phosphoric acid (H_3PO_4). When the level of nutrients is too low, the removal of organic matter can decrease and the process can slow down. On the contrary, when nutrient levels are too high some of the nutrients can be released into the natural water systems, which is not efficient from an environmental or economical perspective. A percentage of the nutrients escape with the treated wastewater into natural waters. The concentration of nitrogen (ammonium) should be 0,5-1 mg/l and phosphorous (phosphate) 0,5-1 mg/l in the aeration tank. (Ahvenainen 2017, 25-27)

5.4 Dissolved oxygen concentration

Dissolved oxygen (DO) is one of the key factors in an activated sludge system. Denitrification, nitrification, and the removal of phosphorous are examples of processes that demand enough dissolved oxygen. The control of dissolved oxygen levels in the aeration tank is one of the most complex functions. Aeration is necessary in an activated sludge system, but it is also the most expensive stage in a wastewater treatment plant (Piotrowski 2015), 45-75% of total plant costs (Chen et al. 2012), because of high energy demand and high cost of the oxygen. When DO levels are too low in the aeration tank, microorganisms cannot function correctly and the mixing of sludge is too low. In other words, when DO levels are too low, sufficient wastewater treatment cannot be achieved. Supplying oxygen to the aeration tank needs automation control so that the oxygen concentration remains stable. The oxygen flow should be adjusted according to the amount in the treated wastewater. When there is a good control system for oxygen flow, economic savings can be achieved. (Piotrowski 2015) Too low DO levels in wastewater will increase the growth of filamentous organisms, which will cause bulking and foaming, and due of this, the SVI will increase. (Chen et al. 2012, 4)

5.5 pH-Level

When pH is not at an optimal level, nitrifying bacteria have difficulties removing ammonia from the activated sludge system. When pH levels are too low, conditions in the activated sludge system are optimal for fungi and filamentous organism growth. These can cause sludge bulking, bad settling of the particles (Mancuso 2021; Springer 2000, 356), and foaming (Comas et al. 2008, 1).

The pH level also affects the dewatering process of sludge. The polymer used will only work under certain pH levels. When the pH-level in sludge is not within these limits, the polymer does not work properly. The alkalinity of wastewater indicates how well water can neutralize acids. Alkalinity also affects the removal of phosphorous. (Mancuso 2021) The pH level can be controlled by using chemicals like calcium oxide (lime) or acids. (Hreiz et al. 2015)

Sulfuric acid is a typical example of a neutralization chemical in the wastewater treatment process. Sulfuric acid forms neutral salts as a result of the neutralization reaction. The reaction is presented in equation 6: (Nemerow 2007, 42)

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O \qquad (6)$$

The biggest problem with sulfuric acid is its corrosiveness, which causes problems when handling the chemical. Storage and feeding equipment can be simple because a small amount of sulfuric acid is enough for neutralization. (Nemerow 2007, 42)

Calcium oxide, also called quicklime, is usually used for neutralizing acidic wastewater and for removing sulphates and metals. Calcium oxide is effective and its chemical reaction is simple. The chemical structure of calcium oxide is CaO. The disadvantages of using quicklime are significantly increasing sludge production and the high-water concentration of the produced sludge. These clog of equipment and pipelines, and thus increases costs. (Hu et al. 2014)

5.6 Bulking and foaming

Bulking is a phenomenon that occurs when particles do not settle correctly at the bottom of the secondary sedimentation tank. Instead, particles flow together with overflow away from the sedimentation tank. (Nesaratnam 1998, 146) Other factors that affect bulking are the number of nitrogen (N) and phosphorous (P) species and/or the level of dissolved oxygen. Filamentous bacteria forms flocs when the number of N or P species and levels of DO are low, and this eventually cause bulking. (Cabrera 2016) The addition of chlorine and hydrogen peroxide is used to destroy filamentous bacteria which will help the system return back to optimal conditions. (Nesaratnam 1998, 147)

Foaming is a phenomenon that occurs when sludge rises to the surface. The risk of foaming increases when the F/M ratio and DO concentration are too low. Another contributing factor for foaming is when the F/M-ratio is high and SRT is low. This is a situation in which there is a large fraction of readily biodegradable organic matter in the wastewater. Also, high SRT combined with a low DO-level is another risk factor for creating foam. (Comas et al. 2008, 3)

6. Case company and measurement method and plan

6.1 Stora Enso Oulu Mill

Stora Enso’s Oulu Mill is located in northern Finland. Operations started in 1935 and the mill has approximately 400 employees at the mill site today. Oulu Mill is an integrated mill that includes wood handling, pulping, kraft liner production, and harbour operations. The produced products are kraftliner and unbleached softwood pulp. Annual production capacities are 450 000 tonnes of kraft liner product and 550 000 tonnes of unbleached pulp. (Stora Enso, Oulu Mill) Prior to autumn 2020, Oulu mill also produced bleached kraft pulp and paper with two paper machines (AFRY 2022, 14).

6.2 Other companies in the same factory area

There are also other companies operating in the same factory area as Stora Enso Oulu Mill. These companies are Karton, Nouryon Finland Oy, and Port of Oulu. The operations and products of these companies also affect the operations of Oulu Mill. This chapter briefly introduces these companies.

6.2.1 Kraton

Kraton is one of the companies that operates on the same factory site as Stora Enso Oulu Mill. Kraton utilizes the crude tall oil that is produced as a side product at the pulping mill. This company distils crude tall oil and produces different distilling products. Kraton has been operating under different company names since 1940. Kraton’s wastewater is first treated in an oil separation tank and flotation process. After this, effluents are fed to Stora Enso’s pulp mill’s wastewater treatment plant. (AFRY 2022, 37-38)

6.2.2 Nouryon Finland Oy

Nouryon Finland Oy produces chemicals for pulp and board production and for wastewater treatment. Stora Enso Oulu Mill uses these chemicals in its own processes. The most important product produced at Nouryon is sodium chloride. The effluents produced at this plant go through a heat exchanger and then they are discharged into the sea. (AFRY 2022, 38)

6.2.3 Port of Oulu

Port of Oulu operates in Stora Enso's factory area. It contains three parts: Oritkari, Nuottasaari, and Vihreäsaari. It receives approximately 550 ships and takes about 3,6 tons of delivery products about 3,6 tons yearly. (AFRY 2022, 38) The most significant commodity groups are products from the forest industry, fuels, and raw materials for the forest industry. (Port Oulu 2022)

6.3 The pulp and board process at Oulu Mill

Oulu Mill produces unbleached kraft pulp and a type of unbleached board called kraftliner. A percentage of the pulp is dried and sold, but the majority is used in its own board production. The pulp and board processes are presented in table 12.

Table 12. Pulp and board processes at Oulu Mill. (AFRY 2022, 42-44)

Department:	Processes:	Other information:
Wood handling	- Wood reception - Measuring station - Log storage - Dry debarking - Chipping - Chip storage and screening	Bark is utilized in the power plant for energy generation. The sludge treatment plant is in the same building as the wood handling facility.
Pulping line	- Cooking - Sorting - Washing - Drying	Some of the pulp is dried for sale but the majority of it is used in its own board mill.

Caustic soda line	- Evaporation plant - Recovery boiler - Causticizing plant - Tall oil cooking plant	Cleaned condensates are cooled down and fed to the wastewater treatment plant. Green liquor sludge is separated and fed to the wastewater treatment plant
Board mill	- Stock preparation - Finishing methods - Broke system - White water system - Coating - Coating kitchen	Produces unbleached board from its own kraft pulp. Only one board machine in use.

6.4 Wastewater treatment

There are two different wastewater treatment plants at Oulu Mill, one for the pulp mill's effluents and one for the board mill's effluents. The process steps of the wastewater treatment plants are presented in table 13:

Table 13. The wastewater treatment plant's process steps in the Stora Enso Oulu mill. (AFRY 2022, 62-63)

Wastewater treatment plant:	Processes:
For pulp mill and Kraton	- Coarse screening - Primary clarifier - Neutralization, urea and liquid nitrogen are also added if needed - Aeration tank - Secondary clarifier - Returned activated sludge system - Sludge treatment with belt filter press for primary sludge and excessive sludge from biological treatment - Dried sludge is burned in the power plant

For board mill	- Primary clarifier - Neutralization - Heat exchanger - Aeration tank - Secondary clarifier - Returned activated sludge system - Tertiary treatment: Phosphorous and COD removal, coagulation of sludge - Sludge treatment by using belt filter press and centrifuge - All clean water is fed to the sea though different canals than treated wastewater

6.5 Measurement methods

Wedge software was used for analysing test phases as a measurement method in this thesis. Wedge is a software designed to improve the analysis of industrial processes. The software is suitable for production management, process and product development, quality management, maintenance, process, control, and mill management. By using this software, the root causes of problems are easier and faster to find. The key features of this program are visualizing, cleansing, analysing, and diagnosing data. (Trimble 2023) Appendix 1 is a Wedge-modelling diagram of a pulp mill’s wastewater treatment plant. It includes biological treatment, sludge treatment, chemical feeding, and modelling of wastewater canals.

Laboratory analyses for different quality parameters were used in the test phases, in addition to Wedge-software. Laboratory measurement methods for different variables are presented in table 14:

Table 14. Variables and measurement methods for laboratory analysis.

Variable	The measurement method
Temperature	Portable thermometer
pH	pH electrode and pH meter
Conductance	Conductivity sensor and meter
Total solid matter	Filtration through membrane filter
Total phosphorous	Reagent + Thermostat + Spectrophotometer
Sodium	Atomic absorption spectroscopy (AAS)

Sulphate	Ion chromatography (IC)
COD	Reagent + Thermostat + Spectrophotometer
Chloride	Ion chromatography (IC)
Redox	Redox electrode and meter

More detailed descriptions of these laboratory analyses are described in Appendix 2. *Laboratory analysis methods and working instructions*. It contains descriptions and instructions for pH, conductance, total solid matter, total phosphorous, sodium, sulphate and chloride, COD, and redox analyses.

6.6 Measurement plans

The measurement plans for all test phases are described in this chapter. There are three different test phases: optimization of the oxygen feed in the aeration tank, optimization of the ferric sulphate feed, and identification of upstream flows.

6.6.1 Test phase 1: Optimization of the oxygen feed in the aeration tank

The main purpose of this test phase was to reduce the oxygen concentration in the aeration tank and save energy. The testing period for this experiment was 15.11.2022-2.1.2023. After this period the adjustment of the oxygen feed was maintained because of favourable results. The aeration tank is divided into aeration tank 1, which has one oxygen measurement, and aeration tank 2, which has three oxygen measurements. The aeration tank already had an automation system that could be used to set a particular value for oxygen level. However, this system was not in use before starting this test phase. Because of this, there was no need to change the target value mechanically. The meter selected was the first one from aeration tank 2. The target value for oxygen concentration was selected to be 2 mg/l and this value was set in the selected measurement.

Meter 1 from the beginning of aeration tank 2 was chosen because it was at the beginning of the aeration tank where the most oxygen was needed and used. Meter 1 from aeration tank 1 could not be chosen because it did not show big changes in oxygen concentration values, while the other meters' values did change a lot. Figure 7 presents more clearly the reasons for choosing this meter.

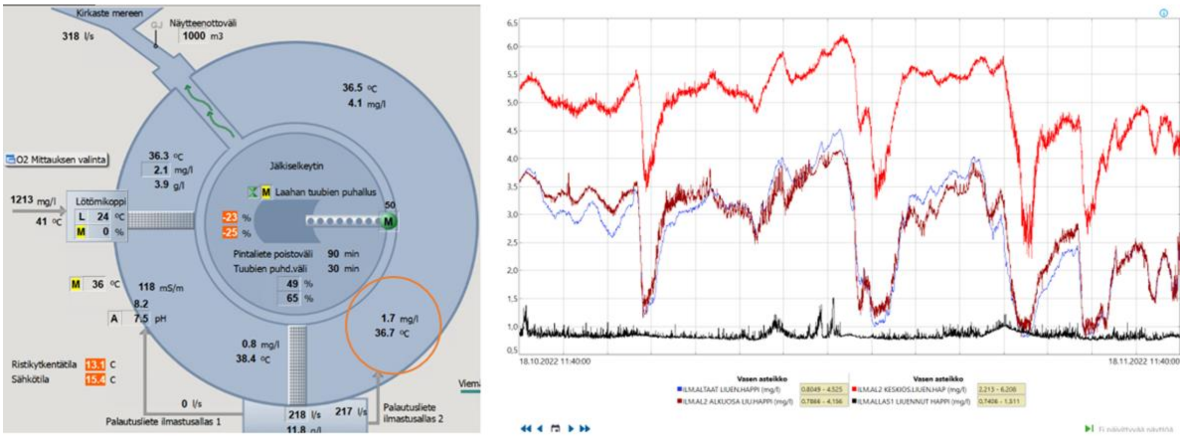


Figure 7. The location of the chosen oxygen concentration measurement and recorded oxygen concentration changes of all meters in the aeration tank.

From figure 7 it can be seen that the concentration of oxygen value changed a lot in all meters of aeration tank 2 (colours: red, brown, and blue graphs). The measurement in the middle of aeration tank 2 always has a higher oxygen concentration than the measurements before or after it. This is because oxygen consumption was greater at the beginning than the end of the aeration tank. The oxygen content was lower at the end of the aeration tank because of the wastewater escaped from the beginning of the aeration tank directly to the end of the aeration tank.

6.6.2 Test phase 2: Optimization of the ferric sulphate feed

Ferric sulphate is used to prevent odours at the wastewater treatment plant of Stora Enso's Oulu Mill. As described in previous chapters, most of the odours at wastewater treatment plants, are caused by hydrogen sulphide. The formation of hydrogen sulphide can be estimated by measuring the redox potential. The formation of hydrogen sulphide happens when the reduction/oxidation potential value is between -50 to -250 mV and when the pH-level is between 6-9.

The purpose of this test phase was to evaluate the reliability of the redox measurement for adjusting the flow of ferric sulphate in wastewater. If the redox measurement was found to be reliable, it could possibly be used as an automatic meter in the control of ferric sulphate's flow in the future. During this test phase, three samples were collected daily for five days. The samples were collected from the coarse screen, the primary clarifier, and from the bridge after the primary clarifier. After collecting samples for that day, the feed of ferric sulphate was adjusted to the next value. The adjusted feeding value of ferric sulphate was valid for 24 hours and after that new samples were collected. The basic value of ferric sulphate feed was 125 ppm, and it was adjusted every 50 ppm by first lowering the value and then increasing it back to the basic value. The changes in ferric sulphate's feed are presented in table 15:

The date	Feed of ferric sulphate [ppm]	Feed of ferric sulphate [l/h]
13.3.2023 – Monday	125 -> 75	145 -> 87
14.3.2023 – Tuesday	75 -> 25	87 -> 29
15.3.2023 – Wednesday	25 -> 75	29 -> 87
16.3.2023 – Thursday	75 -> 125	87 -> 145
17.3.2023 - Friday	125	145

Table 15. Table of ferric sulphate's feed changes during test phase.

Samples were also analysed for temperature, amount of sulphate, conductance, and pH in addition to the redox value. Temperature was measured at the sampling point immediately, and redox value, pH, and conductance as soon as possible in the laboratory. The amount of sulphate was analysed in the laboratory during the same day.

6.6.3 Test phase 3: Identification of upstream flows

The purpose of this test phase was to find the biggest sources of sulphate and at the same time analyse other quality factors of the samples. The samples were collected from ten different wastewater fractions on three different days. The test phase was performed during week 6. The wastewater fractions were:

1. Wastewater from sludge treatment
2. Wastewater from debarking department
3. Wastewater from recovery process
4. Green liquor dregs from recovery boiler
5. Canal water of batch cooking
6. Canal water from pulp drying
7. Overflow of circulation water
8. Overflow of brown circulation water
9. Dirty condensates
10. Dirty condensates and wastewater from continuous cooking process

The wastewater fractions were named according to the different pulp mill areas. All samples were collected in 1000 ml sample containers. All samples were collected on Monday, Tuesday, and Wednesday. On Thursday and Friday the bigger laboratory analyses were performed. Temperature, conductance, and pH were analysed separately from each sample on the same day. The remaining quality factors were analysed from each fraction’s own composite sample. The measured properties and the place and time of measurement of wastewater samples are presented in table 16:

Table 16. Properties to be measured, and place and time of measurement of wastewater samples in test phase 3.

Properties	**Place and time of measurement**
Temperature	At the sampling point, immediately
pH	In the laboratory, on the same day
Conductance	In the laboratory, on the same day
Total solid matter	In the laboratory, on Friday and Thursday
Total phosphorous	In the laboratory, on Friday and Thursday
Sodium	In the laboratory, on Friday and Thursday
Sulphate	In the laboratory, on Friday and Thursday
COD	In the laboratory, on Friday and Thursday
Chloride	In the laboratory, on Friday and Thursday

7. Results and discussion

The results of the test phases are presented in this chapter. The main points of the results are summarized at the end of this chapter.

7.1 Oxygen feed in the aeration tank

Oxygen concentrations in the aeration tank between 1.11.2022 - 2.1.2023 are presented in figure 8. The adjustable measurement (the beginning of aeration tank 2) is represented in burgundy in figure 8. The beginning day (15.11.2022) is circled in green.

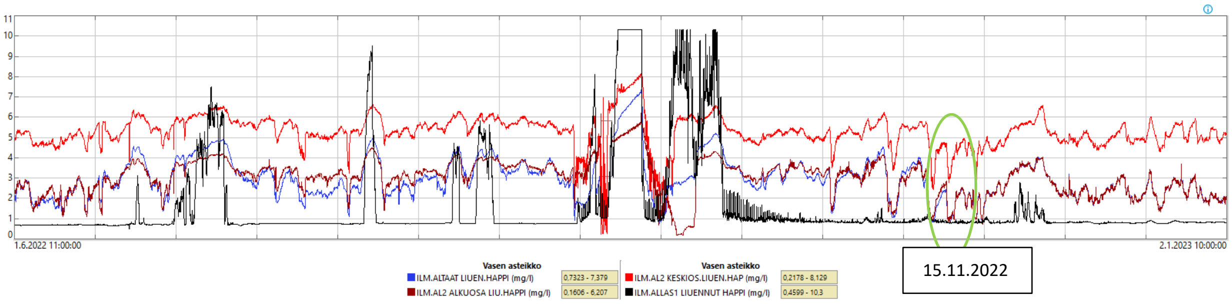


Figure 8. Concentration of oxygen in aeration tank.

Figure 8 shows that the oxygen concentration changed a lot after modification, but that the system tries to keep it close to 2 mg/l. Before modification, the concentration of oxygen was between 3-4 mg/l at the beginning of the aeration tank 2. It can be said that the oxygen concentration in the aeration tank has not changed radically. The power efficacy of the two turbo blowers of the aeration tank are presented in figure 9.

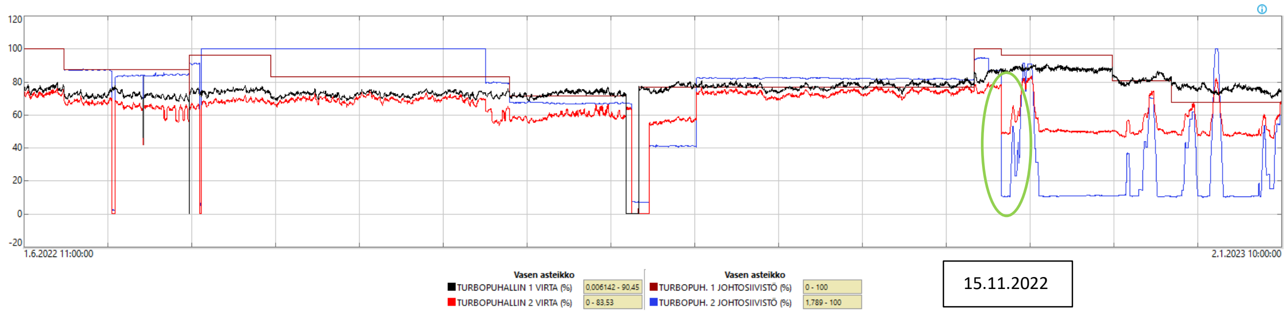


Figure 9. The efficacy and position of inlet guide vanes of the turbo blowers.

Figure 9 shows that power feeding decreased with turbo blower 2 after oxygen feed modification. The position of inlet guide vane 2 is also smaller. This means that energy consumption is lower because the turbo blowers do not have to work as much as before. Oxygen feed changes are presented in figure 10. The starting date of the test is circled in green.

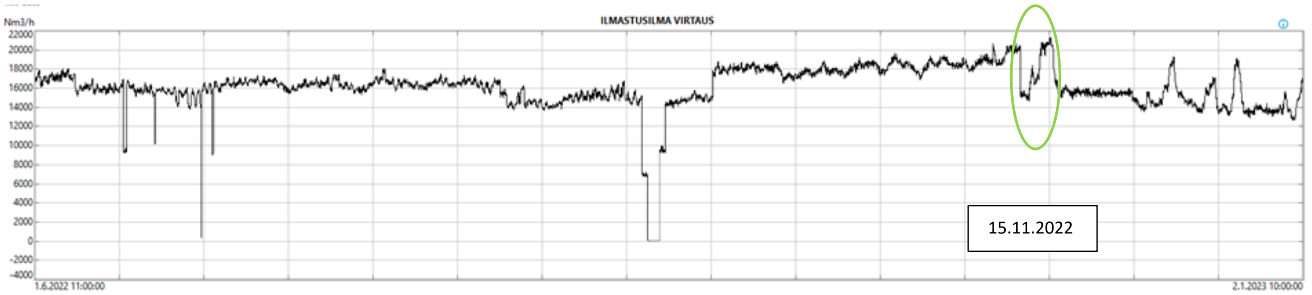


Figure 10. Graph of oxygen feed changes in the aeration tank.

In figure 10, a small decrease in oxygen feeding after setting the target value for dissolved oxygen can be seen. There have not been any markable changes in the number of solid particles, COD, nutrients, or sludge volume index. The modification in oxygen concentration has not negatively affected cleaning efficacy. The modification in oxygen concentration only had positive effects and the desired results, lower oxygen concentration and energy saving, were achieved.

7.2 Optimization of the ferric sulphate feed

During test phase 2, the input flow of ferric sulphate was changed and the consequences were monitored. The assumption was that when the chemical input is reduced, hydrogen sulphide emissions into the air will increase, the redox potential will decrease and the sulphate concentration in the wastewater will increase. When the input of chemical is increased, the opposite phenomenon will occur. All results from test phase 2 are presented in Appendix 3, table 1. The changes in the hydrogen sulphide concentration in the air of the wastewater treatment plant's chemical room are presented in figure 11. The figure only gives assumptions as to how the concentration of hydrogen sulphide changes when ferric sulphate input is changed. There was not an accurate gas meter to measure the air concentration of hydrogen sulphide at the wastewater treatment plant.

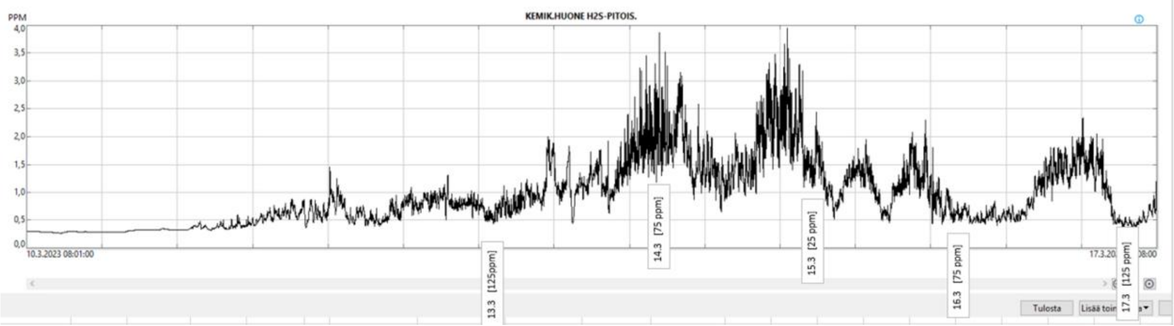


Figure 11. Changes in hydrogen sulphide concentration in the air of the wastewater treatment plant's chemical room.

Figure 11 shows that the concentration of hydrogen sulphide in the air changed as expected during the test phase. The boxes in the graph indicate the sampling days and the amount of ferric sulphate input at the time of taking samples. After taking the samples, the chemical input was changed to the next value as described in the plan of test phase 2.

The phosphorous concentration in the wastewater treatment plant's outflow has changed during two last years, as presented in figure 12. Figure 12 shows the start date of the ferric sulphate feeding with a line.

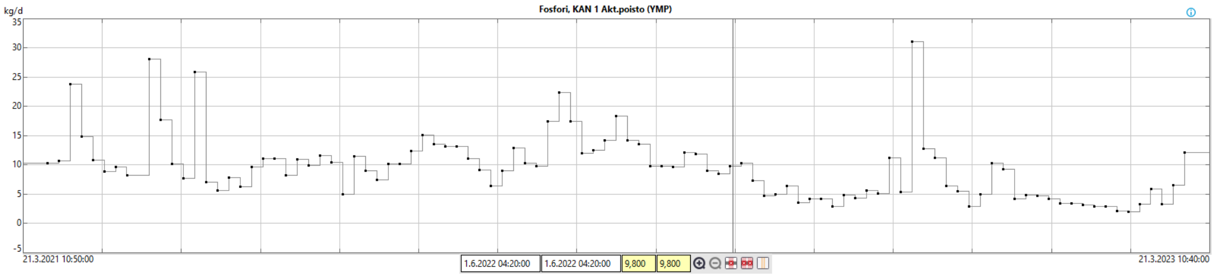


Figure 12. Phosphorous concentration in the wastewater treatment plant’s outflow in canal 1.

From figure 12 it can be seen that the concentration of phosphorous changed after starting the use of ferric sulphate. The concentration of phosphorous is now only half of what it was before dosing started. Appendix 3, figure 5 presents phosphorous reduction changes during the last two years. The reduction of phosphorous is now greater than before the addition of ferric sulphate.

Redox potential changes in the primary clarifier during different input flows of ferric sulphate are presented in figure 13. Appendix 3, figures 6 and 7 also present the results of redox changes in the coarse screen and bridge after the primary clarifier. The coarse screen’s redox potential values describe the quality of the incoming wastewater and its changes during test phase 2.

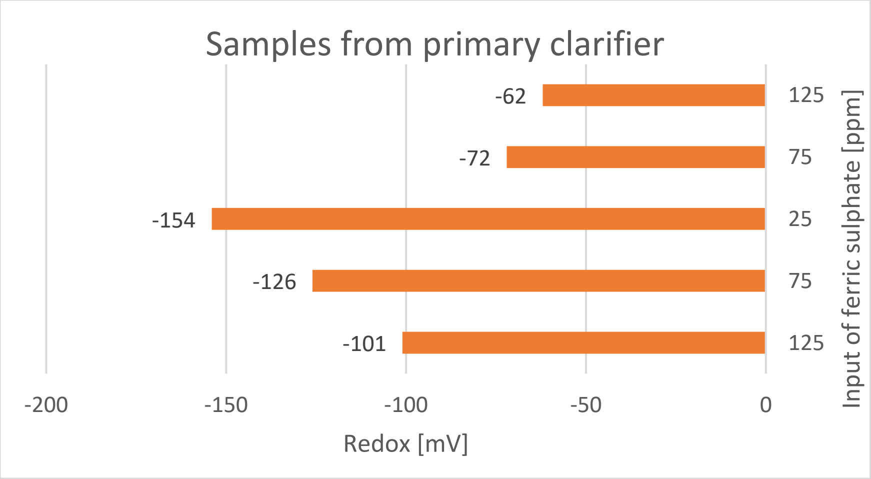


Figure 13. Redox potential values for different input flows of ferric sulphate.

Figure 13 shows that redox potential values change as expected with the input flow of ferric sulphate. When the chemical input flow was reduced in stages (125ppm -> 75 ppm -> 25 ppm), the redox potential value also decreased. When the chemical input flow was increased again (25 ppm -> 75 ppm -> 125 ppm), the redox value also increased. The results confirm the expected relationships between ferric sulphate input flow and redox potential changes. The ORP-value changes in the bridge, after the primary clarifier, were almost identical to those in the primary clarifier, as seen in figure 2 in appendix 3. The samples taken from the bridge on Wednesday were notable. The chemical supply was at its lowest (25 ppm) on Wednesday but the redox potential value was higher than with the 75-ppm input on Tuesday. This phenomenon likely occurred because some of the hydrogen sulphide already in the primary clarifier's wastewater evaporated into the air before the bridge. The differences between sulphate concentration and redox potential values in the primary clarifier and bridge are presented in figure 14 and appendix 3, figure 8. The sulphate concentration changes are noted in orange and the redox potential values in blue in the figures.

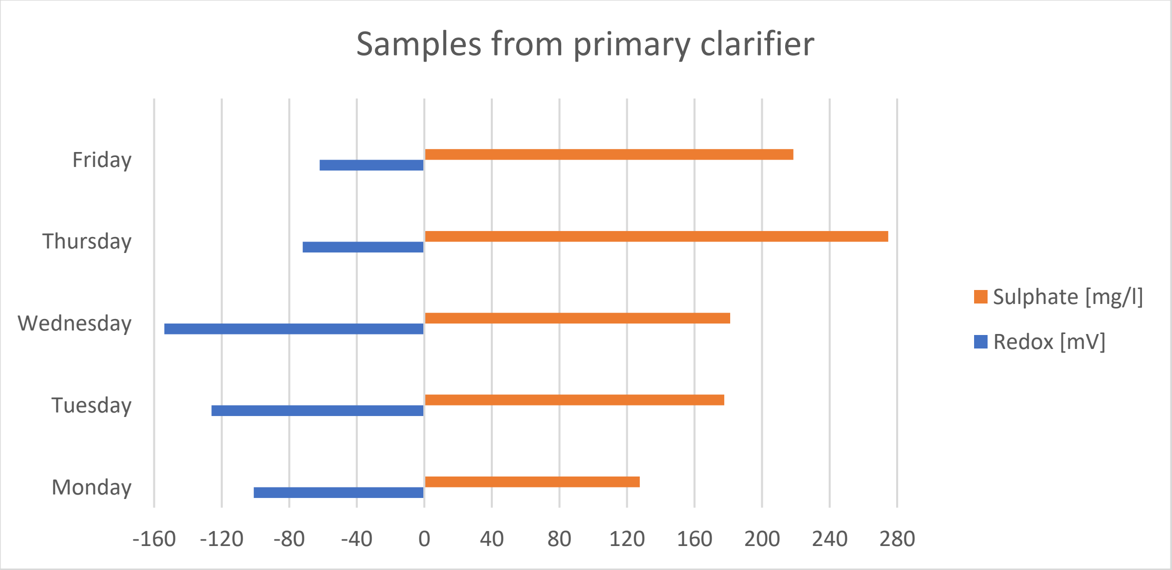


Figure 14. Redox potential values and sulphate concentration of primary clarifier samples during the test phase.

Figure 14 shows that the sulphate concentration changed as expected from Monday to Wednesday. However, on Thursday, the sulphate concentration increased since Wednesday, even though the input of ferric sulphate was already increased. On Friday, the sulphate concentration decreased slightly since Thursday. From this it can be concluded that the sulphate concentration needs more time to return back to normal concentrations. It can be said that sulphate concentration in the wastewater does not react as quickly as the redox potential value. Appendix 3, figure 8 presents the same differences in the samples from the bridge. The results from the bridge were similar to the results from the primary clarifier. The results of redox potential and sulphate concentration changes in the coarse screen are presented in appendix 3, figure 9. The results from the coarse screen describes the quality of the incoming wastewater and its changes during test phase 2.

7.3 Identification of upstream flows

The results from the laboratory analysis are presented in appendix 4, tables 2-5 and in the figures 15-17 below. The first results in tables 15 and 16 describe a situation where the same amount of wastewater flows from each wastewater fraction. Results from COD and total solid matter laboratory analyses are presented in figure 15. The concentration of COD is noted in orange and the concentration of total solid matter in blue.

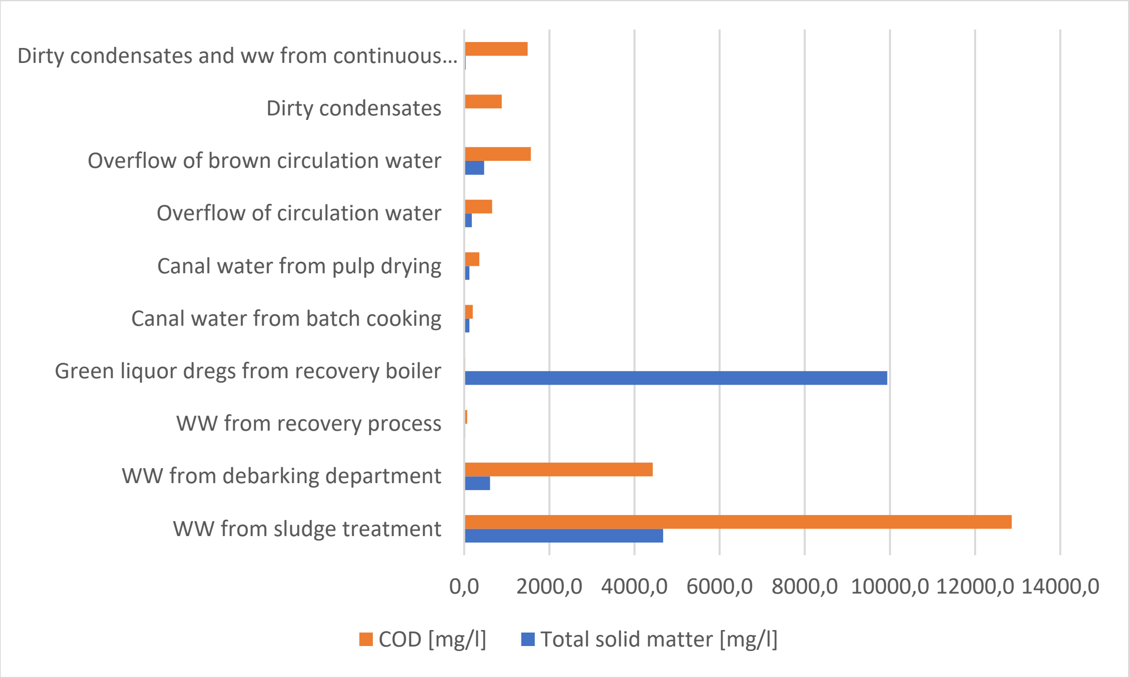


Figure 15. Results from COD and total solid matter analyses from each wastewater fraction.

The results indicating the biggest sources of COD and total solid matter were as expected. Figure 15 shows that the biggest COD sources in upstream flows are wastewater from sludge treatment and from the debarking facility. The biggest sources of total solids matter in upstream flows are the green liquor dregs from the recovery boiler and the wastewater from sludge treatment.

The results of chloride, sodium, sulphate, and total phosphorous laboratory analyses are presented in figure 16 below and in appendix 4, table 4. In figure 16, the concentration of chloride is noted in yellow, sulphate in grey, sodium in orange, and total phosphorous in blue.

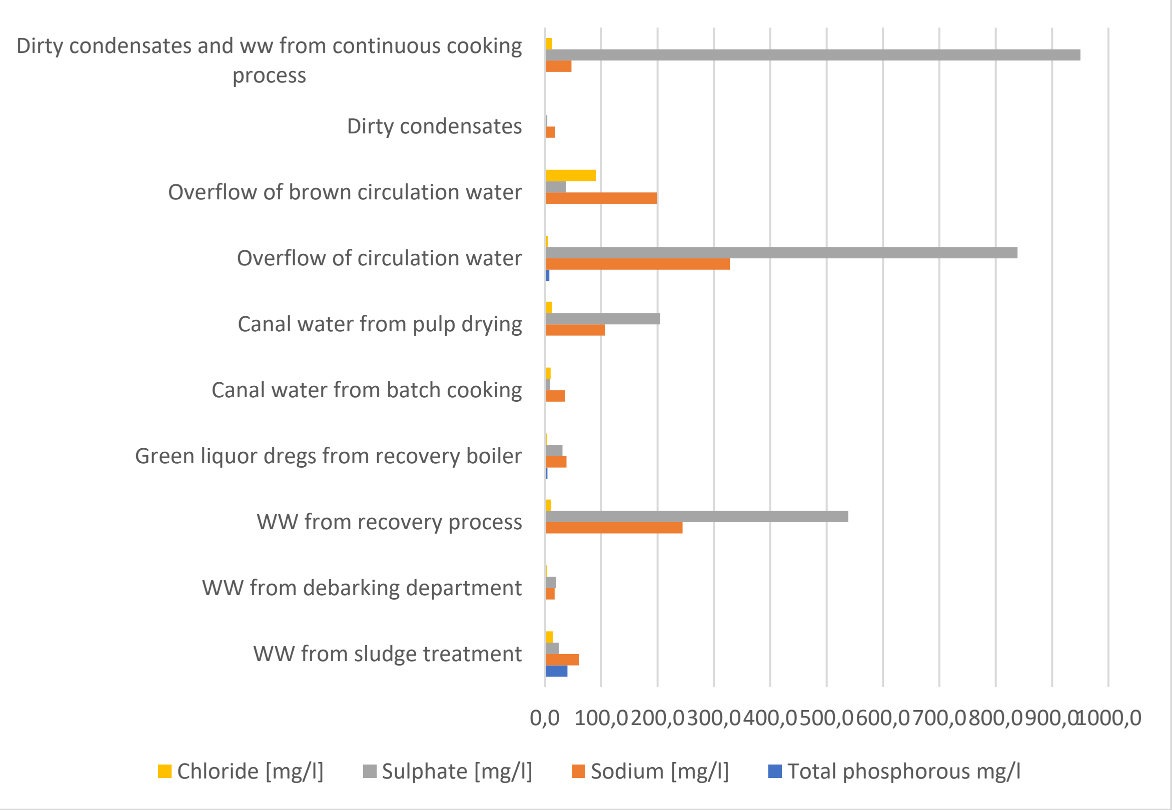


Figure 16. Results of chloride, sulphate, sodium, and total phosphorous analyses from each wastewater fraction.

Figure 16 shows that the sulphate concentration in dirty condensates was low but in wastewater combining dirty condensates and wastewater from the cooking process, the amount of sulphate was high. Therefore the biggest sulphate source was wastewater from the continuous cooking process. Other major sources of sulphate were wastewater from continuous cooking, overflow of circulation water, and wastewater from caustic soda treatment. In other words, these fractions generate the most hydrogen sulphide assuming that the same amount of wastewater would flows from all fractions.

Table 17 shows the estimated flow rate of the upstream sources. There was not a functioning flow meter for most of the sources, which is why the rates of the flow had to be estimated. The results are therefore only approximate and thus do not reflect the real situation in entirely.

Table 17. Estimated flow rates of wastewaters from upstream fractions.

Sampling point	Wastewater flow rate [l/s]
WW from sludge treatment	20,0
WW from debarking	35,0
WW from recovery process	42,0
Green liquor dregs from recovery boiler	5,0
Canal water from batch cooking	5,0
Canal water from pulp drying	25,0
Overflow of circulation water	180,0
Overflow of brown circulation water	105,0
Dirty condensates	75,9
Dirty condensates and ww from continuous cooking process	85,9
Total:	502,9

The highest wastewater flow rates are from circulation water overflow, brown circulation water overflow, and dirty condensates and wastewater from the continuous cooking process. The total flow rate is approximately 503 l/s. Such a flow rate is not typical in normal situations. During normal factory operations, the wastewater flow to the wastewater treatment plant is 300-400 l/s. Figure 17 shows results obtained from upstream analyses in relation to the flow rates.

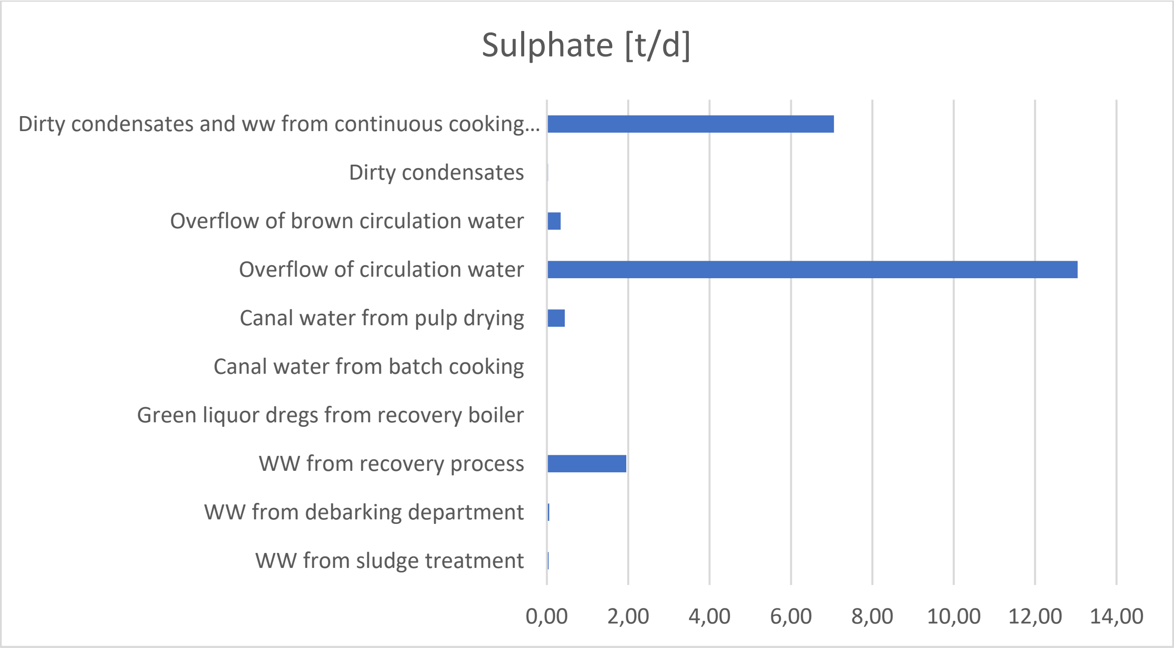


Figure 17. Sulphate concentrations (tonnes/day) in different upstream flow rates.

Figure 17 shows that the biggest sources of sulphate are the overflow of circulation water in the pulp drying process, wastewater from the continuous cooking process and wastewater from the recovery process. Controlling those results for relative flow rates did not change the results. Appendix 4, table 5 shows the results of total solid matter, total phosphorus, sodium, sulphate, chloride, and COD concentrations in proportion to the flow rates.

7.4 Discussion and recommendations

Test phase 1 was successful; all desired results were accomplished. The target was to decrease the concentration of dissolved oxygen and save energy. An automated oxygen concentration control was introduced. With the help of automation and defined target values for oxygen concentration, unnecessary oxygen feed to the aeration tank can be avoided. There is the possibility to save more energy costs by further decreasing more the dissolved oxygen concentration in the aeration tank. The concentration of oxygen is still unnecessarily high in the aeration tank. Also, the aerators in the aeration tank can be rearranged so that there if more oxygen in the beginning of the aeration tank than at the end of it. There could be more aerators at the beginning of the tank than at end of it. More oxygen is needed at the beginning of the aeration tank because the consumption of oxygen is higher there.

Test phase 2, regarding the optimization of ferric sulphate input flow, succeeded but also raised more questions. Attention was drawn to the fact that the redox potential value closely followed the changes in chemical input, but that the sulphate concentration needed a much longer time to normalize. But as explained in the theory paragraphs, ferric sulphate removes hydrogen sulphide from water, not sulphate. The formation of hydrogen sulphide requires sulphate, a suitable redox potential value, and anaerobic conditions. When one of these conditions change, sulphate-reducing bacteria cannot work. Temperature and pH also have an effect, but during this test phase these parameters were kept constant. In future studies, it would be good to have an online redox meter and a more accurate gas meter for the primary clarifier. By having an online redox meter, it would be possible to adjust ferric sulphate input flow. Flow rate meters at upstream points would also help to estimate the need for ferric sulphate at the wastewater treatment plant.

Test phase 3, regarding the identification of upstream flows, gave a lot of important information about the quality of different wastewaters from the pulp mill and the biggest sources of sulphate. The biggest sources of sulphate are the overflow of circulation water in the pulp drying process, wastewater from the continuous cooking process, and wastewater from the recovery boiler. During the test phase, it was succeeded in goal to find the biggest sources of sulphate and the biggest enablers of hydrogen sulphide generation. As a future measure, it would be good to invest in new flow meters in order to obtain a functional flow measurement for each upstream source. This would enable the anticipation of and better and faster resolution of problem situations. In addition, it would be good to know the flow rate from all upstream sources to the wastewater treatment plant. In connection with this test phase, it is also possible to conduct further studies on the quality of wastewater. From different upstream sources. For example, one point of interest could be an examination as to why all of other biggest sulphate sources from the pulp mill also have a lot of sodium, except wastewater from the continuous cooking process.

8. Conclusion

Today, the Oulu pulp mill produces unbleached sulphate pulp instead of bleached sulphate pulp. As a result of this production change, the amount and quality of wastewater was changed significantly, which is why the operation of the wastewater treatment plant had to be optimized again. After the production change, less wastewater is generated, so the same water and sludge circulates longer at the wastewater treatment plant.

In this thesis, the odour problems of the primary clarifier were investigated and discussed and the fractions that are fed to the primary clarifier, as well as the possibility to optimize the oxygen content of the aeration are investigated. The work does not consider, for example, Kraton's wastewater, which is fed directly to the aeration basin. All of the desired results were achieved, and a lot of valuable information was collected. The main goal was to find ways to save energy and costs by optimizing different parameters. The goal was also to find out the main sources of sulphate and investigate the effect of ferric sulphate at the wastewater treatment plant. An important part of this work was also the modelling of the wastewater treatment plant, which was made with Wedge software. Online results and laboratory results for various measurements were quick to find from the model created. From the results, it was easy to build graphs and calculate the necessary values. The modelling remains at the mill for everyday use.

With the help of optimising and automating the oxygen feed, energy consumption was decreased, and the oxygen content of the aeration basin was adjusted downward. It is possible to adjust the oxygen concentration even further down, for example between 1,5-1,8 mg/l. In addition, it would be important to think about the possibility of moving more aerators to the beginning of the aeration basin, where most of the oxygen in the wastewater is consumed. From the Wedge software, it can be seen that the oxygen concentration in the middle and end of the aeration basin 2 is still unnecessarily high. This work shows that it is important to be familiar with the flows that are fed to the wastewater treatment plant. It would be good to know the quality and flow rate of the flows from different wastewater fractions and to analyse them regularly. It is also important to find out and investigate the reasons why the overflow levels of circulation water and brown circulation water are still so high at the moment. It is important to find ways to improve the situation and at the same time reduce the amount of wastewater produced.

Odour problems are caused by many different compounds, but the most common cause is hydrogen sulphide. It can be said that ferric sulphate is a good chemical to prevent odours caused by hydrogen sulphide. However, it is important to know that ferric sulphate does not remove sulphate but precipitates the already formed hydrogen sulphide from the wastewater. The correct dosage of ferric sulphate is still being determined, but in this thesis one possible parameter was found. Redox was an accurate signifier of changes in ferric sulphate feed and changes in conditions with the primary clarifier. However, it must be noted that in test phase 2, a table model redox meter was used in the laboratory, so the uncertainty caused by the delay must be considered in the results. More accurate and reliable results could have been obtained by measuring the redox value directly at the sample collection point with a hand-operated meter. Another effective way to reduce or prevent the generation of hydrogen sulphide with the primary clarifier would be to feed oxygen to the water. The downside to this procedure is the high cost. With this method, the anaerobic conditions would be changed to aerobic and the sulphate-reducing bacteria would not be able to work. (Pulkkinen 2014, 13–14)

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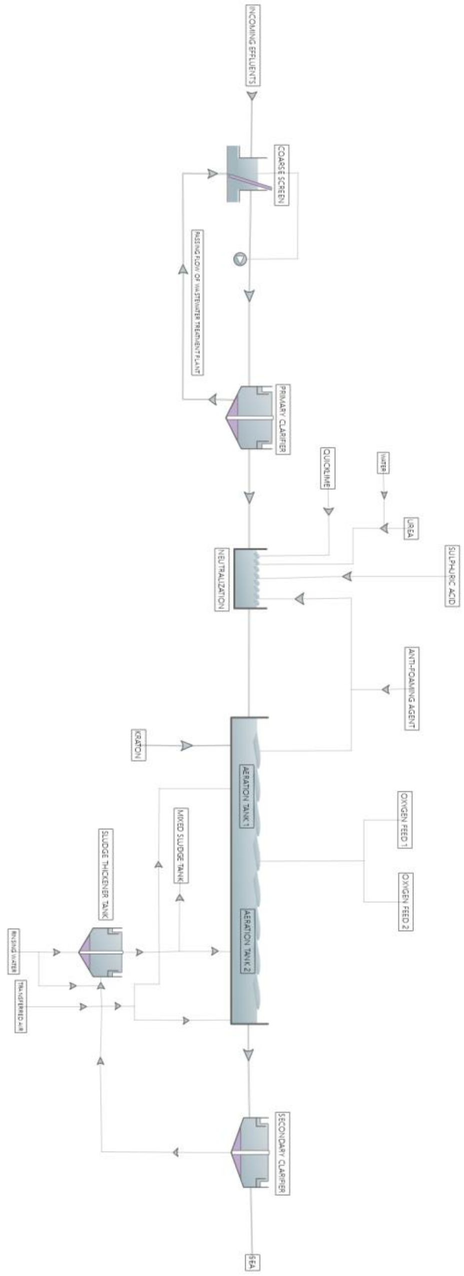
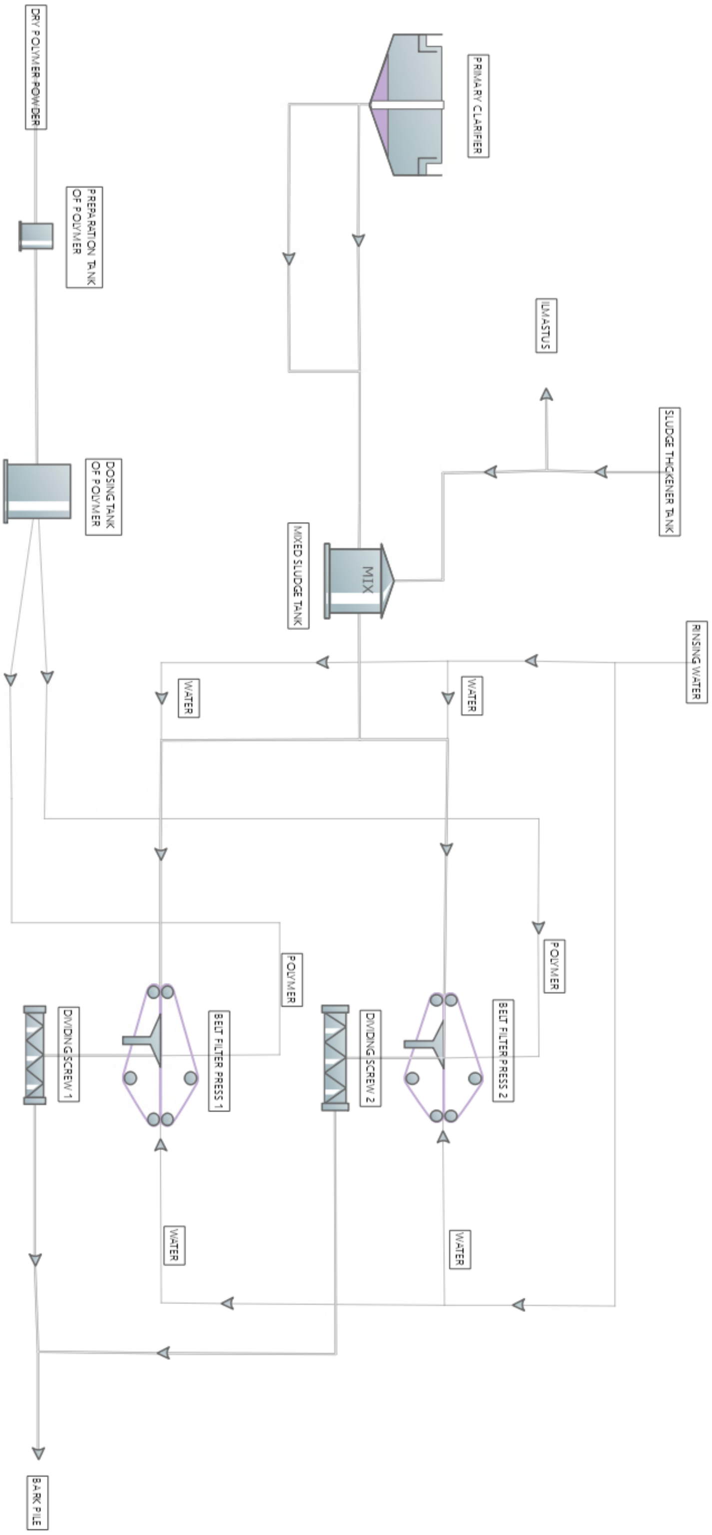
Appendices

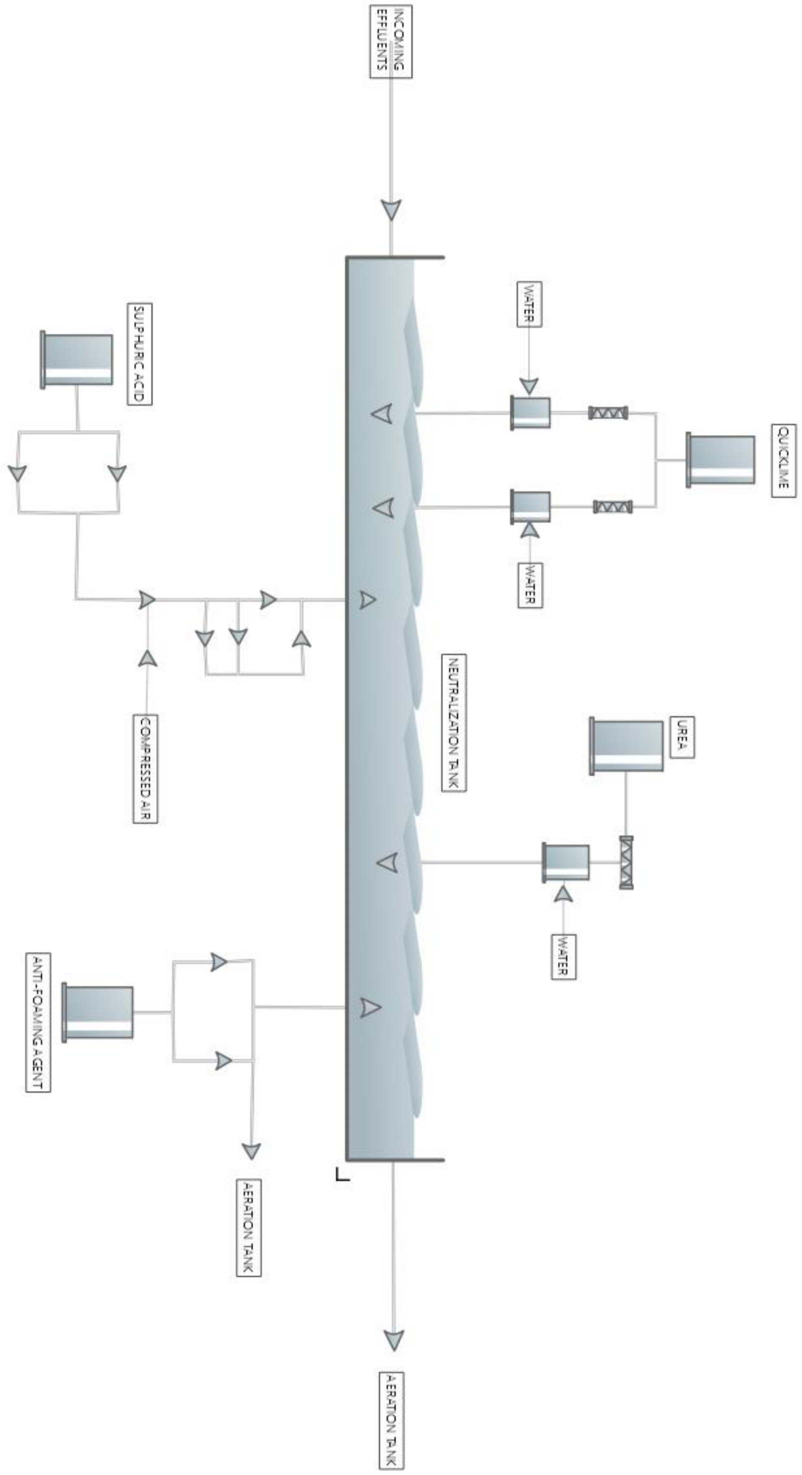
Appendix 1. Wedge-model from a pulp mill’s wastewater treatment plant



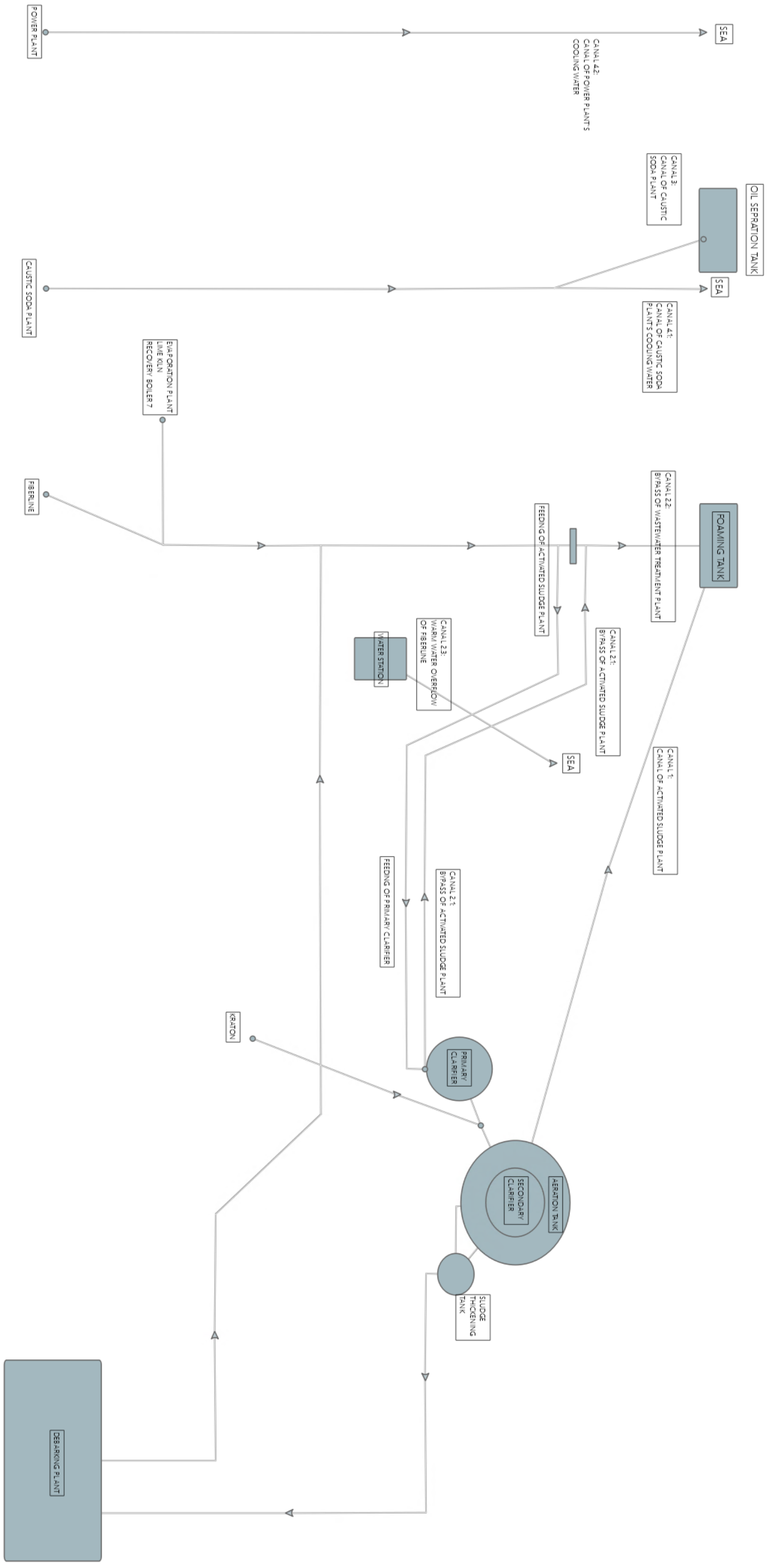
Appendix. Figure 1. Wedge-model from biological treatment in a wastewater treatment plant.



Appendix. Figure 2. Wedge-model from sludge treatment in a wastewater treatment plant.



Appendix. Figure 3. Wedge-model from chemical feeding in a wastewater treatment plant.



Appendix. Figure 4. Wedge-model from canal routes in a pulp mill area.

Appendix 2. Laboratory analysis methods and working instructions

pH analysis

pH was measured using a Lab pH meter inoLab pH7110 and SenTix 81 pH-electrode.

Conductance analysis

Conductance was measured using a WTW inoLab Cond 720 conductivity meter and TetraCon 325 Probe conductivity electrode.

Total solid matter analysis

Stora Enso’s total solid matter working instructions are based on standard SFS-EN 872.

Analysis equipment:

- Glass microfiber filters: Whatman GF/A: 110 mm or 47 mm depending on sample
- Millipore filtering system
- Whiteribbon Whatman 589: 110 mm
- Buchner funnel
- Glass filter suction flask
- Tweezer
- Baking tray

Procedure:

1. Mix the sample well and measure the required amount of the sample. The amount of each sample are presented in the table
2. Write down the volume of the sample taken
3. Filter the sample using a glass microfiber filter
4. Dry the sample in a drying oven at 105 °C for at least two hours
5. Weigh the dried sample at 0,1 mg accuracy

Amount of taken sample:	**Total weight - weight of filter = total solids weight**
Sample 1: 40 ml	674,9 mg – 488,0 mg = 186,9 mg
Sample 2:55 ml	515,8 mg – 483,4 mg = 33,4 mg
Sample 3:500 ml	499,9 mg – 487,9 mg = 12,0 mg
Sample 4: 100 ml	1480,9 mg -487,2 mg= 993,7 mg
Sample 5: 500 ml	543,9 mg -483,0 mg= 60,9 mg
Sample 6:121 ml	500,6 mg – 485,7 mg= 14,9 mg
Sample 7: 122 ml	504,1 mg – 482,4 mg=21,7 mg
Sample 8:70 ml	519,3 mg – 486,4 mg=32,9 mg
Sample 9:1000 ml	489,5 mg -485,0 mg = 4,5 mg
Sample 10:220 ml	491,1 mg – 483,0 mg= 8,1 mg

Total phosphorous analysis

Determination of phosphorous concentration in wastewater:

- Stora Enso’s working instructions are based on standard EN ISO 6678:2004
- Phosphorous comes only from wood raw material, i.e. the wastewater treatment plant does not separately add phosphorous nutrient

Total phosphorous analysis:

- Based on oxidation of the sample under acidic conditions and the formation of a blue complex compound. The absorbance measured from the complex is proportional to the phosphorous concentration in the sample

Dilution factors for upstream flows:

1. Wastewater from sludge treatment	Dilution factor: 10 (10ml/100 ml distilled water)
2. Wastewater from debarking	Dilution factor: 10 (10ml/100 ml distilled water)
3. Wastewater from recovery process	Dilution factor: 2 (100ml/100 ml distilled water)
4. Green liquor dregs from recovery boiler	Dilution factor: 20 (5ml/100 ml distilled water)
5. Canal water of batch cooking	Dilution factor: 2 (100ml/100 ml distilled water)
6. Canal water from pulp drying	Dilution factor: 2 (100ml/100 ml distilled water)
7. Overflow of circulation water	Dilution factor: 2 (100ml/100 ml distilled water)
8. Overflow of brown circulation water	Dilution factor: 2 (100ml/100 ml distilled water)
9. Dirty condensates	Dilution factor: 2 (100ml/100 ml distilled water)
10. Dirty condensates and wastewaters from continuous cooking process	Dilution factor: 2 (100ml/100 ml distilled water)

Analysis equipment:

- Thermoreactor: Merck TR 620 or TR 320
- Spectrophotometer: HACH Lange DR 3900, measuring range 0,05-1,5 mg/l of phosphorous
- Reagent tubes: HACH Lange LCK 349

Reagents:

- Reagent B: Consists of 16 % sulphuric acid
- DosiCap C-zip: Consists of sodium persulfate, sodium metaborate and lithium sulphate

Procedure of total phosphorous analysis:

1. Carefully remove the foil from the screwed-on DosiCap Zip and make all necessary marks on the tube
2. Unscrew the DosiCap Zip and pipet 2,0 ml of sample
3. Screw the DosiCap Zip back on the tube upside-down and shake the tube until reagent has been dissolved from the zip
4. Heat tube in the thermostat: 60 minutes at 100 °C
5. After heating at 100 °C, let tubes cool down at 50 °C in the thermoreactor
6. Allow the tube to cool down at room temperature
7. After cooling down, pipet reagent B 0,2 ml into the tube
8. Close the tube immediately with grey DosiCap C-Zip and shake the tube a couple of times until the reagent has been dissolved
9. After 10 minutes, invert tube a few more times. The measurement must be done 10-30 minutes after adding reagent

10. Clean the tube carefully, insert the tube into spectrophotometer
11. Spectrophotometer will measure the concentration of phosphorous automatically

Sodium analysis

At Stora Enso Oulu Mill's laboratory SpectrAA 220 atomic absorption spectrometer is used as an AAS device. There is no standard way to prepare samples. All preparation decisions have to be made considering all samples individually.

Atomic absorption spectrometry (AAS) is used for analysing elements in liquid. This device detects elements by comparing an element's characteristics of wavelengths of electromagnetic radiation from different light source. All elements have different reaction times to light and different wavelengths and these reactions are measured against standards. (Thermo Fisher Scientific, 2023) When atoms react to the light's specific wavelength, energy is absorbed by the atom. The flame of the AAS is the component where all atoms' light absorption occurs. (Agilent 2023)

Sulphate and Chloride analysis

Stora Enso Oulu Mill's laboratory uses Thermo Scientific DIONEX ICS-1100 642 as an ion chromatography analysis device. This device consists of an IonPac AS14A- column and gives the possibility to analyse, among other things, F, CH3COO, Cl, NO2 Br, NO3, PO4, SO3, SO4 and C2O4.

Ion chromatography (IC) is used to analyse liquid form samples. There are two types of IC: anion or cation exchange chromatography. The basic principle of IC is to separate differently sized and charged molecules from each other. Separation happens in the column and it is based on the molecule's different interactions with column's resin. (Measurlabs 2023) The ions are measured by an electrical conductivity detector in the column of the IC. The detector is the element that produces the chromatogram from the results, which are based on conductivity versus time. Ions make peaks on this graph and the peaks and ions can be recognized by using standardized results. (Gordon et al. 2011) The IC usually consists of liquid eluent, high-pressure pump, sample injector, guard and separator column, chemical suppressor, conductivity cell and data collection system. (Thermo fisher scientific 2012)

Dilution factors of samples are presented in the table:

Sample 1: Coarse screen	Dilution factor: 100
Sample 2: Primary clarifier	Dilution factor: 100
Sample 3: Bridge (after primary clarifier)	Dilution factor: 100

Dilution factors for the chloride and sulphate analysis of test phase 3's samples are presented in the table:

1. Wastewater from sludge treatment	Dilution factor: 1
2. Wastewater from debarking	Dilution factor: 1
3. Wastewater from recovery process	Dilution factor: 1(Chloride) and 10 (sulphate)
4. Green liquor dregs from recovery boiler	Dilution factor: 1
5. Canal water of batch cooking	Dilution factor: 1
6. Canal water from pulp drying	Dilution factor: 20 (sulphate) and 1 (chloride)
7. Overflow of circulation water	Dilution factor: 1 (chloride) and 25 (sulphate)
8. Overflow of brown circulation water	Dilution factor: 100 (chloride) and 1 (sulphate)
9. Dirty condensates	Dilution factor: 1
10. Dirty condensates and wastewater from continuous cooking process	Dilution factor: 1 (chloride) and 100 (sulphate

COD analysis

Principle:

- COD (Chemical oxygen demand) describes how much oxygen is consumed for the complete chemical decomposition of the organic matter contained in the wastewater.
- COD is a combination of slowly and rapidly decomposing organic matter
- In COD analysis a strong chemical oxidizer (bichromate) is used
- COD-tubes used are between 0-150 ppm and 0-1500 ppm

Dilution factors of samples are presented in the table:

1. Wastewater from sludge treatment	Dilution factor: 20
2. Wastewater from debarking	Dilution factor: 10
3. Wastewater from recovery process	Dilution factor: 1
4. Green liquor dregs from recovery boiler	Dilution factor: 1
5. Canal water of batch cooking	Dilution factor: 1
6. Canal water from pulp drying	Dilution factor: 1
7. Overflow of circulation water	Dilution factor: 1
8. Overflow of brown circulation water	Dilution factor: 2
9. Dirty condensates	Dilution factor: 2
10. Dirty condensates and wastewater from continuous cooking process	Dilution factor: 2

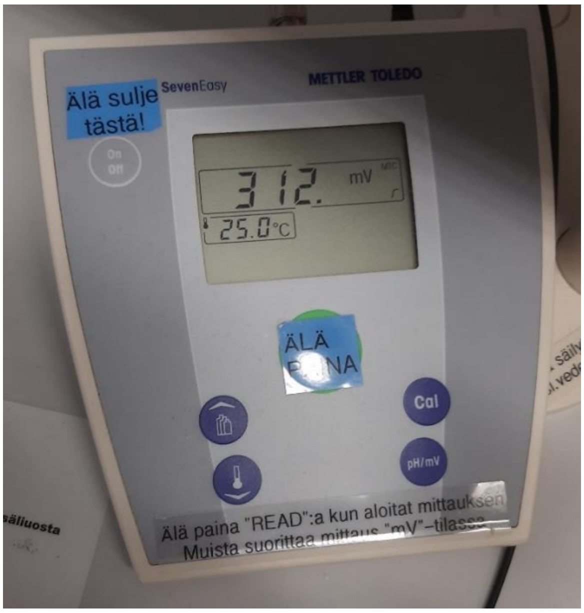
Procedure of COD analysis

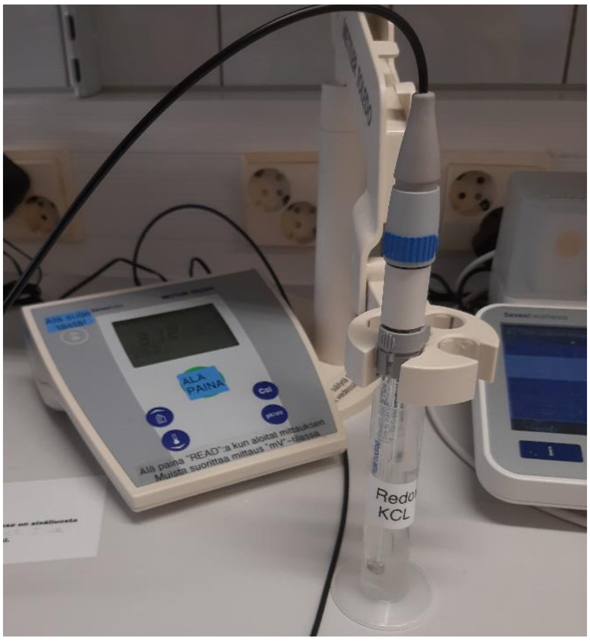
1. Mix the sample carefully and open the COD tube
2. Pipet 2 ml of the sample in the reagent tube
3. Close the tube and mix the tube with Vortex genie about 15 seconds
4. If the sample is green after this, the sample needs to dilute again
5. Make the zero-sample from distilled water (2 ml to the COD tube)
6. Put all tubes in the thermometer and let them warm up at 148 °C for two hours

7. Turn the tubes upside-down one more time after warming
8. Use the COD-measurement to measure COD concentration in the samples

Redox analysis

Redox potential was measured using a SevenEasy Mettler Toledo pH and ORP measurement and InLab Redox-L ORP combined electrode.

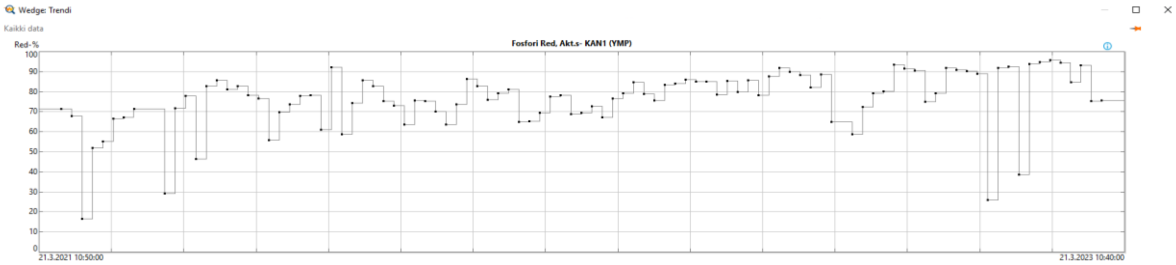




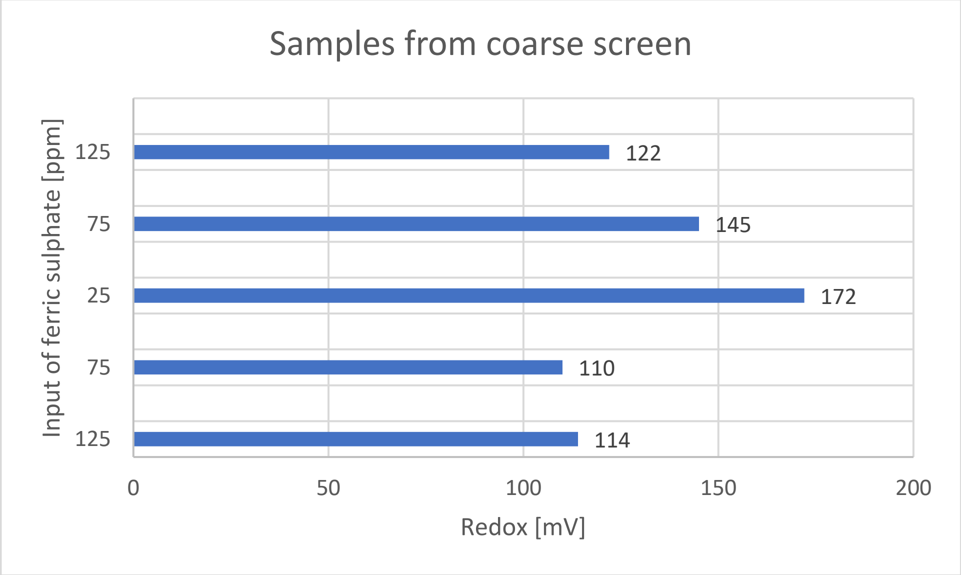
Appendix 3. Test phase 2 results

		Ferric sulphate							
		Input [ppm]	Input [l/h]	Redox [mV]	pH	Conductivity [uS/cm	Conductivity [mS/m	Temperature[°C]	Sulphate [mg/l
Sample from coarse screen (without ferric sulphate)	**Monday**	125	145	114	8,69	767	76,7	41,7	183,76
	Tuesday	75	87	110	7,97	716,3	71,63	42,3	186,29
	Wednesday	25	29	172	8,02	885,4	88,54	41	245,46
	Thursday	75	87	145	7,64	799,3	79,93	41,4	267,97
	Friday	125	145	122	7,8	540,7	54,07	40,1	145,85
Sample from primary clarifier	**Monday**	125	145	-101	6,94	703,1	70,31	37,6	127,55
	Tuesday	75	87	-126	6,76	763,8	76,38	40,6	177,57
	Wednesday	25	29	-154	7,12	800	80	43,1	181,08
	Thursday	75	87	-72	7,09	884,5	88,45	41,8	274,69
	Friday	125	145	-62	6,92	837,5	83,75	40,4	218,5
Sample after primary clarifier (bridge) (ferric sulphate has already taken effect)	**Monday**	125	145	-79	6,86	710,2	71,02	40,7	126,84
	Tuesday	75	87	-132	6,67	783,8	78,38	41,7	178,06
	Wednesday	25	29	-97	7,05	797,2	79,72	42,7	178,67
	Thursday	75	87	-47	7	913,4	91,34	42,4	254,66
	Friday	125	145	-30	6,86	851,9	85,19	40,8	223,22

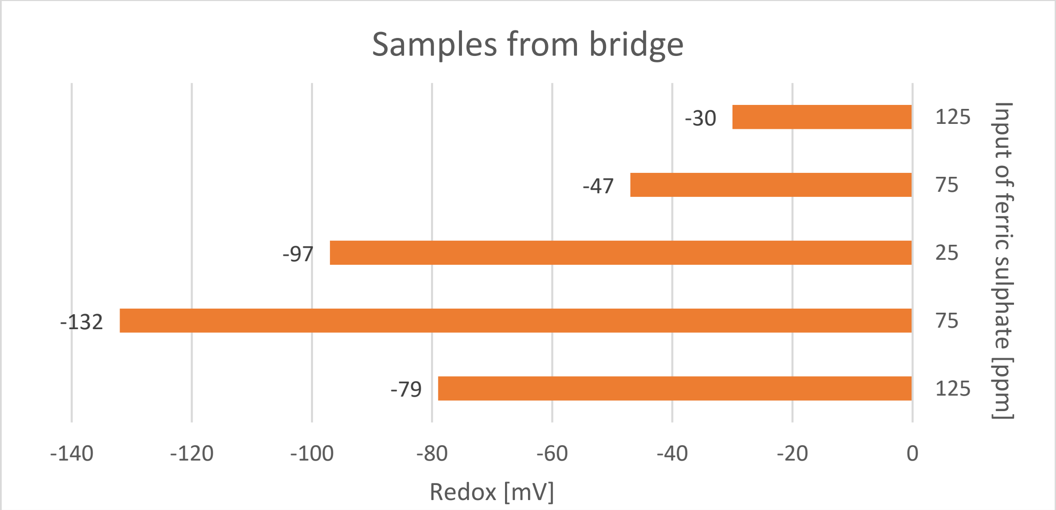
Appendix. Table 1. Table of all results of test phase 2



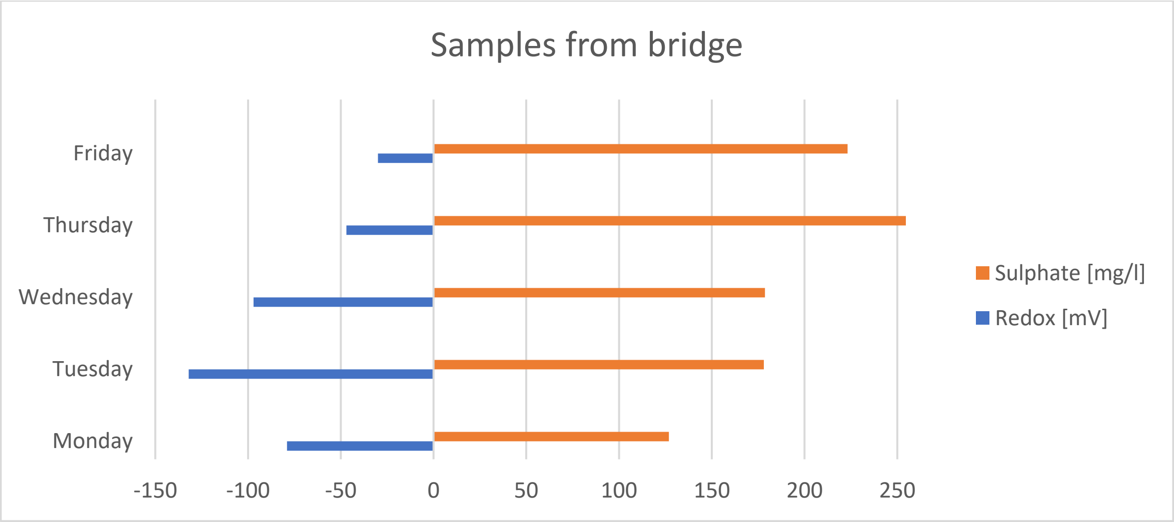
Appendix. Figure 5. Phosphorous reduction changes between canal 1 and activated sludge plant’s input flow during the last two years.



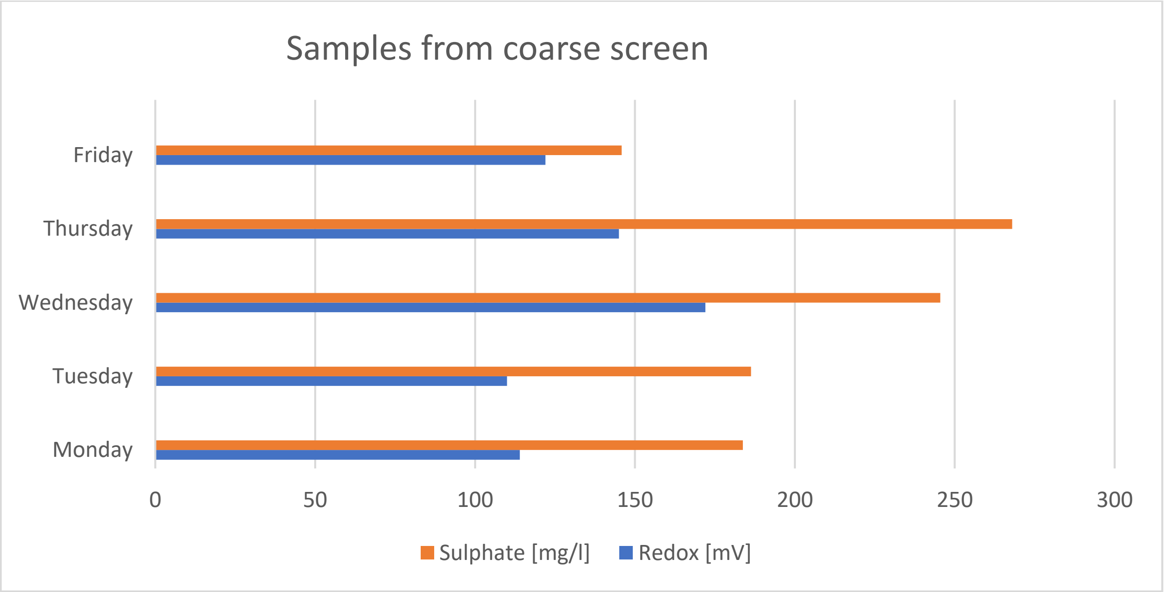
Appendix. Figure 6. Redox potential changes during test phase 2 in samples from coarse screen.



Appendix. Figure 7. Redox potential changes during test phase 2 in samples from bridge after primary clarifier.



Appendix. Figure 8. Sulphate concentration and redox potential changes in samples from bridge.



Appendix. Figure 9. Sulphate concentration and redox potential changes in samples from coarse screen.

Appendix 4. Test phase 3 results

Sampling point	Sampling point	Temperature [°C]	pH	Conductance [mS/m]
WW from sludge treatment	1	18,6	7,2	58,3
WW from debarking department	2	38,5	5,1	12,0
WW from recovery process	3	23,8	10,0	121,1
Green liquor dregs from recovery boiler	4	59,5	9,5	33,4
Canal water from batch cooking	5	18,8	8,2	17,5
Canal water from pulp drying	6	43,9	6,7	55,0
Overflow of circulation water	7	55,5	5,8	167,5
Overflow of brown circulation water	8	50,8	8,5	86,5
Dirty condensates	9	54,0	9,1	10,5
Dirty condensates and ww from continuous cooking process	10	34,9	6,9	171,8

Appendix. Table 2. Temperature, pH and conductance results from test phase 3 samples.

Sampling point	Sampling point	Total solid matter [mg/l]	COD [mg/l]
WW from sludge treatment	1	4672,5	12860,0
WW from debarking department	2	607,3	4430,0
WW from recovery process	3	24,0	68,0
Green liquor dregs from recovery boiler	4	9937,0	26,0
Canal water from batch cooking	5	121,8	202,0
Canal water from pulp drying	6	123,1	354,0
Overflow of circulation water	7	177,9	656,0
Overflow of brown circulation water	8	470,0	1564,0
Dirty condensates	9	4,5	882,0
Dirty condensates and ww from continuous cooking process	10	36,8	1492,0
	Total:	**16174,9**	**22534,0**

Appendix. Table 3. Total solid matter and COD concentration results from test phase 3 samples

Sampling point	Sampling point	Total phosphorous mg/l	Sodium [mg/l]	Sulphate [mg/l]	Chloride [mg/l]
WW from sludge treatment	1	40,0	60,6	25,0	13,9
WW from debarking department	2	0,9	17,4	19,4	3,8
WW from recovery process	3	0,3	244,5	538,5	10,9
Green liquor dregs from recovery boiler	4	4,5	38,4	31,4	3,3
Canal water from batch cooking	5	0,2	35,7	9,3	10,3
Canal water from pulp drying	6	2,0	106,9	204,6	12,3
Overflow of circulation water	7	8,0	328,0	838,8	5,8
Overflow of brown circulation water	8	1,9	198,8	37,2	90,8
Dirty condensates	9	0,0	17,8	4,3	0,3
Dirty condensates and ww from continuous cooking process	10	0,4	47,3	950,5	12,5
	Total:	**56,8**	**1095,4**	**2658,9**	**164,0**

Appendix. Table 4. Total phosphorous, sodium, sulphate, and chloride concentration results from test phase 3 samples

Sampling point	Total solid matter [t/d]	Total phosphorous [kg/d]	Sodium [t/d]	Sulphate [t/d]	Chloride [kg/d]	COD [t/d]
1	8,07	69,12	0,10	0,04	24,02	22,22
2	1,84	2,61	0,05	0,06	11,58	13,40
3	0,09	1,05	0,89	1,95	39,70	0,25
4	4,29	1,96	0,02	0,01	1,43	0,01
5	0,05	0,10	0,02	0,00	4,44	0,09
6	0,27	4,32	0,23	0,44	26,48	0,76
7	2,77	123,95	5,10	13,04	90,36	10,20
8	4,26	17,33	1,80	0,34	824,01	14,19
9	0,03	0,00	0,12	0,03	1,64	5,78
10	0,27	3,06	0,35	7,06	93,08	11,07
	21,94	223,51	8,68	22,98	1116,74	77,98

Appendix. Table 5. Total solid matter, total phosphorous, sodium, sulphate, chloride, and COD concentration results from samples as a proportion of flow rates from wastewater fractions.