



**A BIOLOGICAL PROCESS FOR CONTROLLING CHEMICAL BALANCE IN A  
KRAFT MILL**

Lappeenranta–Lahti University of Technology LUT

Master's programme in Sustainability Science and Solutions, Master's thesis

2025

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Pulp and Paper Sustainability Lead, M.Sc. (Tech.) Antti Pietiläinen

## ABSTRACT

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LUT School of Energy Systems

Environmental Technology

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Keywords: sulfate reduction, kraft mill, anaerobic digestion, chemical balance, Na/S balance

This Master's thesis examines the potential of anaerobic digestion as a sulfate reducing method from sulfate-containing side streams of a kraft mill. The aim was to find out whether a kraft mill can become sulfur self-sufficient, and under what conditions, what are the most important factors that affect anaerobic digestion and how these factors affect the efficiency and end result of the process. Furthermore, it was investigated how efficiently anaerobic digestion can reduce sulfate emissions at the mill and recover useful by-products while maintaining the sodium/sulfur balance of the kraft mill. The results of a third-party laboratory experiment and sodium/sulphur balances of two hypothetical kraft mills were utilized in the study.

The results of laboratory experiment show that up to 100% of sulfate can be reduced if the process conditions remain optimal for sulfate reducing bacteria. With anaerobic digestion, a kraft mill can become sulfur self-sufficient if sulfuric acid produced with SulfoLoop would be used to replace fossil-based sulfuric acid used in the production of kraft pulp. Based on the laboratory experiment the following factors showed as the most important factors for the efficiency and outcome of the process: the sulfate concentration of the sample, the ratio of chemical oxygen demand and sulfate, the content of organic and fatty acids and the process conditions. Calculations carried out for two hypothetical kraft mills show that the addition of an anaerobic digester to the mill does not affect the mill's Na/S balance. The calculations can also be used to conclude that anaerobic digestion is an effective way to reduce sulfate emissions and recover sulfur. Anaerobic digestion can be found to be a suitable method for reducing sulfate from sulfate-containing side streams of a kraft mill, and it is supported by both laboratory tests and hypothetical calculations.

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Tässä diplomityössä tutkitaan mädätyksen potentiaalia sulfaatin pelkistyksessä sellutehtaan sulfaattipitoisista sivuvirroista. Tarkoituksena oli selvittää voiko sulfaattisellutehtaasta tulla rikkiomavarainen, ja missä olosuhteissa, mitkä ovat tärkeimmät tekijät, jotka vaikuttavat mädätykseen ja miten nämä tekijät vaikuttavat prosessin tehokkuuteen sekä lopputulokseen. Lisäksi tutkittiin, kuinka tehokkaasti mädätys voi vähentää tehtaan sulfaattipäästöjä ja ottaa talteen hyödyllisiä sivutuotteita kuitenkin samalla ylläpitäen sulfaattisellutehtaan natrium/rikki -tasapainoa. Työssä hyödynnettiin muun muassa kolmannen osapuolen suorittaman laboratoriokokeen tuloksia sekä kahden hypoteettisen sulfaattisellutehtaan Na/S-tasetta.

Laboratoriokokeiden tulokset osoittavat, että jopa 100 % sulfaatista saadaan pelkistettyä, mikäli prosessiolosuhteet pysyvät sulfaattibakteereille optimaalisina. Mädätyksen avulla sulfaattisellutehtaasta voi tulla rikkiomavarainen, jos SulfoLoopin avulla tuotetulla rikkihappolla saadaan sulfaattisellun valmistuksessa käytetty fossiiliperäinen rikkihappo korvattua. Laboratoriokokeiden avulla voidaan todeta prosessin tehokkuuden ja lopputuloksen kannalta merkittävimmiksi seuraavat tekijät: näytteen sulfaattipitoisuus, kemiallisen hapenkulutuksen ja sulfaatin suhde, orgaanisten happojen pitoisuus sekä prosessiolosuhteet. Kahdelle hypoteettiselle sulfaattisellutehtaalle toteutetut laskelmat osoittavat, että hapettoman mädättämön lisääminen tehtaan yhteyteen ei vaikuta tehtaan Na/S-taseeseen. Laskelmien avulla voidaan myös todeta mädätyksen olevan tehokas keino sulfaattipäästöjen pienentämiseen ja riikin talteen ottamiseen. Mädätyksen voidaan todeta soveltuvan menetelmänä sulfaatin pelkistämiseen ja sitä tukevat niin tehdyt laboratoriokokeet kuin hypoteettiset laskelmat.

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*Martta Harsia*

## SYMBOLS AND ABBREVIATIONS

### Roman characters

$c$	concentration	[g/l, mg/l]
$M$	molar mass	[g/mol]
$m$	mass	[kg, t]
$q_v$	volume flow	[m <sup>3</sup> /ADt]
wt-%	mass percentage	[%]
$x$	mass of x in substance	[kg <sub>x</sub> /kg <sub>substance</sub> ]
%S	sulfur content in sulfate	[%]

### Greek characters

$\rho$	density	[kg/m <sup>3</sup> ]
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### Subscripts

d	desired
max	maximum
r	required
re	recovered

### Chemical compounds and elements

Ba	Barium
Ca	Calcium
CaCO <sub>3</sub>	Calcium carbonate

CaO	Calcium oxide, lime
Ca(OH) <sub>2</sub>	Calcium hydroxide
CH <sub>4</sub>	Methane
CH <sub>3</sub> COOH	Acetate
Cl	Chlorine
ClO <sub>2</sub>	Chlorine dioxide
ClO <sub>3</sub> <sup>-</sup>	Chlorate
CO <sub>2</sub>	Carbon dioxide
H <sub>2</sub>	Hydrogen
HCl	Hydrochloric acid
HCO <sub>3</sub> <sup>-</sup>	Hydrogen carbonate
H <sub>2</sub> O	Water
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
H <sub>2</sub> S	Hydrogen sulfide
HS <sup>-</sup>	Bisulfide
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
K	Potassium
MgSO <sub>4</sub>	Magnesium sulfate
Na	Sodium
Na <sub>2</sub> CO <sub>3</sub>	Sodium carbonate
NaClO <sub>3</sub>	Sodium chlorate
NaHS	Hydrosulfide
NaHSO <sub>4</sub>	Sodium bisulfate
Na <sub>3</sub> H(SO <sub>4</sub> ) <sub>2</sub>	Sodium sesquisulfate

NaOH	Sodium hydroxide, caustic soda
Na <sub>2</sub> S	Sodium sulfide
Na <sub>2</sub> SO <sub>4</sub>	Sodium sulfate
O <sub>2</sub>	Oxygen
OH <sup>-</sup>	Hydroxide
P	Phosphorous
S	Sulfur
S <sup>2-</sup>	Sulfide
SO <sub>2</sub>	Sulfur dioxide
SO <sub>3</sub>	Sulfur trioxide
SO <sup>(2-)</sup> <sub>4</sub>	Sulfate

#### Abbreviations

AD	Anaerobic Digestion
ADt	Air Dry metric ton of pulp
BSW	Brown Stock Washing
CNCG	Concentrated Non-Condensable Gas
COD	Chemical Oxygen Demand
DNCG	Diluted Non-Condensable Gas
ECF	Elemental Chlorine Free
ESP	Electrostatic Precipitator
EU	European Union
g	gas
HW	Hardwood

Na/S	Sodium/Sulfur
NCG	Non-Condensable Gase
NPEs	Non-Process Elements
P&P	Pulp & Paper
SBR	Sulfate Reducing Bacteria
SW	Softwood
TCF	Totally Chlorine Free
TRS	Total Reduced Sulfur
WSA	Wet-gas Sulfuric Acid
WWTP	Wastewater Treatment Plant

#### Units

Temperature [°C]

Time [d]

Volume [ml, m<sup>3</sup>]



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# 1 Introduction

Industrial processes have been found to be one of the main factors contributing to the depletion of freshwater resources, alongside with human-induced climate change (Chowdhary et al. 2020, p. 236). Freshwater, which does not contain salts and originates from sources such as rivers or lakes, is becoming increasingly scarce. This issue is prevalent across Asia and Northern and Sub-Saharan Africa and now also affects Southern Europe (WISE 2024). The shortage of freshwater will significantly impact water-intensive sectors, like industry and agriculture, demanding adaptation to these new conditions. Increased evaporation and disrupted precipitation patterns are examples of the consequences of freshwater scarcity. Evaporation and precipitation have a relevant role in the hydrological cycle. Disruptions in this natural cycle could cause imbalance followed by degradation of freshwater sources. (Gleick & Cooley 2021, pp. 319, 330-331; Mazzucato et al. 2024, pp. 44, 49.)

The pulp and paper (P&P) industry will be particularly affected by the need to adapt to these changes, as it is recognized as a major contributor to the increasing scarcity of freshwater (Chowdhary et al. 2020, pp. 236-237). This industry is globally known to be one of the most water-consuming industries. An average pulp mill consumes freshwater around 20-40 cubic meters per air dried ton of pulp ( $\text{m}^3/\text{ADt}$ ) and typically releases its treated wastewater back to waterbodies (Sousa et al. 2023, p. 63). Freshwater is preferred in pulp mills due to its more conventional treatment compared to salt water. As the availability of freshwater diminishes, it is most likely that the environmental regulations and requirements related to water use and wastewater quality will become stricter. Effluents from kraft mills contain many pollutants such as sulfate, biological oxygen demand, and chemical oxygen demand (COD) (Chowdhary et al. 2020, p. 237). In order to reduce water consumption in the pulp industry, these pollutants need to be removed and water more circulated in pulp mills. If there are harmful pollutant in the effluents, the change towards closed water circulation in a pulp mill is impossible. (Esmaeeli & Sarrafzadeh 2022, p. 1.)

Sodium/Sulfur (Na/S) balance is one of the most important chemical balances of the kraft mill. The recovery and recycling of cooking chemicals containing sodium (Na) and sulfur (S) is crucial to make the kraft process economically feasible. To maintain the optimal Na/S balance in a kraft mill different chemicals, makeup chemicals, and by-products from other

onsite processes are added to the chemical recovery process. (Saturnino 2012, pp. 5-6.) The Na/S balance is often described with sulfidity which tells the amount of sodium sulfide in the cooking chemical (Fardim 2011, p. 277). The reduction degree and causticizing degree affect sulfidity which must be considered while discussing the Na/S balance. Sulfidity tends to be higher in mills using softwood compared to mills using hardwood in pulping. (Know-Pulp n.d.) Typically, sulfidity is between 30-45% (Andritz 2025a).

## 1.1 Background

This master's thesis is done in collaboration with Andritz. Andritz is a globally leading supplier of plants, equipment, automation solutions, and services for hydropower stations, the pulp and paper industry, the metalworking and steel industries, as well as environmental and green energy-focused sectors. Andritz has developed a process called SulfoLoop, which aims to produce sulfuric acid ( $\text{H}_2\text{SO}_4$ ) more sustainably than current sulfuric acid production methods from fossil-based sulfur (Brimstone, not treacle 2022). In the process the sulfuric acid is produced on-site in kraft mills. Sulfur needed in SulfoLoop could originate from sulfate reduction by anaerobic digestion (AD) furthermore to current sulfur from non-condensable gases (NCGs) and externally bought fossil-based sulfur. This sulfate would be obtained from sulfate-rich pulp mill streams. The streams utilized would be bleaching effluent, electrostatic precipitator (ESP) ash and other sulfate containing wastes and side streams. In the thesis the focus is on bleaching effluent and ESP ash. Sulfate reducing bacteria (SRB) can utilize sulfate ( $\text{SO}_4^{2-}$ ) as a terminal electron acceptor in their metabolism, reducing it to hydrogen sulfide ( $\text{H}_2\text{S}$ ). Followed by AD, hydrogen sulfide is then oxidized in SulfoLoop, and sulfuric acid is produced. (Andritz 2024d.) Figure 1 presents a simplified drawing of biological sulfate reduction process.

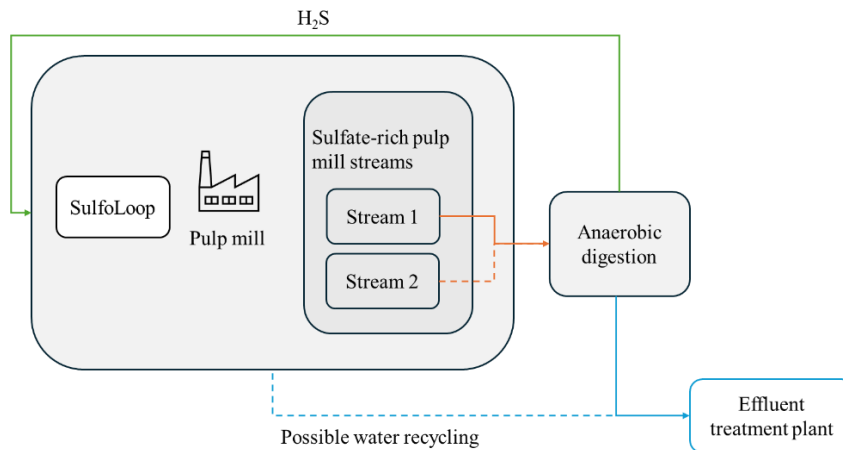


Figure 1. Biological sulfate reduction

Currently 80% of total sulfur used in industry originates from oil and gas refining as a by-product. The demand of fossil-based sulfur has been estimated to decline due to climate change. On the other hand, the demand of sulfur has been estimated to grow from 246 million tons to 400 million tons by 2040. This creates opportunities for new developing production methods, such as the SulfoLoop process, and the application of anaerobic digestion for the reduction of sulfate. These methods enable the effective management of sulfur containing compounds, resulting in the production of hydrogen sulfide and sulfuric acid. (Maslin et al. 2022, pp. 501, 503.) The demand of sulfuric acid will most likely also increase, as it is a highly important chemical in different industrial processes such as pulping and in the manufacture of fertilizer. It has been estimated that as human population expands so does the demand of fertilizer. (Brimstone, not treacle 2022.)

Sulfate ( $\text{SO}_4^{2-}$ ) is an anion, which is naturally found in water bodies. Seawater contains the most sulfates, while freshwater contains only approximately 0,1-1% of the seawater's level. (Karjalainen et al. 2021, p. 1.) Pulp production is one of the main human-induced causes of elevated sulfate concentration in the water bodies. Currently, the European Union (EU) does not monitor sulfate emissions to water bodies regularly, as it does not have an environmental quality standard guideline for sulfate. (Karjalainen et. al 2023, p. 1.) However, this does not mean that sulfate discharges into water bodies are not regulated in EU countries. In Finland, for example, the Supreme Administrative Court of Finland rejected the environmental permit of a pulp mill because its sulfate concentrations in wastewater were too high. In this case, sulfate emissions could not exceed an annual average of 55 t/day. (KHO:2019:166.)

Physical and chemical reactions of sulfate in a solution do not differ between various kinds of receiving water bodies. More relevant is the temperature of the discharged water as elevated temperatures accelerate chemical and biological reactions of sulfates. Also, the solubility of oxygen is reduced which weakens the status of the aquatic ecosystem even further. High concentrations of sulfate have also been found to displace oxygen. It has been noted that elevated concentrations of sulfates in brackish water (Baltic Sea) are one of the main reasons for intensive stratification, oxygen depletion, and formation of sulfides and hydrogen sulfide. (Aluehallintovirasto 2023, p. 168.)

Karjalainen et al. (2023, p. 1) noted that elevated sulfate concentrations in freshwater might harm aquatic life. Furthermore, Zak et al. (2021, pp. 1,10) found that elevated sulfate concentrations in freshwater bodies affect the biogeochemical cycle of carbon, nitrogen, and phosphorus. For example, eutrophication within freshwater bodies was found to have increased due to the disruption of the natural phosphorus cycle. The impacts of elevated sulfate emissions in seawaters are rarely researched due to naturally high sulfate levels. The sulfate level in seawater is approximately 2,7 g/l compared to freshwater 0-0,63 g/l depending on the type of freshwater source. (Zak et al. 2021, p. 4.) In Europe, most of the pulp mills are located close to a river or a lake as 86,7% of consumed freshwater is surface water (CEPI 2024, p. 28). Sulfates are not currently removed from discharged effluents, but as awareness increases, this is likely to change. The change is crucial, especially since the effluents from pulp mills are often discharged into the water system from which the freshwater was originally taken. (Andritz 2025b.)

Nowadays the majority of companies in the P&P industry in Europe have taken into account issues related to sulfates in discharged effluents and freshwater consumption. This has been recognized by implementing sustainable water usage and effluent treatment into their main strategy. For example, Metsä Group and Altri which is a Portuguese pulp manufacturing company have set a target to recover and utilize 100% of side streams generated in the pulping process by 2030 (Altri 2021, p. 63; Metsä Group 2020, p. 8). An Austrian P&P company MM Group has set a concrete target to reduce its water consumption by 30% by the end of 2030 compared to 2019. MM Group has also set targets to support this goal by improving process water consumption. (MM Group 2023, p. 37.) Among Finnish P&P companies at least Metsä Group, Stora Enso, and UPM have set a target to improve recovery and recycling to reduce water consumption at their production (UPM 2023, p. 92). From these companies,

Metsä Group and Stora Enso have also set a concrete target for reducing water use. Metsä Group has set a target to decrease the use of process water by 25% by 2030 compared to 2018 and Stora Enso similar reduction target by reducing 17% by 2030 compared to 2019. (Metsä Group 2020, p. 8; Stora Enso 2024, p. 38.) UPM has also set a concrete target to reduce the volume of wastewater by 30% by 2030 compared to 2008 (UPM 2023, p. 92).

In Finland, the location and the type of receiving water body impact to the limit value of sulfates in discharged effluents. For a pulp mill locating in the coastal area of the Baltic Sea, in Northern Finland near Kemi the limit value of sulfates in discharged effluents is 1 200 mg<sub>SO<sub>4</sub></sub>/l and in total in a year 39 000 t, while a battery material factory's similar values for the same ocean but in Southern Finland near Hamina are 30 900 mg<sub>SO<sub>4</sub></sub>/l and in a year 96 400 t (Aluehallintovirasto 2020, pp. 90-91). These values are set for effluents discharged to the Baltic Sea and are multiples compared to the guiding limit value for fresh water's 100 mg<sub>SO<sub>4</sub></sub>/l. (Aluehallintovirasto 2024, p. 168.)

## 1.2 Research questions of the study

This thesis aims to investigate could anaerobic digestion be a viable method to reduce sulfate to hydrogen sulfide from kraft mill waste streams. The transition from fossil-based sulfur to non-fossil-based sulfur creates pressure and opportunities to investigate alternative sources and recovery methods of sulfur. New studies generate opportunities to examine and improve these alternative sources and recovery methods and gain crucial information on the topic. In more detail, the focus of the study is on the empirical part, analyzing the laboratory experiment results and comparing Na/S balances for two hypothetical kraft mills with and without AD. The aim is to analyze anaerobic digestion from sulfate reducing point of view. The research questions of this thesis are the following:

1. In which type of conditions can a kraft mill become sulfur self-sufficient? How does the addition of anaerobic digestions impact to the sulfur self-sufficiency?
2. What are the main parameters that affect anaerobic digestion? How do these parameters affect the efficiency and the outcome of the process?
3. How effectively can anaerobic digestion reduce sulfur emissions and recover useful by-products while simultaneously maintaining the Na/S balance of a kraft mill?

The research questions create a structure for the study, which aims to conduct a comprehensive analysis of AD as a sulfate reducing method with the help of results from laboratory experiment and calculations for two hypothetical kraft mills. The goal is to identify how does the addition of AD impact the kraft pulping process and the main factors affecting the AD process. To support this goal, the theory part of the thesis will investigate the role of sulfur in kraft pulping process, sulfur in the water circulation of a kraft mill and anaerobic effluent treatment of kraft mill wastewater.

### 1.3 Structure of the thesis

This thesis is divided into two main parts, of which the first part is a literature review, and the second part is an empirical review. The literature part is again divided into three chapters. These chapters include basic information about sulfur in the kraft pulping process, sulfur in kraft mill water circulation, and knowledge about anaerobic effluent treatment. The first theory chapter explains the basics of the pulping process, focusing on relevant unit processes from Na/S balance point of view. The second chapter deals with sulfur in the water circulation of a kraft mill, different substances in effluents and their properties and factors limiting the closure of kraft mill water circulation. The last theory chapter explains the basic principles of anaerobic effluent treatment, mainly focusing on sulfate reduction from pulp mill effluents and side streams.

The second part of the thesis consists of empirical research. The goal of this section is to explore and reveal the answers to the research questions of the study. This is conducted by interpretation of samples taken from one part of the kraft pulping and completing calculations for the hypothetical kraft mills. Results from the calculations are utilized to investigate the effect of AD to the Na/S balance of a kraft mill. Laboratory experiment results are utilized to analyze the viability and efficiency of AD as a sulfate reducing method. Also, the possible sulfur self-sufficiency of a kraft mill is investigated with all of these results.

At the end of the thesis, the conclusion part presents the findings of the thesis and provides answers to the research questions. If there occurs a need for further research, that is also included in the previous discussion part. The summary part summarizes the whole thesis and briefly goes through both the theory and the empirical parts.



## 2 Sulfur in kraft pulping process

In this chapter the kraft pulping process is explained in general. The focus is on relevant unit processes from Na/S balance point of view since these processes use sulfur-containing chemicals and therefore may be a source for sulfur recovery. These processes include cooking and bleaching. Chemical recovery is also under comprehensive examination due to its importance to the chemical balance of the kraft mill and its high loads of sulfates in effluent.

### 2.1 Kraft pulping process

Pulping can be conducted either chemically or mechanically. From these chemical pulping is the leading pulping method. Chemical pulping can be divided into sulfite and sulfate processes of which the kraft (sulfate) process is more commonly used. (CEPI 2024, pp. 8-9.) Approximately 80% of the global chemical pulp is produced with kraft process (Suhr et al. 2015, p. 195). Therefore, when discussing pulping, this refers to kraft pulping and if not, it has been mentioned in the context.

The kraft pulping process can be divided into two main steps: pulp line also known as fiber line and chemical recovery. The first step in fiber line, wood handling, includes bark removal, chipping, and screening. This is followed by pulp production which includes cooking, washing and screening, oxygen delignification, bleaching, and drying. After the fiber line, there is chemical recovery. Chemical recovery consists of three steps which are evaporation, incineration, and recausticizing. (Suhr et al. 2014, pp. 196-204.) Figure 2 presents a schematic kraft process by Andritz.

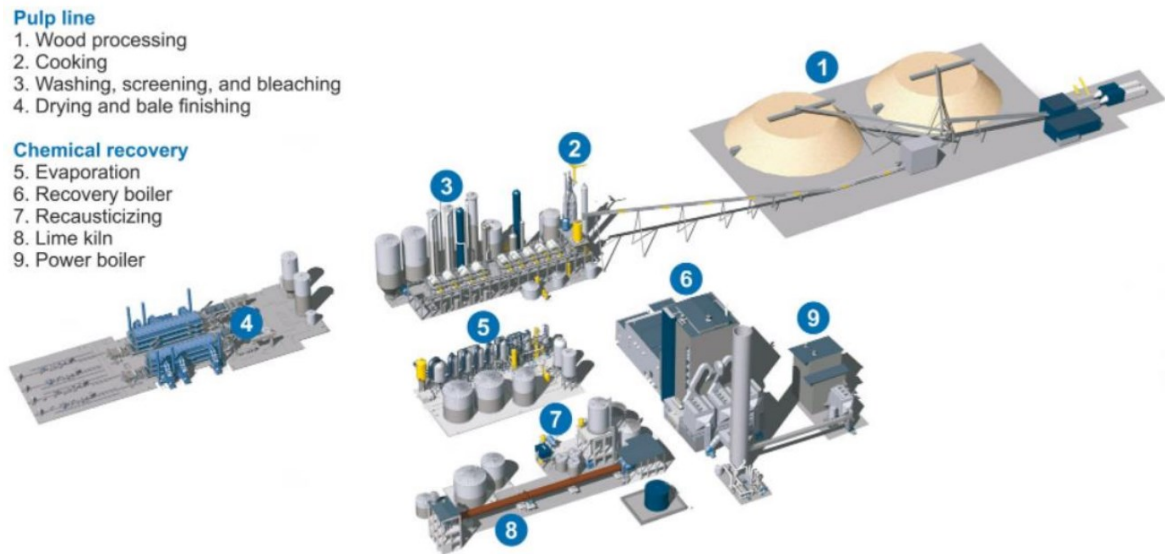


Figure 2. Kraft process by Andritz (Andritz 2024c)

### 2.1.1 Na/S balance

Controlling of Na/S balance is crucial to maintain high pulp yield, pulp quality and to control gaseous sulfur emissions (Mahecha-Botero et al. 2021, p. 102). Sulfur and sodium enter kraft pulping process alongside with chemicals, wood and water (Andritz 2025a; Suhr et al. 2015, 214). Makeup chemicals added to the process to cover the lack of sodium are typically sodium hydroxide (cooking & white liquor), sodium sulfate (evaporation/black liquor/recovery boiler) and sodium carbonate (reausticizing/green liquor) (Andritz 2025a). Alongside with sodium sulfate sulfur is also added to the process by mixing it with green liquor. Some sodium and sulfur also enter the process alongside with sludge generated in chlorine dioxide plant. This is only relevant input for mills utilizing chlorine dioxide in their process. The sludge is formed mainly from sodium bisulfate ( $\text{NaHSO}_4$ ) or sodium sesquisulfate ( $\text{Na}_3\text{H}(\text{SO}_4)_2$ ) and can be utilized as a makeup chemical (Saturnino 2012, p. 10). Sulfur from tall oil plant originates from sulfuric acid utilized in the tall oil production and sodium originates from sodium salts of tall oil (Tikka 2008, p. 360). (Mahecha-Botero et al. 2021, p. 100.) Sulfur also enters the process alongside with fuels used in recovery boiler and white liquor plant (lime kiln), magnesium sulfate ( $\text{MgSO}_4$ ) utilized in brown stock washing (BSW) and in ash leaching sulfuric acid is utilized (Andritz 2025a; Suhr et al. 2015, p. 214). Figure 3 presents the most common sodium and sulfur containing chemical inputs to the liquor

circulation. Liquor circulation is the circulation of chemicals which dissolve in alkali. These chemicals contain sodium, sulfur, and some foreign substances. (KnowPulp n.d.) In the figure blue arrows represent sodium and red arrows represent sulfur.

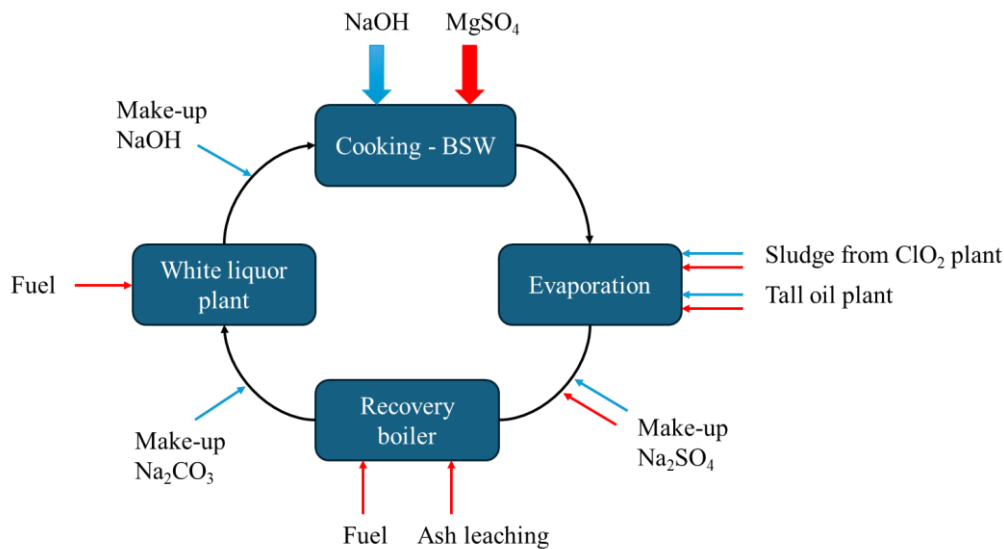


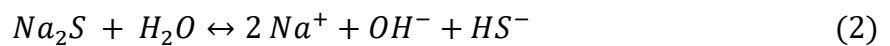
Figure 3. Most common inputs of sodium and sulfur containing chemicals into liquor circulation (Andritz 2025a)

## 2.2 Cooking

Cooking is one of the most crucial unit operations when it comes to pulping. Conventionally chemical pulp is produced either with continuous cooking or batch cooking. The main difference between these methods is that continuous cooking takes place in a single digester and the chips are fed continuously while batch cooking takes place in several different digesters step by step. (KnowPulp n.d.)

Cooking aims to remove lignin, so the wood chips would defibrate easily. Lignin is a binding material, and its purpose is to bind the wood fibres together. The removal of lignin is conducted with heat and chemicals. Cooking must be conducted in such a way that the cellulose fibres would be damaged as little as possible. (KnowPulp n.d.) The process itself takes place in one or several digesters. The temperature inside of a digester is usually between 150-170 °C. The chemicals used in cooking are fed into the digester warm to ease the process. The temperature of these chemicals is usually 80-100 °C. (Fardim 2011, p. 203.)

The cooking chemical used in kraft pulping is white liquor, which is a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S). White liquor is fed to the digester where the dissolving of lignin appears. The reaction between lignin and white liquor generates weak black liquor. (Tran & Vakkilainen 2008.) Equations 1 and 2 present the dissolving of sodium hydroxide and sodium sulfide in the cooking process (Andritz 2025a). In the equation OH<sup>-</sup> equals to hydroxide and HS<sup>-</sup> to bisulfide. Some of the dissolved hydrogen sulfide generates concentrated non-condensable gases (CNCGs) with other total reduced sulfur (TRS) compounds. The rest of the dissolved hydrogen sulfide transfers to the evaporation plant in black liquor. As the black liquor is evaporated, hydrogen sulfide still remaining transfers into CNCGs. (Hovikorpi & Vakkilainen 2019, p. 298.)



### 2.3 Bleaching

In the bleaching phase brightness and cleanliness of pulp are improved. The aim is to remove residual lignin remaining after cooking, as it is one of the main contributing factors in the colouring of the pulp. Brightness can be improved either by removing or brightening colour-causing substances. Removal of colour-causing substances is typically done with alkaline and chlorine chemicals such as chlorine dioxide (ClO<sub>2</sub>). Whereas brightening of colour-causing substances is done with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and oxygen. (Fardim 2011, p. 460; Suhr et al. 2015, pp. 201-203.)

Bleaching is one potential input of sulfur which can be explained by the bleaching chemicals used and their production method. Sulfur-containing chemicals are used at least in the production of chlorine dioxide. Chlorine dioxide is a common bleaching chemical used in elemental chlorine free (ECF) bleaching. (Saturnino 2012, pp. 9-10.) The sludge originating from ClO<sub>2</sub> plant contains sulfate and sodium which can be seen in figure 3. The last step of bleaching is washing, where the chemicals that do not remain in the bleached pulp end up in effluents exiting the process (Fardim 2011, p. 499). Figure 4 illustrates a schematic drawing of the unit processes in the bleaching phase. Although in total chlorine free (TCF) bleaching

sulfur containing chemicals are not utilized, there still are sulfates in the effluents. This can be explained for example by the sulfur carried by the pulp. (Suhr et al. 2015, p. 214.)

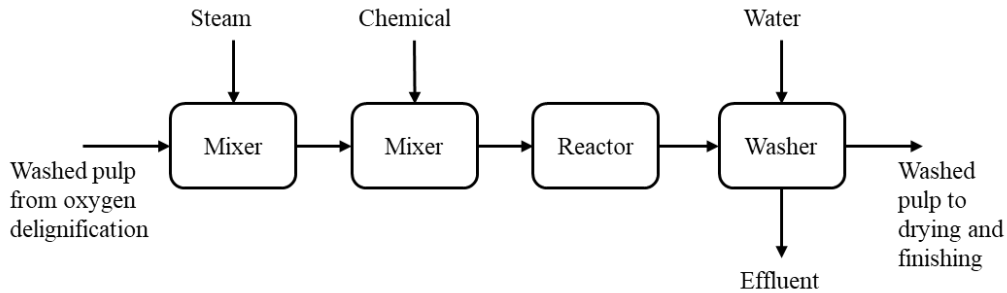


Figure 4. Unit operations in bleaching (Fardim 2011, p. 499)

Nowadays bleaching includes several stages and using a single-stage method is not possible. The reason for this is that single-stage bleaching does not remove all the colour. As mentioned before, some bleaching chemicals are selective on which type of colour-causing substances the chemical either removes or brightens (Sharma et al. 2020, p. 5). Some of the bleaching chemicals also create new coloured structures and that is one other reason single-stage bleaching is not possible. One example of these colour-causing chemicals is chlorine dioxide. This is why chlorine dioxide is rarely the last step of bleaching. (Fardim 2011, p. 462.)

Bleaching methods can be divided into two main categories which are called elemental chlorine free and totally chlorine free. In ECF no molecular of gaseous chlorine is used and in TCF chlorine is not used in any form. Chlorine dioxide is the most used chemical in ECF mills added with some other bleaching sequences such as ozone. In TCF the process typically consists of oxygen, ozone or peracetic acid, and hydrogen peroxide sequences alongside alkali sequence to remove lignin. TCF as a bleaching method has increased its popularity due to environmental concerns and the desire to reduce the pollutant load on effluents and

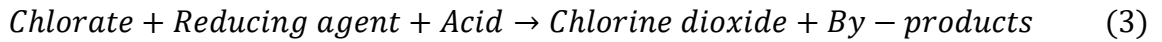
to close the water circulation at the mill. (Fardim 2011, p. 549; Suhr et al. 2015, pp. 202-203.)

### 2.3.1 Elemental chlorine free bleaching

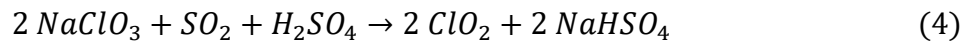
ECF bleaching is currently the dominant bleaching concept (Sousa et al. 2023, p. 63). Chlorine dioxide is now one of the most commonly utilized ECF bleaching sequences (Sharma et al. 2020, p. 5). The first step in the bleaching is typically pH adjustment which can be done either by adding hydrochloric acid (HCl) or sulfuric acid to the pulp. Sulfuric acid is more commonly used in the pH adjustment. (Halinen 2025.) There are many reasons for ClO<sub>2</sub>'s rising popularity such as improved brightness of the pulp, higher pulp strength, and decreased environmental load in effluents compared to other similar methods. As the awareness of environmental issues related to the use of chlorine-based bleaching chemicals keeps rising, it is most likely that the use will continue to decline more exponentially in the future (Sousa et al. 2023, p. 63). (Suhr et al. 2015, pp. 201, 203.)

Chlorine dioxide is highly used in pulp and paper industry due to its characteristics. Solubility to water is high as it is 8-10 g/l in 20 °C. This high solubility ensures that when chlorine dioxide is diluted with water, the majority of it can be effectively used in the bleaching process. Chlorine dioxide is a strong oxidizer that benefits in the removal of remaining lignin in pulp. The production yield of chlorine dioxide is notably high, reaching up to 97% when reduced from chlorate. This makes chlorine dioxide economically feasible for bleaching chemicals. (KnowPulp n.d.; Työterveyslaitos 2022.)

ClO<sub>2</sub> can only be produced as a dilute gas because it is a highly reactive gas. For this among other safety and economic reasons, manufacturing of the gas usually takes place on site. The prepared ClO<sub>2</sub> gas is mixed with water to create a dilute solution (6-8 g/l) which then can be utilized in the bleaching process. The preparation of ClO<sub>2</sub> can be conducted either from chlorite or chlorate. The most cost-effective way is to reduce chlorate as the preparation from chlorite is aimed for small-scale production. The reduced chlorate gas is then diluted with water so it can be utilized in the next reaction. (Työterveyslaitos 2022.) The reaction that occurs when starting with chlorate (ClO<sub>3</sub><sup>-</sup>) is presented in equation 3. Chlorate is often used in the form of sodium chlorate (NaClO<sub>3</sub>) in the production of chlorine dioxide. (Fardim 2011, pp. 525-526; Suhr et al. 2015, p. 207.)



As a reducing agent sulfur dioxide (SO<sub>2</sub>) can be used. The reaction occurs in acidic conditions, which facilitates the reduction. Mostly used acids are sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and HCl. As a by-product sulfur and sodium containing substances can be formed such as sulfuric acid, sodium sulfate, and sodium bisulfate (Fardim 2011, p. 526). Equation 4 presents the reaction where sodium chlorate is reduced with sulfur dioxide and sodium bisulfate is formed as a by-product (Saturnino 2012, p. 10). (Suhr et al. 2015, p. 208.)



Operating conditions in chlorine dioxide bleaching are typically quite acidic as the pH is between 1.5 and 3.5. Temperature is between 40-60 °C and operating pressure is usually the ambient pressure. The chlorine dioxide bleaching sequence usually lasts 20 to 60 minutes depending on the brightness of the treated pulp. The consumption of chlorine dioxide is determined by the kappa number. The kappa number tells the amount of remaining lignin in the pulp and the smaller the number the less residual lignin (Suhr et al. 2015, p. 198). The amount of chlorine dioxide dozed is 1.5-2.3 times the kappa number per air dried metric ton (ADt) of pulp. (KnowPulp n.d.)

### 2.3.2 Total chlorine free bleaching

Hydrogen peroxide is the main bleaching chemical used in TCF bleaching. TCF has increased its popularity as a bleaching method in the pulp and paper industry. One of the main reasons for this interest can be explained by the decomposition of hydrogen peroxide. When hydrogen peroxide decomposes it generates only water and oxygen. For this reason, hydrogen peroxide can be referred to as a green chemical since the decomposition does not generate harmful pollutants. (Chen 2008.)

Typically, the first step in TCF bleaching is a pH adjustment. Either HCl or sulfuric acid is used to adjust the pH, from which sulfuric acid is more common. Other than that sulfur in effluents from TCF bleaching plant originate from water and wood used in pulping and the pulp treated itself. (Halinen 2025.) Bleaching with hydrogen peroxide is based on improving the brightness of residual lignin as mentioned before. The method is called the “lignin saving” method and it does not dissolve the residual lignin in pulp. Peroxide reacts with lignin by oxidizing it as it is also a strong oxidizer. Peroxide is also selective as it only oxidizes the group of lignin chromophores which is the colour-forming group. After the oxidation reaction, the chromophores are colourless, and the brightness of the pulp has been improved. (KnowPulp n.d.)

TCF bleaching with hydrogen peroxide sequence occurs in alkaline conditions. Hydrogen peroxide is typically utilized as a weak acidic water solution with a peroxide concentration of 50% (KnowPulp n.d.). All the operating conditions depend on the characteristics of the treated pulp. The operating pH ranges somewhere between 10 to 12. The temperature is between 60-80 °C and the operating time varies from 2 to 4 hours. The dosing of hydrogen peroxide depends on the following process conditions: operating temperature, pH, and caustic soda load. Caustic soda load means NaOH added to the bleaching process. Furthermore, the end type of the pulp treated, and its consistency affect these process conditions listed. (Ramos et al. 2008.) NaOH can be added to the process in case there is a lack of sodium (Andritz 2025a).

## 2.4 Chemical recovery

Chemical recovery aims to recover cooking chemicals and energy. The recovery line consists of evaporation, recovery boiler, and white liquor preparation. In evaporation, weak black liquor from the washing phase is concentrated into strong black liquor by heating and water evaporation. This is followed by a recovery boiler where the remaining strong black liquor is combusted to recover chemicals (Na and S) and energy. As a combustion product smelt is generated from black liquor combustion. The smelt consists mainly of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) but there is also small concentration of sodium sulfide (Sousa et al. 2023, p. 59). From the smelt green liquor is first separated and then directed to a lime kiln & recausticizing plant. (Suhr et al. 2015, pp. 204-206.) Figure 5 presents the relevant input and



output flows of chemical recovery at a typical kraft mill where chlorine dioxide is used in the bleaching phase.

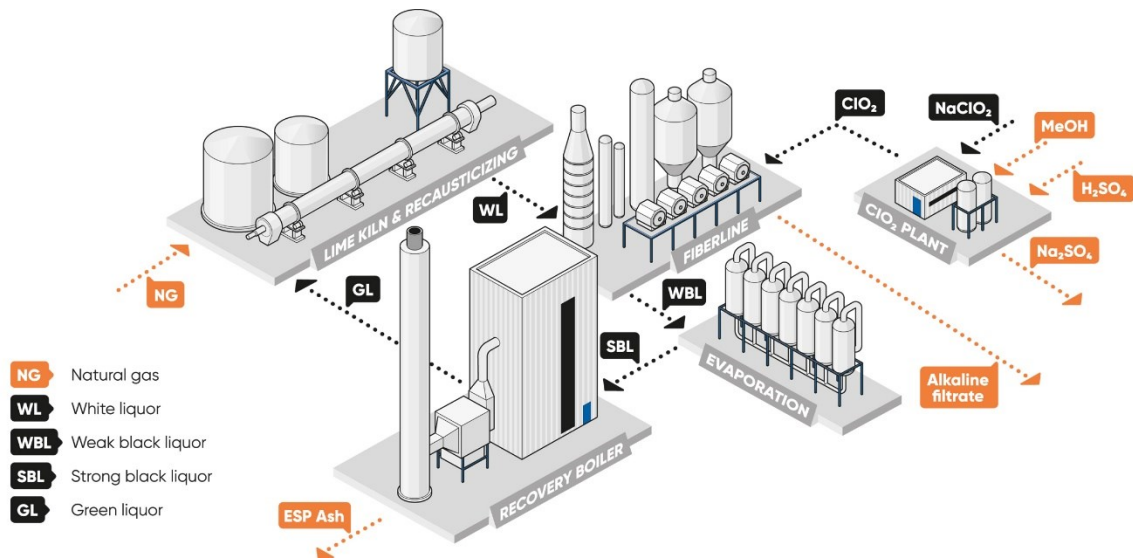


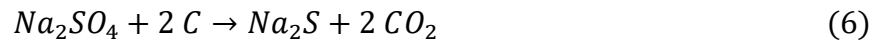
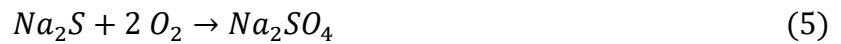
Figure 5. Chemical recovery (Andritz 2024a)

### 2.4.1 Recovery boiler

A recovery boiler is designed to recover chemicals and to produce steam and electricity. The need for the circulation of chemicals originates from high expenditures of cooking chemicals. Cooking chemicals used in kraft pulping contain for example sodium compounds whose price has driven toward chemical recovery. One of the aims of a recovery boiler is to circulate these chemicals from by-products back into the process. The efficiency of this is described with reduction efficiency which tells how well sodium sulfate can be reduced back to sodium sulfide. The reduction efficiency has an impact on the Na/S balance. (Andritz 2025a.) Another function of the recovery boiler is incineration of the organic matter generated during the process and the recovery of the heat generated in the combustion. (Fardim 2011, p. 204; Balint et al. 2023.)

Sodium sulfide which is used as a cooking chemical oxidizes to sodium sulfate. The oxidation appears while organic compounds in black liquor are combusted in the recovery boiler. Combustion aims to release sulfur and sodium. To recover sodium as sodium sulfide back to the cooking process it needs to be reduced. This reduction from sodium sulfate to

sodium sulfide takes place in the recovery boiler. In case there is a lack of sodium and sulfur in the process, sodium sulfate can be added as a makeup chemical (Andritz 2025a). Sodium sulfate reacts with organic carbon and then sodium sulfide is generated. Most of the sulfate is reduced as sulfide in well-operated recovery boilers. These operations appear simultaneously under high temperature and pressure (Tran & Vakkilainen 2008). (Neto 2021, p. 23.) Equation 5 presents the oxidation of the sodium sulfide and equation 6 presents the reduction of sodium sulfate. In the equations  $O_2$  equals to oxygen,  $C$  equals to carbon and  $CO_2$  to carbon dioxide.



Sodium sulfate, sodium carbonate, and sodium sulfide are generated as inorganic black liquor combustion products more commonly known as smelt. Sodium carbonate and sodium sulfide are recovered from the bottom of the recovery boiler as a smelt which is then further treated in recausticizing (Bajpai 2018, p. 438). Recovery boiler fly ash which consists mainly of sodium sulfate and some sodium carbonate is collected from the flue recovery boiler gases with electrostatic precipitator (ESP). One of the aims of ESP is to recover mainly sodium sulfate and also some sodium carbonate as ESP ash (Bajpai 2018, pp. 437-438). The ash generated in ESP contains high loads of sulfates and it is disposed from recovery boiler with effluents. Effluents from recovery boiler are directed to the wastewater treatment plant (WWTP) of the mill, where the concentration of nutrients can be reduced and harmful pollutant removed if necessary. (KnowPulp n.d.)

#### 2.4.2 White liquor preparation

White liquor preparation is a critical process from a chemical recovery point of view. The primary goal is to convert sodium-containing substances, such as green liquor, back to sodium hydroxide. This conversion allows the recovery of sodium so it can be recirculated to the pulping process as sodium hydroxide. (Neto 2021, 24.) Sodium sulfide is simultaneously

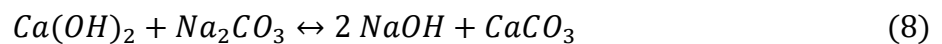
present through whole white liquor preparation, but it does not react with any other substance (Tran & Vakkilainen 2008).

White liquor preparation consists of two phases called recausticizing and lime regeneration (Tran & Vakkilainen 2008). In recausticizing, smelt from the recovery boiler is treated to recover sodium. Sodium hydroxide is regenerated from sodium carbonate in recausticizing. This conversion is achieved by dissolving the smelt in water or weak white liquor to produce green liquor. Green liquor serves as a raw material for white liquor preparation which then can be returned to the pulping process. (Suhr et al. 2015, p. 206.)

In recausticizing sodium carbonate in green liquor is converted into sodium hydroxide as mentioned before. This conversion is conducted by mixing sodium carbonate with calcium hydroxide. Calcium hydroxide ( $\text{Ca(OH)}_2$ ) is prepared when lime ( $\text{CaO}$ ) from lime kiln reacts with water in green liquor. This reaction is presented in equation 7. (Hart et al. 2021, p. 18.)



Causticizing efficiency describes the amount of sodium carbonate that reacts into sodium hydroxide (Sanchez 2007, p. 11). In green liquor, sodium sulfide is simultaneously present, but it does not react with calcium hydroxide. Sodium hydroxide is then prepared by adding the prepared calcium hydroxide to green liquor containing sodium carbonate. As a by-product, calcium carbonate ( $\text{CaCO}_3$ ) is formed (Neto 2021, p. 24). Equation 8 presents this reaction. (Hart et al. 2021, p. 18.)



Calcium carbonate is then combusted in the lime kiln and converted into lime and this lime is then used again in recausticizing (Hart et al. 2021, p. 37). The conversion of calcium carbonate into calcium oxide ( $\text{CaO}$ ) is called lime regeneration (KnowPulp n.d.). Figure 6 illustrates the loop of white liquor preparation.

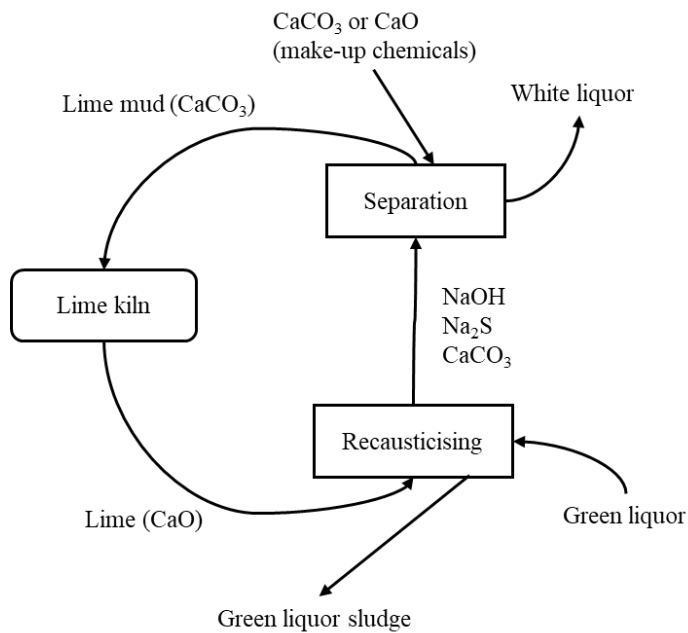


Figure 6. White liquor preparation (Suhr et al. 2015, p. 205)

In recausticizing sodium is an essential part of the process. Occasionally, sodium from green liquor is not enough for the white liquor preparation due to chemical losses. (Suhr et al. 2015, p. 195.) In these cases, make-up chemicals are utilized as replacement chemicals to cover chemical losses in the process (Suhr et al. 2015, p. 845). The most common make-up chemical used in white liquor preparation is sodium carbonate (Andritz 2025a). Sodium hydroxide is typically used if there is a lack of sodium in the prepared white liquor (Andritz 2025a).

### 3 Sulfur in kraft mill waters

In this chapter, the focus is on sulfur in kraft mill waters. First different kind of harmful substances in kraft mill effluents are presented followed by the water circulation in a kraft mill. Lastly, factors limiting the closure of water circulation in a kraft mill are explained.

#### 3.1 Effluent characteristics in kraft pulping

As the pulp industry has been found to have major impacts on freshwater scarcity, the change of freshwater consumption habits in the industry is necessary (Chowdhary et al. 2020, pp. 236-237). Esmaeeli & Sarrafzadeh (2023, p. 2) addressed that freshwater consumption habits vary between mills due to the uneven distribution of technologies and the current situation of freshwater reserves. In Europe, freshwater consumption of a kraft mill is typically lower compared to the rest of the world. In the process, this freshwater gets contaminated with different harmful substances alongside valuable chemicals. Sulfates are one of the main ions in kraft mill effluent after wastewater treatment (Suhr et al. 2015, p. 66). In some ecosystems, sulfates are considered toxic in high concentrations but in kraft pulping, sulfur is a valuable element (Karjalainen et al. 2023, p. 2). High loads of sulfates have been found at least from bleaching effluents and ESP ash (Andritz 2025a). (Chowdhary et al. 2020, p. 244.)

Effluents from a kraft mill contain many different types of pollutants. Various ways influence the type and amount of pollutants in the effluent. Used chemicals and raw materials are the main origin of chemical and pollution loads in the wastewater. (Dahl 2008, pp. 13-14.) These pollutants are one of the main reasons why closed circulation is not currently possible at pulp mills. One of the most contributing factors is the scaling of poorly soluble compounds in the effluents of bleaching plants in different equipment. Usually, wastewaters generated before bleaching are treated in the evaporation plant and wastewaters after bleaching are treated in the WWTP. Bleaching effluents cannot usually be treated in the evaporation plant due to their high loads of chlorine (Halinen 2025). (Huber et al. 2014, p. 41.)

Bleaching effluents contain elements that, when reacting with certain substances, can impact the process negatively. This is one of the main reasons why bleaching effluents cannot be recycled at the mill without proper treatment. These elements are called non-process

elements (NPEs). In kraft pulping, these substances include aluminium, barium, cadmium, phosphorus, potassium, calcium, chlorine, copper, lead, magnesium, manganese, silicon, iron, and nitrogen (Ulmgren 1997). Of the above, calcium and barium can, for example, form scale deposits in the bleach plant. The scale deposits are one of the main reasons why bleaching effluents cannot be recycled in a pulp mill without treatment. (Bajpai 2018, pp. 530-536.)

### 3.2 Water circulation at a kraft mill

Water consumption of whole pulping industry has been under comprehensive examination in the last decades due to growing freshwater water scarcity (Huber et al. 2014, p., 36). Reduction of freshwater consumption in a kraft mill is profitable from environmental and economical point of view (Suhr et al. 2015, p. 365). The increase in internal water circulation has been found to be one of the most efficient ways to reduce water consumption and effluent volume in a kraft mill (Suhr et al. 2015, p. 123). On the other hand, Bajpai (2018, p. 532) found that as the degree of internal water circulation increases so does the technical issues. Higher degree of closed water circulation has also been found to negatively impact to the Na/S balance (Mahecha-Botero 2021, p. 100). All these negative consequences summed lead to decrease of benefits gained from internal water circulation.

In order to reduce the volume of effluent in a kraft mill the recovery of valuable chemicals and harmful pollutants needs to be improved to make it economically feasible (Mahecha-Botero 2021, p. 100). It is known that the sulfate concentration is high in the discharged kraft mill wastewater. One way to reduce the organic load in effluents while simultaneously recovering sulfur is anaerobic digestion which will be discussed more comprehensively in chapter 4 (Lohani & Havukainen 2018). Sodium is also present in high concentration in the discharged wastewater as sodium sulfate is a common residual from kraft mill unit processes. Sodium sulfate is generated for example in the ClO<sub>2</sub> plant and recovery boiler. (Neto 2021, p. 23; Fardim 2011, p. 526.)

As discussed in chapter 2, some chemicals utilized in the process end up to the water circulation of a kraft mill as they dissolve and do not remain in the pulp (Andritz 2025b; Fardim 2011, p. 499). Figure 7 illustrates the most relevant water streams in a kraft mill. In the figure brown arrows indicate the water in pulp mass if nothing else is mentioned. Black arrow

indicates the water in black liquor, light grey arrow indicates the water in white liquor and dark grey arrows indicate the possible water in ash if there is a separate ESP ash treatment method. Red arrows indicate the water in bleaching effluent, blue arrows indicate the water in condensate and green arrows indicate the water in treated effluent. Figure 7 also points out that bleaching is the only outlet point of effluents from a kraft mill. Therefore, all the dissolved chemicals in water circulation end up to the WWTP. From closed water circulation point of view this is also the most crucial water stream to focus. To close the water circulation in a kraft mill, the focus needs to be in the water management of the bleach plant. (Huber et al. 2014, pp. 36-37.)

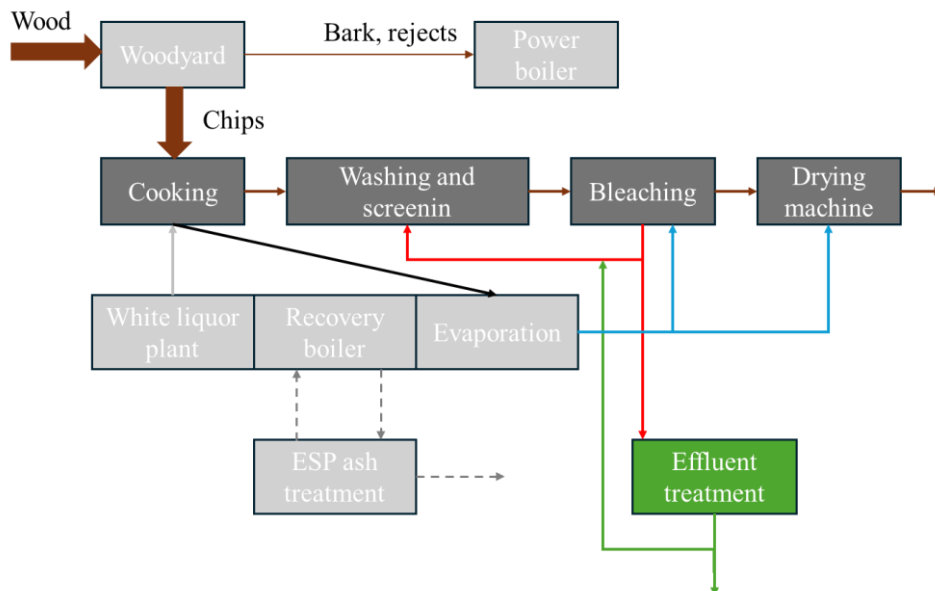


Figure 7. Conventional simplified water circulation of a kraft mill (Andritz 2025b)

In kraft mills using TCF bleaching cooking, washing and bleaching has been found to contribute the most to the generation of effluents (Sousa et al. 2023, p. 60). From figure 8 can be seen that effluents from these processes are guided to WWTP via bleach plant which makes this effluent stream a good possible source of sulfur. In chapters 2.1 and 2.2 the importance of cooking and bleaching to the Na/S balance was explained. As these effluent streams are highly relevant when it comes to the volume of effluent it is justified to focus on bleaching effluent stream to reduce the water consumption and pollution load in a kraft mill (Huber et al. 2014, p. 37; Sousa et al. 2023, p. 60). The pollution load of bleaching effluent

stream is one of the main concerns when discussing closure of kraft mill water circulation. Main issue causing pollutants are NPEs as mentioned before. (Bajpai 2018, p. 533.)

When NPEs are under control the closing or partial closing of the kraft mill water circulation is possible. In practice, this means the closure of water circulation of bleaching plant. Counter-current washing has been found to be the most suitable way to achieve closed water circulation. The counter-current washing method is based on washing the bleached pulp with fresh water added to the process and then recycled back to previous process steps. Figure 8 demonstrates in more detail the idea of the counter-current washing method. In the picture, the blue arrows represent the direction of water, and the green arrows represent the direction of the pulp. (Huber et al. 2014, p. 37; Suhr et al. 2015, pp. 119-121.)

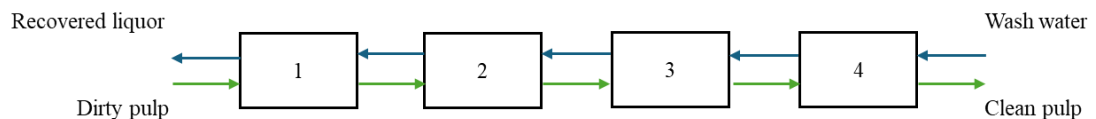


Figure 8. Counter-current washing method (Suhr et al. 2015, 268, 601)

### 3.3 Factors limiting the closure of water circulation

NPEs are one of the main factors limiting the closure of water circulation in a kraft mill. The amount of NPEs depend on the characteristics of wood used in pulping as it has been found to be the main source of NPEs in the process. For example, hardwood (eucalyptus) contains higher concentrations of chlorine compared to softwood (pine & spruce) from the Nordics (Halinen 2025). Also, chemicals used in pulping determine which NPEs may occur in the process and how do these substances affect it. The chemicals used vary from one pulping method to other and for example the amount of chlorine differs depending on if it is ECF or TCF bleaching. Besides wood and chemicals, one relevant source of NPEs is freshwater taken from waterbodies (Ulmgren 1997). (Bajpai 2018, p. 533.)

When chemicals utilized in pulping dissolve into water or another liquid, they dissolve into ions. Similar reactions appear in the cooking process where the structure of the wood degrades. The recovery boiler ash contains potassium (K) and chlorine (Cl) but in the case of closed water cycles the amounts of these elements would increase considerably. Increased



amounts of K and Cl would lead to plugging and corrosion of the recovery boiler, reduced recovery boiler capacity and efficiency, and corrosion issues in digester and evaporators. From an environmental perspective, increased amount of nutrients (nitrogen and phosphorus) in the discharged effluents could lead to eutrophication, negatively affecting water ecosystems. (Suhr et al. 2015, pp. 219, 269; Ulmgren 1997.)

### 3.3.1 Bleaching

The most common NPEs in bleach plant are calcium (Ca), barium (Ba), sulfate, carbonate and oxalate. Ions listed above form compounds which can cause deposits and scaling in bleaching equipment. These compounds are calcium carbonate, calcium oxalate and barium sulfate. Deposits can be prevented by many means, such as removing metals (Ba and Ca) by acid washing or chelation. (Huber et al. 2014, p. 36.) Every effort is made to avoid these deposits, because if deposits occur, often the entire bleaching plant must be stopped so that the deposits can be removed. This, then might lead to production losses, which are tried to avoid. (Suhr et al. 2015, pp. 268-269.)

In TCF-bleaching manganese, iron and copper are the main issue causing NPEs. Manganese and copper work as a catalyst for hydrogen peroxide and therefore reduce the bleaching efficiency. Low concentrations of these NPEs are accepted but controlling these concentration levels is essential from the operating efficiency point of view. (Ulmgren 1997.) NPEs also increase the consumption of bleaching chemicals, and certain impurities interfere the bleaching reaction. The reaction can be interfered either by reducing the effectiveness of the bleaching chemical or by decomposing the bleaching chemical (Suhr et al. 2015, p. 365). These impurities may cause precipitation if, for example, alkaline and acidic filtrates are mixed. On the other hand, if the pH is kept neutral this precipitation may be avoided (Halinen 2025). Among NPEs, calcium and magnesium in particular limit the recycling of bleaching effluents due to their high scaling potential (Tran & Vakkilainen 2008).

Bleaching effluents cannot usually be circulated at the mill due to the chlorine-based compounds used there. These compounds could cause corrosion and plugging in the recovery boiler if bleaching effluents were circulated/recycled. This is one of the main reasons why it has not yet been possible to completely close the water cycle in bleaching plants. Choosing chlorine-free or low-chlorine bleaching methods can contribute to the complete closure of

bleaching water cycles. If possible, TCF bleaching should be used instead of ECF bleaching. (Bajpai 2018, pp. 530–533.)

### 3.3.2 Chemical recovery

In the cooking phase most of the NPEs released originate from the wood utilized as a raw material. These NPEs are then transferred to the chemical recovery along with the black liquor. The most relevant NPEs causing issues in the lime cycle are phosphorous, magnesium, aluminum and silica. Phosphorous reacts with calcium to create calcium phosphate which accumulates in the lime cycle. This accumulation leads to increased amounts of magnesium, aluminum and silica in the lime cycle, ultimately decreasing the efficiency of the process. (Suhr et al. 2015, p. 269; Ulmgren 1997.)

Recovery boiler ash contains potassium and chlorine and the ash is further collected with ESP. If the water circulation of a kraft mill were to be closed, it would considerably increase the amount of ESP ash removed from the process. This is due to the excess amounts of Cl, K, Na and S that need to be removed. Conventionally ESP ash dumping has been used to control different balances in a kraft mill such as the Na/S balance and the K/Cl balance. The K/Cl balance has been found to greatly impact to the Na/S balance, making ESP dumping crucial from the chemical circulation perspective. (Naukkarinen & Tikka 2025.) The amount of Na and S needed to remove from the process can be determined using the Na/S balance, which indicates how much ESP ash should be removed by dumping. (Ulmgren 1997.)

The recovery boiler cannot withstand elevated temperatures if there are high concentrations of potassium and chlorine in the liquor circulation. That is one of the reasons why controlling the Cl/K balance is almost as important as controlling of Na/S balance. (Halinen 2025.) More ash may be dumped if potassium and chlorine cannot be efficiently removed by other methods, which also results in the removal of sulfur and sodium. Chloride and potassium can be removed from ESP ash for example by ash re-crystallization (ARC) which is a chloride removal system developed by Andritz. (Naukkarinen & Tikka 2025.)

## 4 Anaerobic effluent treatment

In this chapter, anaerobic effluent treatment is explained. The treatment method that the chapter focuses is anaerobic digestion. Concerning anaerobic digestion, the focus is on anaerobic digestion as sulfate reduction method and parameters affecting the process. SulfoLoop process is also presented and the technology behind it is explained.

### 4.1 Anaerobic digestion

Anaerobic digestion (AD) is a process based on degradation of organic matter by bacteria in the absence of oxygen. AD is a multi-step process which is illustrated in figure 9. The process itself appears in a bioreactor (Khan et al. 2016, p. 744). As can be seen from the figure, in AD different microorganisms break down product from earlier phase into more simple compounds. Typically, when discussed about AD it is referred as the production method of biogas (methane) and digestate which can be utilized as a fertilizer (Timonen et al. 2019, p. 1567). This is because methanogenesis is usually the dominant process compared to sulfate reduction process. Other relevant aims of AD are reduction of organic matter in wastewaters and reduction of organic waste (Yin & Wu 2024, pp. 22-23). The process consists of four steps which are hydrolysis, acidogenesis, acetogenesis and methanogenesis. These processes can either occur in the order listed or simultaneously (Meedoga et al. 2018, p. 3). As a result of methanogenesis methane ( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ), water ( $\text{H}_2\text{O}$ ) and humus are produced. Hydrogen sulfide and carbon dioxide are formed as products from sulfate reduction. (Lohani Sunil & Havukainen 2018.)

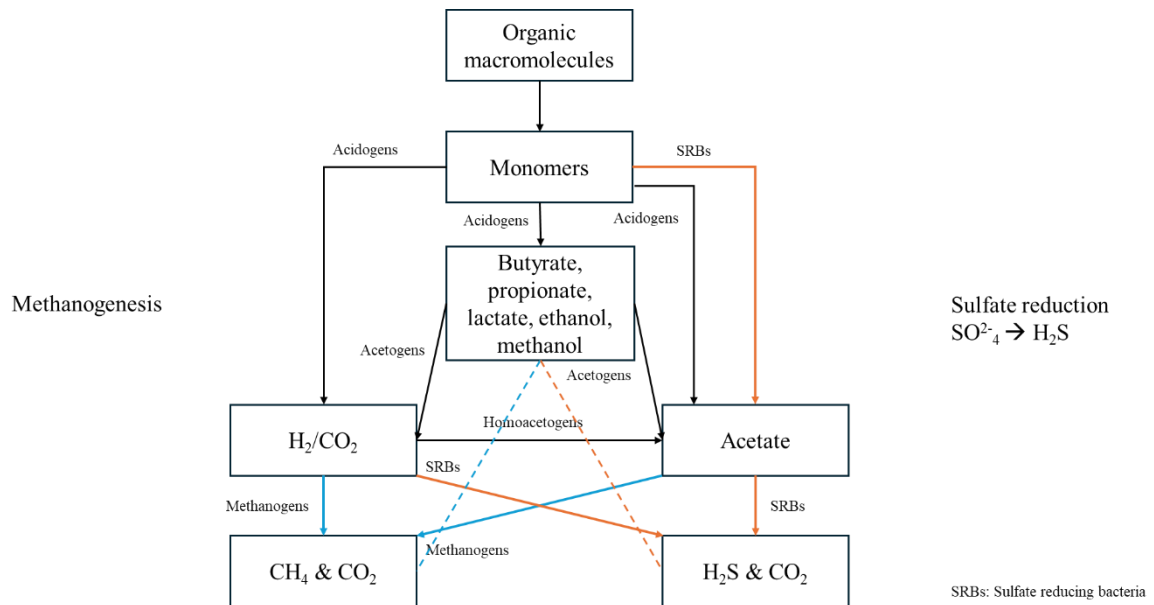


Figure 9. Simplified AD process (Lohani & Havukainen 2018; Meegoda et al. 2018, p. 3)

In the first step of anaerobic digestion which is called hydrolysis organic macromolecules such as carbohydrates, proteins and fats are degraded into simpler monomers by hydrolytic bacteria. Monomers produced in hydrolysis are further broken down by acidogenic bacteria in phase called acidogenesis. Products from this phase are for example volatile fatty acids (butyrate and propionate), organic acids (lactate), alcohols (methanol and ethanol) alongside with carbon dioxide and ammonia (Zhang et al. 2015). Acetogenesis is followed by acidogenesis where the products of acidogenesis are converted into acetate, hydrogen and carbon dioxide. This conversion is conducted by acetogenic bacteria. (Lohani Sunil & Havukainen 2018.)

The last phase of AD can be either methanogenesis or sulfate reduction. These phases compete and certain conditions determine which phase is dominant. One of the main contributors is the carbon to sulfate ratio (Niu & Wu 2024, p. 117). Methanogenesis is dominant if the content of organic matter (carbon) is higher than sulfate content. Sulfate reduction, on the other hand, is the dominant phase if the presence of sulfate exceeds a certain level. (Ueki et al. 1992, p. 195.) This result occurs normally for wastewaters containing high loads of sulfate. Other relevant contributing factor is the chemical oxygen demand (COD) to sulfate ratio. If the ratio is below 0,66 COD/SO<sub>4</sub><sup>2-</sup>, sulfate reduction is the dominant phase and SRBs are the only microorganisms consuming organic matter. Therefore, AD is suitable method

for sulfate reduction for wastewaters containing more sulfates than COD. (Niu & Wu 2024, pp. 122, 124.)

AD has been studied if it would be economically feasible way to recover nutrients and other valuable products back to use in the pulp industry. The pulp industry has a lot of wastewater and sludge streams that could be treated with AD. Studies have shown that AD could be an efficient way for the pulp and paper industry to recycle nutrients. (Zhang et al. 2015, p. 8751.) Pulp and paper industry waste streams are types of streams that can be used to produce biogas by using AD. This is because P&P waste streams contain a lot of organic matter and thus create optimal conditions for microbes. (Zhang et al. 2015, p. 8753; Niu & Wu 2024, pp. 119–120.) In general animal manure and other biodegradable wastes and side streams are commonly utilized in the production of biogas (Timonen et al. 2019, p. 1567). Wastewater from chemical pulping often contains a lot of sulfates which inhibit the production of biogas but contribute to sulfate reduction. (Zhang et al. 2015, p. 8757.) Currently, research is underway to determine which types of AD reactors would be best suited for pulp and paper industry wastewater for sulfate reduction. Nowadays, however, commercial practices are still limited, and research has mainly focused on AD as a biogas production method. (Zhang et al. 2015, p. 8763.)

#### 4.1.1 Methanogenesis

In methanogenesis methanogenic bacteria produce methane and carbon dioxide from hydrogen ( $H_2$ ) or carbon dioxide and acetate ( $CH_3COOH$ ). The formation of methane and water from hydrogen and carbon dioxide is presented in equation 9 and equation 10 presents the formation from acetic acid to methane and carbon dioxide. (Lohani & Havukainen 2018.)



If the aim of AD is to produce biogas, there are several factors affecting the process. There are two different digestion ways called mesophilic and thermophilic. The main difference

between these methods is temperature which can be seen also from table 2. Temperature alongside with pH is one of the most crucial factors when it comes to the process conditions (Yin & Wu 2024, p. 22). If the temperature is not optimized, it might inhibit the biological process or have some other negative impacts to the process. Optimized temperature will lead to improved solubility of organic matter and therefore optimized conditions for the microorganisms. Temperature can also affect to the retention time either by increasing it or decreasing it. pH is especially relevant factor from the methane production yield point of view. It is important to optimize pH as especially low pH radically inhibits the microorganisms. (Khan et al. 2016, pp. 744-745.) Retention time affects for example to the size of the reactor either by increasing or decreasing the size of the reactor. The activity of methanogenic bacteria is affected by retention time and therefore it is crucial from the process efficiency point of view. Table 2 gathers the most important parameters for methanogenesis. (Lohani & Havukainen 2018.)

Table 1. Optimal process conditions for biogas production (Lohani & Havukainen 2018)

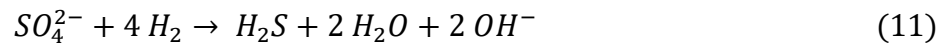
Parameter	Value	Unit
Temperature, mesophilic	30-38	°C
Temperature, thermophilic	50-60	°C
pH	7.0-7.2 (can vary between 6.2-8.0)	-
Retention time	10-30	d

#### 4.1.2 Sulfate reduction

The aim of sulfate reduction is to reduce sulfate ions in treated effluent to hydrogen sulfide. In sulfate reduction, the sulfate reducing bacteria (SRB) break down mainly hydrogen, carbon dioxide or acetate into hydrogen sulfide and carbon dioxide. This process works as an inhibitor for methane production in AD as it generates hydrogen sulfide which is toxic for the microbes (Niu & Wu 2024, p. 117). SRBs are anaerobic microorganisms which can utilize sulfate in assistance of their respiration. (Lohani & Havukainen 2018.) Muyzer & Stams (2008, pp. 1, 8) found that SRBs can live in a wide range of environmental conditions such as in marine and freshwater sediments. It was also noticed that SBRs are one of the main factors in natural carbon and sulfur cycles.

Sulfate reduction appears mainly as the last step of AD, but it can also happen during acidogenesis and acetogenesis (Lohani & Havukainen 2018). In acidogenesis the conversion of organic matter (organic carbon) to acetate is conducted with incomplete SBR. Other type of SRB which converts organic matter (organic carbon) to carbon dioxide is called complete SRB. (Niu & Wu 2024, p. 118.) To thrive and grow, SRBs require sulfate, nutrients (nitrogen and phosphorus) and some source of organic carbon. These conditions provide an optimal anaerobic environment for the sulfate reducing bacteria. If the amounts of sulfate and carbon are optimal, the growth of SRB is exponential and sulfate reduction in AD is optimized. Even though SRB can utilize organic carbon they need assistance to break down common macromolecules. (Niu & Wu 2024, pp. 119-120.)

Equations 11 and 12 present the formation of hydrogen sulfide. In equation 11, hydrogen sulfide is formed from hydrogen and in equation 12 from acetic acid. In these processes sulfate reducing bacteria act as catalyst. As a consequence from reduced sulfates, pH and buffer capacity of the solution are increased. (Lohani & Havukainen 2018.) In equation 12,  $\text{HCO}^{3-}$  equals to hydrogen carbonate.

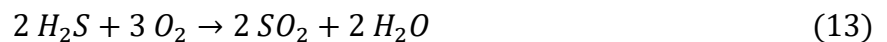


## 4.2 SulfoLoop

Andritz has developed an innovative technology to produce sulfuric acid from kraft mill waste streams. The process is called SulfoLoop, and it is an on-site production method of sulfuric acid in kraft mills. Installation of onsite sulfuric acid plant has been found to be an efficient way to control the Na/S balance of a kraft mill (Mahecha-Botero 2021, p. 100). Traditionally excess sulfur is dumped as ESP ash which consists mainly of sodium sulfate and some sodium carbonate. Either sulfur (S) or sodium (Na) are not recovered although both elements are highly utilized in kraft mills in different chemicals. The aim of SulfoLoop is to recover sulfur, which is a valuable element in pulping. This is conducted with a target of decreasing or even eliminating the amount of ESP ash dumping. In SulfoLoop, ESP ash could be utilized as a raw material for AD to produce hydrogen sulfide for  $\text{H}_2\text{SO}_4$  production.

The production method used is Wet-gas Sulfuric Acid (WSA). The plant produces concentrated commercial-quality  $H_2SO_4$  from concentrated non-condensable gases (CNCG). (Andritz 2024d.)

WSA process is a wet gas catalytic method. The aim of the process is to produce concentrated sulfuric acid by condensing wet process gas. Benefits gained from this process are lack of need for gas drying, the amount of wastewater generated is reduced and sulfur loss is reduced. WSA process begins with  $SO_2$  production at the operating temperature of the oxidation catalyst in the  $SO_2$  converter. The operating temperature is approximately  $410\text{ }^\circ\text{C}$  (Schlesinger et al. 2011, p. 227). If  $SO_2$  is already present in the feed, only preheating is needed. In other cases, sulfur containing feeds must be oxidized to  $SO_2$  by combustion in a waste heat boiler. Hydrogen sulfide in this case would originate as a product from anaerobic digestion. Equation 13 presents the combustion process for hydrogen sulfide (Mahecha-Botero et al. 2020, p. 103). (Andritz 2024b; Topsoe 2024.)



In kraft mills  $SO_2$  is extracted from the mill's concentrated non-condensable gases (CNCGs). After combustion, the gas is cooled down in a gas cooler simultaneously as excess heat is recovered to the steam drum. This step is followed by oxidation of  $SO_2$  to sulfur trioxide ( $SO_3$ ). The conversion is conducted in one or more catalyst beds and heat is also recovered from this step. Equation 14 presents the oxidation reaction (Mahecha-Botero et al. 2020, p. 103). (Andritz 2024b; Topsoe 2024.)



After the final oxidation step, the gas mixture is cooled to  $290\text{ }^\circ\text{C}$  (Schlesinger et al. 2011, p. 227) and followed by reaction with  $SO_3$  and water vapor forming sulfuric acid in gas (g) phase. Equation 15 presents the reaction between  $SO_3$  and water vapor (Mahecha-Botero et al. 2020, p. 103). (Andritz 2024b; Topsoe 2024.)





In the last step of WSA the sulfuric acid gas is first cooled down in a WSA condenser. Clean gas from the gas mixture exits the condenser at the top while sulfuric acid is collected at the bottom. The sulfuric acid gas is first cooled and then sent to storage as liquid sulfuric acid. Figure 10 illustrates the SulfoLoop process described above. (Andritz 2024b; Topsoe 2024.)

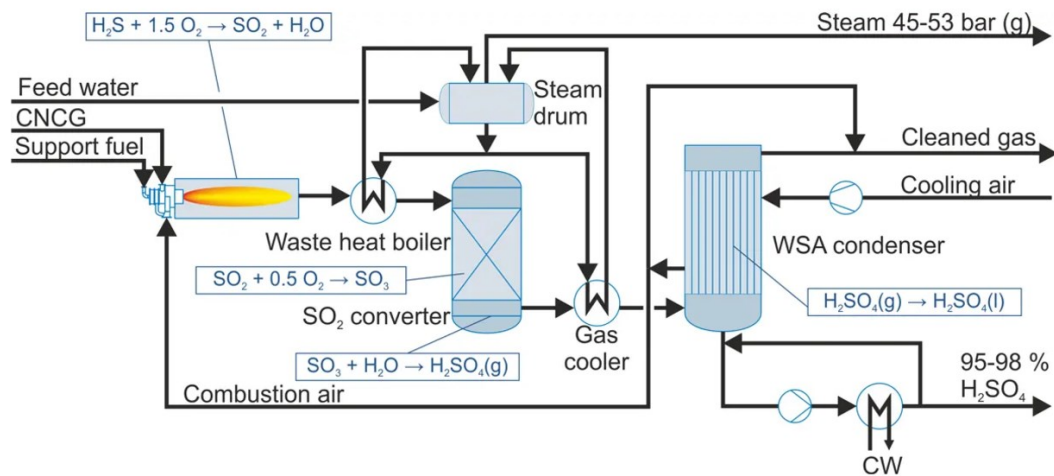


Figure 10. SulfoLoop process (Andritz 2024b)

In kraft mills the WSA process is a viable method to treat CNCGs (Andritz 2024d). Non-condensable gases (NCGs) can be divided into CNCGs and diluted non-condensable gases (DNCGs). NCGs are odorous and hazardous sulfur-containing gases originating from the kraft process. (Mahecha-Botero et al. 2021, p. 102.) The primary source of NCGs is chemical reactions and processes involved in breaking down wood chips and chemicals. NCGs originate from various stages of the kraft process including cooking and evaporation (Halinen 2025). The main components in these gases are TRS compounds such as hydrogen sulfide. (Hovikorpi & Vakkilainen 2019, p. 297.)

CNCGs contain high concentrations of TRS compounds while DNCGs contain only small concentrations of TRS compounds. The benefit of CNCGs is that there are high

concentrations of sulfur in small volumes of CNCGs. In modern chemical pulp mills CNCGs typically contain 2-5 kg S/ADt which makes them a good source of sulfur (Mahecha-Botero et al. 2021, p. 103). The sulfur content is usually higher for hardwood (eucalyptus) than softwood (pine, spruce) due to the different lignin composition (Hovikorpi & Vakkilainen 2019, p. 298). The main difference between these gases is that CNCGs can be burnt and DNCGs cannot. (Hovikorpi & Vakkilainen 2019, p. 297.) Conventionally CNCGs are burnt in the recovery boiler but if SulfoLoop technology is integrated to a kraft mill those gases would be combusted in a waste heat boiler (Andritz 2024d; Hovikorpi & Vakkilainen 2019, p. 298).

## 5 Methodology

In this chapter, the empirical part of the study is explained. First laboratory experiment conducted for this thesis is explained followed by the explanation of calculation methodology utilized in the thesis.

### 5.1 Laboratory experiment

For the empirical part of this study six different effluent samples were analysed by external company. These samples were collected from somewhere in the kraft pulping process. In this laboratory experiment the reduction potential of sulfate into sulfide in anaerobic conditions was investigated. The main purpose was to demonstrate that the samples do not exhibit inhibition or toxicity. Different scenarios were determined such as in case COD is present, is sulfate reduction still possible. The composition of the samples varies as some of the samples only contain bleaching effluent while some samples contain ash alongside with effluent. Table 3 presents an overview of the samples. For the samples two different bleaching effluents (K and D) were collected from somewhere in the bleach plant and two different ashes (K and D) were collected from ESP. These effluents and ESP ash were chosen because they contain sulfates and organic matter according to previous knowledge and testing. This mixture of ESP ash and bleaching effluent is referred as solution later on in the text.

Table 2. Overview of the analysed samples

Sample	Composition
Sample 3	Bleaching effluent K
Sample 4	Bleaching effluent K + Ash K
Sample 5	Bleaching effluent D
Sample 6	Bleaching effluent D + Ash D

Figure 11 shows the appearance of the four different samples under examination. In the figure the samples are organised as sample 3 being in the left and sample 6 being in the right in the line. The samples were stored at 4 °C and all showed a small amount of settled solids.

The color for all samples is brown-yellow sample 4 being the darkest and sample 6 the lightest by color.

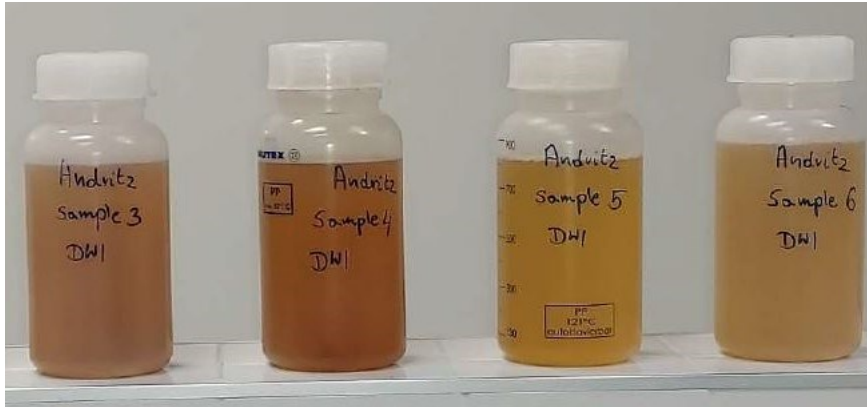


Figure 11. Appearance of the four samples

In table 4 can be seen some characteristics of the samples. The ratio of chemical oxygen demand (COD) and  $\text{SO}_4$  can be determined by dividing the concentration (mg/l) of COD with the concentration of sulfates in the sample solution. As mentioned in chapter 4.1, the optimal ratio of COD and  $\text{SO}_4$  required to reduce sulfate as sulfide is 0,66 or below (Niu & Wu 2024, pp. 124). In case all of the COD present could be used for sulfate reduction, 100% of the sulfates would reduce. To make the process more efficient, more COD is required for the reduction of sulfate than the theoretical value. In the samples the presence of lactic acids, acetic acids, propionic acids and butyric acids were noticed. The concentration of these acids was noticed to be higher for sample 3 and sample 4.

Table 3. Characteristics of the samples

Parameter	Sample 3	Sample 4	Sample 5	Sample 6	Unit
COD	2575	2495	1260	1123	mg/l
$\text{SO}_4$	9297	15685	6568	12930	mg/l
COD/ $\text{SO}_4$	0,28	0,16	0,19	0,09	-

The experiment was conducted in a test bottle (300 ml) as a batch experiment with anaerobic granular biomass present. Granular biomass utilized in the experiment is comparable to biomass originating from a fully operational sulfate reduction plant. The aim was to increase the sulfide concentration to a level where the activity of methanogens is strongly inhibited.

As a result, the amount of sulfides produced indicates if the solution is suitable for sulfate reduction.

The experiment began by adding 186 ml of tested solution to a test bottle. To ensure optimal conditions for sulfate reduction, sufficient amounts of nutrients and a buffer solution were added to the samples. In any of the samples there was not sufficient amount of COD so acetic acid was added to establish the activity of the SRBs. In these cases, acetic acid functioned as an electron donor. Next sodium hydrosulfide (NaHS) was mixed to the sample to the sample to increase the sulfide concentration to a level that will inhibit the activity of methanogenic bacteria. The amount of sulfides produced indicates if the sample is suitable for sulfate reduction. Followed by sulfide optimization is pH adjustment to neutral (7). Then small amount of settled anaerobic biocatalyst was added followed by gentle flushing the headspace of the bottle with nitrogen. Lastly, the test bottle was placed in an incubator at 35 °C.

Sulfate, sulfide and COD concentrations were simultaneously measured as the experiment. To compare the test results, sodium sulfate solution was used as a blank sample to test the activity of the applied anaerobic biocatalyst.

## 5.2 Na/S balance determination

Two hypothetical mills and their Na/S balances are under examination. As Mill 1 a kraft mill using softwood (SW) as raw material and ECF bleaching using  $\text{ClO}_2$  as bleaching chemical is chosen. As Mill 2 a kraft mill using hardwood (HW), more specifically eucalyptus (euca) as raw material and TCF as a bleaching method is chosen. In the base scenario, bleaching effluents are directed to the WWTP and discharged to water bodies after treatment and ESP ash/ARC purge are mixed to wastewater exiting recovery boiler and directed to WWTP. This assumption is made based on theory part and the information presented there. Figure 12 presents a schematic drawing of the Na/S circulation in the base scenario. In the figure the size of an arrow indicates the mass of the input, red arrows represent sulfur and blue arrows represent sodium.

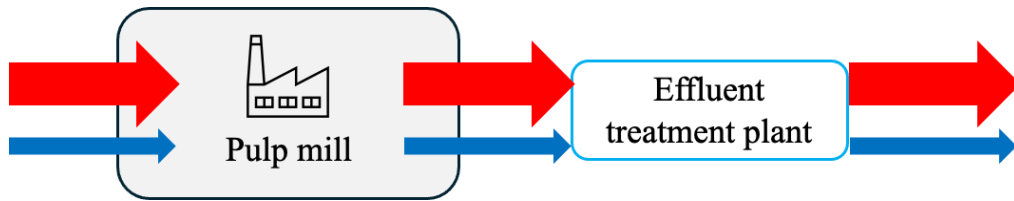


Figure 12. Na/S circulation in the base scenario

In Mill 1, the sludge (by-product) from the  $\text{ClO}_2$  plant is directed to evaporation. As the lignin concentration is higher for SW compared to hardwood (HW) there is a need for tall oil plant in SW kraft mill. The fuels needed in lime kiln are produced with bark gasification and therefore there is no need for natural gas. No ash treatment is needed as the concentration of chlorines is lower for SW compared to HW. For this hypothetical ECF kraft mill there are excess sulfur in the process which needs to be removed by ash dumping and the CNCGs generated in the process are directed to SulfoLoop. In contrast in Mill 2, there is no need for  $\text{ClO}_2$  plant and thereby no  $\text{ClO}_2$  sludge is not generated. Lack of  $\text{ClO}_2$  sludge also eliminates the need for bisulfite. The lime kiln in this mill uses natural gas, and ash treatment is necessary due to the chlorine content in eucalyptus. The ash treatment method at this mill is ash re-crystallization (ARC). Since there is no excess sulfur, there is no need for ash dumping, and less CNCGs are directed to the SulfoLoop. Table 4 gathers sodium and sulfur inputs and outputs for both hypothetical mills in the base scenario.

Table 4. Sodium and sulfur inputs and outputs for ECF and TCF kraft mills

<i>Parameter</i>	<b>SW ECF+Sulfoloop</b>		<b>Euca TCF+Sulfoloop</b>		Unit
Pulp production	1 000 000		250 000		ADt/year
	2817		704		ADt/d
Operation days	355		355		d/a
<b><i>Inlet</i></b>	<b>Na</b>	<b>S</b>	<b>Na</b>	<b>S</b>	
Water	0,05	0,02	0,05	0,02	kg/ADt
Wood	0,40	0,10	0,35	0,09	kg/ADt
MgSO <sub>4</sub> to O <sub>2</sub> -delignification	-	0,25	-	0,25	kg/ADt
ClO <sub>2</sub> plant by-product	5,00	3,50	-	-	kg/ADt
Tall oil plant H <sub>2</sub> SO <sub>4</sub>	-	4,90	-	-	kg/ADt
Lime kiln gas	-	-	-	0,005	kg/ADt
Bark Gasification	0,03	-	-	-	kg/ADt
Alkali to CNCG scrubber for bisulfite	0,30	-	-	-	kg/ADt
<b><i>TOTAL</i></b>	<b>5,78</b>	<b>8,77</b>	<b>0,40</b>	<b>0,37</b>	kg/ADt
<b><i>Outlet</i></b>	<b>Na</b>	<b>S</b>	<b>Na</b>	<b>S</b>	
Wash loss in bleaching	4,90	1,35	4,20	0,90	kg/ADt
Screening rejects	0,03	0,01	0,08	0,02	kg/ADt
Dregs	0,15	0,05	0,10	0,02	kg/ADt
Grits	0,10	0,03	0,10	0,02	kg/ADt
Purge from ARC	-	-	4,00	2,13	kg/ADt
Ash Dump	2,83	1,91	-	-	kg/ADt
Bisulfite to bleaching waste acid	0,30	0,35	-	-	kg/ADt
CNCG for H <sub>2</sub> SO <sub>4</sub>	-	5,00	-	1,80	kg/ADt
RB and LK emissions	0,03	0,07	0,09	0,20	kg/ADt
<b><i>TOTAL</i></b>	<b>8,33</b>	<b>8,77</b>	<b>8,57</b>	<b>5,09</b>	kg/ADt
<b><i>TOTAL without ash dump</i></b>		<b>6,86</b>		<b>5,09</b>	kg/ADt
Na loss	2,55	-	8,17	-	kg/ADt
S loss	-	0,00	-	4,73	kg/ADt
<b>Na<sub>2</sub>SO<sub>4</sub> makeup</b>	<b>0,00</b>	-	<b>20,97</b>	-	<b>kg/ADt</b>
Na in Na <sub>2</sub> SO <sub>4</sub>	0,00	-	6,79	-	kg/ADt
<b>Additional NaOH makeup</b>	<b>2,55</b>	-	<b>1,38</b>	-	<b>kg/ADt</b>

The aim is to remove the necessity of ash dumping for Mill 1 and the necessity of ARC purge disposal for Mill 2 and to recover sulfur from different waste streams without impacting the Na/S balance of the mill. This can be conducted by adding anaerobic digestion to treat ESP ash and ARC purge mixed with bleaching effluents while simultaneously recovering sulfur. This mixture of ESP ash or ARC purge with bleaching effluent is referred as solution later in the text. As AD cannot recover sodium, it will be directed to the WWTP alongside with residuals generated in the process. Therefore, sodium ends up to the water bodies similarly as in the base scenario without AD.

In order to determine the amount of ESP ash and ARC purge that can be treated with AD, some calculations must be conducted. In the equations ESP ash and ARC purge are referred as ash because the calculations apply for both residuals. In the calculations it is assumed that 100% of the sulfate reduces to sulfide in anaerobic digestion as the laboratory experiment indicated that is possible. The calculations begin with determining the mass of ash generated in the recovery boiler. In the base scenario, it assumed that ESP ash and ARC purge are disposed from recovery boiler alongside with solids to be removed from the process. Therefore, the mass of ash generated,  $m_{ash}$ , can be calculated as follows in equation 16.

$$m_{ash} = m_{solids} * x_{ash} \quad (16)$$

where,  $m_{ash}$  = mass of ash generated [kg/ADt]  
 $m_{solids}$  = mass of solids produced [kg/ADt]  
 $x_{ash}$  = amount of ash in solids [kg<sub>ash</sub>/kg<sub>solids</sub>]

Then the mass of sulfates in ESP ash,  $m_{SO_4, ash}$ , can be calculated, as the amount of sulfate in ash is known. Equation 17 presents this calculation.

$$m_{SO_4, ash} = x_{SO_4} * x_{ash} \quad (17)$$

where,  $m_{SO_4, ash}$  = mass of sulfate in ash [kg/ADt]  
 $x_{SO_4}$  = amount of sulfate in ash [kg<sub>SO<sub>4</sub></sub>/kg<sub>ash</sub>]

The amount of sulfur in sulfate, %S, can be determined with the percentage of sulfur in sulfate (McMurry et al. 2016, 121). The percentual amount of sulfur is calculated with equation 18.



$$\% S = \frac{M_S}{M_{SO_4^{2-}}} \quad (18)$$

where,  $\%S$  = amount of sulfur in sulfate [%]

$M_S$  = molar mass of sulfur [g/mol]

$M_{SO_4}$  = molar mass of sulfate [g/mol]

Then the mass of sulfur produced,  $m_{S, ash}$ , can be calculated with equation 19.

$$m_{S,ash} = m_{SO_4,ash} * \% S \quad (19)$$

where,  $m_{S, ash}$  = mass of sulfur in ash [kg/ADt]

To fulfill the amount of sulfur desired, the mass of sulfates required,  $m_{SO_4, r}$ , that equals to it needs to be calculated. With equation 20 the mass of sulfates needed to fulfil the wanted amount of sulfur is calculated. This also equals to the amount of sulfates that was previously discharged to water bodies alongside ash in treated wastewater.

$$m_{SO_4, r} = \frac{m_{S, d}}{\% S} \quad (20)$$

where,  $m_{SO_4, r}$  = mass of sulfates required [kg/ADt]

$m_{S, d}$  = mass of sulfur desired [kg/ADt]

Lastly, the mass of ash required,  $m_{ash,r}$ , can be calculated as the mass of required sulfate and amount of sulfate in ash is known. Equation 21 presents the equation for the amount of ash required.

$$m_{ash,r} = \frac{m_{SO_4,r}}{x_{SO_4}} \quad (21)$$

where,  $m_{ash,r}$  = mass of ash required [kg/ADt]

When determining the volume flow of the solution, optimal mass percentages of ash and effluent, and saved sulfate load in discharged effluents, some assumptions are made. In this case solution refers to the mix of ash and bleaching effluent. It is assumed that the density of the solution is 1000 kg/m<sup>3</sup> which is close to the density of water at 25 °C (997 kg/m<sup>3</sup>). This assumption is justified by the fact that the solution is mostly (99 wt-%) of bleaching effluent, which consists mainly of water. The total volume flow of bleaching effluent that can be utilized is approximately 8 m<sup>3</sup>/ADt, which is the amount of bleaching effluent generated. Therefore, the total volume flow of the solution can be calculated with the maximum mass of the ash and bleaching effluent. The bleaching effluent under examination is assumed to be the same for Mill 1 and Mill 2. Taking all these assumptions into consideration, the total volume of the solution,  $q_V$ , can be calculated. Equation 22 is used in the determination of the total volume.

$$q_V = \frac{m_{effluent} + m_{ash,r}}{\rho} \quad (22)$$

where,  $q_V$  = volume flow of the solution [m<sup>3</sup>/ADt]

$m_{effluent}$  = mass of the bleaching effluent [kg/ADt]

$\rho$  = density of the solution [kg/m<sup>3</sup>]

Finally, the mass percentages of ash and bleaching effluent in the solution can be calculated with equation 23.

$$wt - \%_i = \frac{m_i}{m_{effluent} + m_{ash,r}} \quad (23)$$

where,  $wt - \%_i$  = mass percentage of substance i [%]

$m_i$  = mass of the substance i [kg/ADt]

The mass of sulfates from the bleaching effluents recovered with AD instead of discharging into water bodies alongside with wastewater can be calculated as the volume flow of the effluent and the sulfate concentration are known. Equation 24 presents the amount of sulfate load avoided in the discharged wastewater.

$$m_{SO_4, re} = q_{V, effluent} * C_{effluent} \quad (24)$$

where,  $m_{SO_4, re}$  = mass of sulfates recovered [kg/ADt]

$q_{V, effluent}$  = volume flow of the effluent [m<sup>3</sup>/ADt]

$C_{effluent}$  = sulfate concentration of the effluent [mg/l]

The mass of sodium leaving the process alongside with wastewater can be calculated with equation 25.

$$m_{Na} = m_{ash,r} * x_{Na} \quad (25)$$

where,  $m_{Na}$  = mass of sodium [kg/ADt]

$x_{Na}$  = amount of sodium in ash [kg<sub>Na</sub>/kg<sub>ash</sub>]

With the results from the laboratory experiment the aim is to also calculate the total volume flow of the solution with the limitation of sulfur leaving. This volume flow,  $q_V$ , is comparable to the volume flows for Mill 1 and Mill 2 and therefore the results can be compared. The total volume flow can be calculated with equation 26.

$$q_{V,max} = \frac{m_{ash,r}}{\%S * (c_{solution} - c_{effluent})} \quad (26)$$

where,  $c_{solution}$  = sulfate concentration of the solution [mg/]

## 6 Results and discussion

In this chapter, the results and discussion part of the study are explained. First laboratory results are interpreted followed by calculations related to the hypothetical kraft mills. These calculations include determination of new Na/S balance with the addition of anaerobic digestion process and comparative calculations based on the laboratory samples.

### 6.1 Laboratory experiment results

The samples were diluted to get more realistic results in sulfate reduction. In all samples the concentration of COD was insufficient, so addition of acetate was necessary. Table 5 presents an overview of the sulfate reduction rate for the different samples. The reduction rate is determined with the initial concentration and final concentration. The final concentration is reached in several days and it differs 1-2 days between the samples. This creates limited accuracy to the results. These results can give an indication of the activity, but true activity can be demonstrated only in a continuous experiment as it is more realistic compared to batch experiment. The volumetric loading of sulfate for all the samples is also presented. This value indicates the mass of sulfate reduced per volume per day.

Table 5. Laboratory experiment results

Parameter	Sample 3	Sample 4	Sample 5	Sample 6	Unit
Sulfate reduction rate	0,23	0,38	0,16	0,16	g SO <sub>4</sub> /g VSS/day
Volumetric loading	6,4	11,3	4,4	4,4	kg SO <sub>4</sub> /m <sup>3</sup> /day

## 6.2 Na/S balances with anaerobic digestion

General values needed in the calculations for determining the amount of ESP ash and ARC purge and the volume of the solution are presented in table 6. It has been assumed that ESP ash and ARC purge are generated the same amount.

Table 6. General values

Parameter	Value	Unit
$m_{\text{solids}}$	1,5	$t_{\text{solids}}/\text{ADt}$
$X_{\text{ash}}$	100	$g_{\text{ash}}/\text{kg}_{\text{solids}}$
$M_{\text{S}}$	32	g/mol
$M_{\text{SO}_4}$	96	g/mol
$C_{\text{effluent}}$	7558	mg/l
$q_{\text{V, effluent}}$	8	$\text{m}^3/\text{ADt}$
$\rho_{\text{solution}}$	1000	$\text{kg}/\text{m}^3$

Sulfate content in ESP ash is  $0,525 \text{ kg}_{\text{SO}_4}/\text{kg}_{\text{ESP}}$  and in ARC purge  $0,440 \text{ kg}_{\text{SO}_4}/\text{kg}_{\text{ARC}}$ . For sodium, the content in ESP ash is  $0,322 \text{ kg}_{\text{Na}}/\text{kg}_{\text{ESP}}$  and in ARC purge  $0,274 \text{ kg}_{\text{Na}}/\text{kg}_{\text{ARC}}$ . The desired amount of sulfur recovered originating from ESP ash with AD is  $1,91 \text{ kg}/\text{ADt}$  for Mill 1 and from ARC purge  $2,13 \text{ kg}/\text{ADt}$  for Mill 2. Table 7 gathers these specific values used in the calculations for Mill 1 and Mill 2.

Table 7. Specific values for Mill 1 and Mill 2

Parameter	Mill 1	Mill 2	Unit
$X_{\text{SO}_4, \text{ESP}}$	0,525 (52,5)	-	$\text{kg}_{\text{SO}_4}/\text{kg}_{\text{ESP}}$ (%)
$X_{\text{SO}_4, \text{ARC}}$	-	0,440 (44,0)	$\text{kg}_{\text{SO}_4}/\text{kg}_{\text{ARC}}$ (%)
$X_{\text{Na}, \text{ESP}}$	0,322 (32,2)	-	$\text{kg}_{\text{Na}}/\text{kg}_{\text{ESP}}$ (%)
$X_{\text{Na}, \text{ARC}}$	-	0,274 (27,4)	$\text{kg}_{\text{Na}}/\text{kg}_{\text{ARC}}$ (%)
$m_{\text{S, d, ESP}}$	1,91	-	kg/ADt
$m_{\text{S, d, ARC}}$	-	2,13	kg/ADt

The aim is to eliminate the need of ash dumping at the ECF mill utilizing softwood. Therefore, the maximum amount of sulfur recovered from ESP ash through anaerobic digestion should equal the amount of sulfur currently dumped in ESP ash. The amount of ESP ash treated with AD cannot exceed this limit, as it would lead to sulfur losses in the process which are tried to be avoided. Table 7 shows that the desired amount of sulfur recovered from ESP ash is 1,91 kg/ADt. For Mill 2, the amount of sulfur recovered from ARC purge through anaerobic digestion equals the amount of sulfur leaving the process alongside the ARC purge. This is due to the lack of sulfur in the process, which eliminates the need for ash dumping because of excess of sulfur or sodium. In this case, the aim of ARC is the removal of chlorine. From table 7, it can be seen that the amount of sulfur desired to recover from ARC purge is 2,13 kg/ADt.

For Mill 1 the required mass of ESP ash to fulfil the desired amount of sulfur is approximately 7% from the total amount of ESP ash generated. The required mass of ARC purge for Mill 2 to fulfil the desired amount of sulfur is approximately 10% from the total amount of ARC purge generated. From this amount of ash, the amount of sodium leaving the process alongside with residuals generated in AD for Mill 1 is 32,2% and for Mill 2 27,4%. The total volume flow of the solution is approximately 8,0 m<sup>3</sup>/ADt for both mills and the optimal amount of ESP ash is 0,14 wt-% in Mill 1 and for ARC purge 0,18 wt-% in Mill 2. Therefore, the optimal amount of effluent in the solution is 99,86 wt-% in Mill 1 and 99,82 wt-% in Mill 2.

With the addition of anaerobic digestion sulfate emission to water bodies can be avoided. Sulfate emissions from bleaching effluent and ash avoided in discharged wastewater for Mill 1 and Mill 2 are approximately 48% less compared to base scenario. This value includes the amount of sulfates from the bleaching effluent and ash directed to AD because these effluents would otherwise be directed to the WWTP. When the pulp production capacity of the mill is taken into consideration yearly sulfate emissions avoided are over 100% for Mill 1 and approximately 50% for Mill 2 less compared to a sulfate limit value set for Kemi pulp mill. The total amount of sulfur produced with AD is 47,5% for Mill 1 and 48,0% for Mill 2 of the sulfur in bleaching effluent and ash

After completing the calculations, a new Na/S balance can be conducted. Figure 13 presents a schematic drawing of the Na/S circulation with the addition of anaerobic digestion. In the

figure the size of an arrow indicates the mass of the input, red arrows represent sulfur and blue arrows represent sodium.

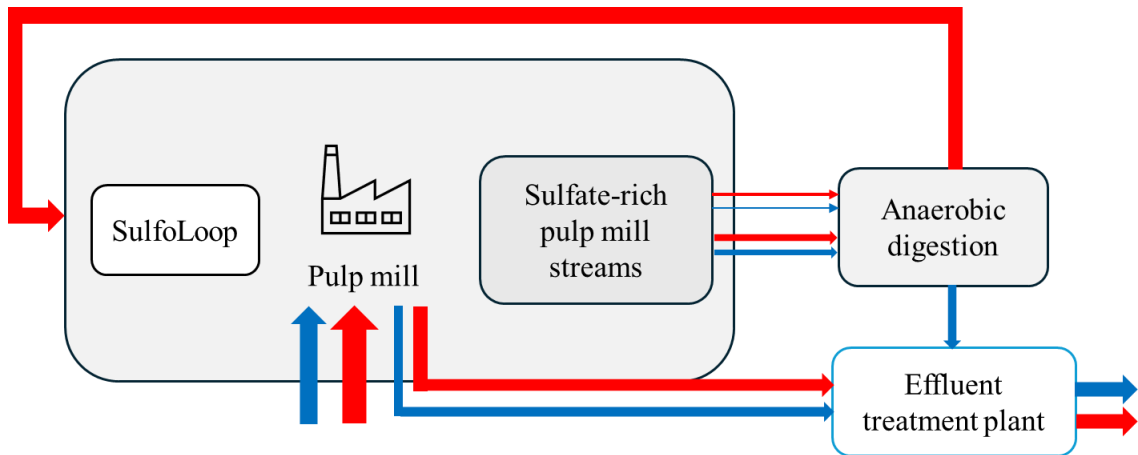


Figure 13. Na/S circulation with the addition of AD

### 6.3 Calculations based on laboratory experiment

Table 8 presents the maximum volume flows of the solution based on the samples used in the laboratory experiment. The volume flows are calculated based on the maximum amount of sulfur in ESP ash and ARC purge. The maximum amount of sulfur in ESP ash for Mill 1 is 1,91 kg/ADt and and for ARC purge for Mill 2 2,13 kg/ADt. The maximum volume flows are presented only for sample 4 and sample 6 because they are the samples that contain ash and therefore have a limiting factor for the maximum volume.

Table 8. Volume flows based on laboratory experiment

Volume flow, $q_{v, \max}$	Sample 4	Sample 6	Unit
Mill 1	0,897	0,901	$\text{m}^3/\text{ADt}$
Mill 2	1,000	1,004	$\text{m}^3/\text{ADt}$

Table 9 presents the maximum mass of sulfate and sulfur recovered from solutions like the tested samples per ADt. These amounts for Mill 1 and Mill 2 are based on the maximum volume flows presented in table 8. In the calculations, the amounts for sample 3 were



calculated with the volume flow of sample 4 and for sample 5 with the volume flow of sample 6. Samples 3 and 5 consist only of bleaching effluent and therefore there are no limiting factors and are calculated with these chosen flows to be more comparable with each other. The maximum amount of sulfate and sulfur are determined with the assumed maximum volume flow of bleaching effluent ( $8 \text{ m}^3/\text{ADt}$ ) and the amount of ESP ash generated ( $150 \text{ kg}/\text{ADt}$ ). When comparing the calculated values for Mill 1 and Mill 2 with the maximum values of sulfate and sulfur it can be noted that they are approximately only 11,2% of total amount of sulfate and sulfur.

Table 9. Amount of sulfate and sulfur per air dried ton of pulp

Sample	Mill 1		Mill 2		Maximum	
	kg SO <sub>4</sub> /ADt	kg S/ADt	kg SO <sub>4</sub> /ADt	kg S/ADt	kg SO <sub>4</sub> /ADt	kg S/ADt
Sample 3	8,34	2,78	9,30	3,10	74,38	24,79
Sample 4	14,07	4,69	15,69	5,23	125,48	41,83
Sample 5	5,92	1,97	6,60	2,20	52,54	17,51
Sample 6	11,65	3,88	12,99	4,33	103,44	34,48

## 6.4 Discussion

The laboratory experiment conducted was a batch experiment, whereas in industry the process is typically a continuous process. This inconsistency most likely affects the results and their reliability. Batch tests may not accurately replicate the continuous process, potentially leading to differences in microbial activity, sulfate reduction rates, and overall, in the process itself. Therefore, the results gained from the laboratory experiment should be interpreted with caution, and further studies as continuous experiment are recommended to validate these findings. With taking this into account, it should be noted that as the results from this laboratory experiment are used as grounds for some assumptions made in the calculations, it also creates uncertainty to the calculation results.

Laboratory experiment results show that the sulfate reduction rate of sample 4 is the best of the samples, even though its COD/SO<sub>4</sub> ratio is not the lowest. It is noticed that a good COD/SO<sub>4</sub> ratio does not necessarily correlate with the fact that the lower the number, the

better the sulfate reduction rate. It seems that more is influenced by the sulfate concentration of the sample before anaerobic digestion. Samples 3 and 4 also contain more lactic acids, acetic acids, propionic acids and butyric acids compared to samples 5 and 6. This may have some effect on the rate of sulfate reduction since these organic and fatty acids are typically products from acidogenesis and are further broken down by SRBs directly into hydrogen sulfide and carbon dioxide. The results indicate that presence of these organic acids may enhance sulfate reduction by providing available substrates for SRB. In general, better sulfate reduction rate and volumetric loading are in samples 3 and 4 compared to samples 5 and 6.

When comparing the Na/S balance (base scenario) presented in table 4 and Na/S circulation presented in figure 12 to new Na/S circulation in figure 13, it can be seen that the addition of anaerobic digestion onsite does not directly impact to the Na/S balance of a mill. The Na/S balance stays constant, only change in the Na/S circulation is that sodium and sulfur previously in ash dump or ARC purge are now in anaerobic digestion. The consumption of makeup chemicals stays constant which means there are no occurring lacks of sulfur or sodium. It can be noticed when comparing Na/S circulation presented in figure 12 and in figure 13 that the external input of sulfur is smaller with the addition of AD. Even though there were no changes in the values of the Na/S balance, it does not mean that there were no impacts. With the addition of AD, sulfur from bleaching effluents that was previously discharged to water bodies alongside wastewater, is now recovered and can be further converted to sulfuric acid onsite with SulfoLoop process.

Sulfur ends up to the AD process mainly from by-products of other processes, as a make-up chemical or with fuel, and furthermore with small amounts in water and wood. The sulfur from sulphuric acid comes mainly from by-products of other processes, such as sludge from chlorine dioxide plant and residual from tall oil plant. Therefore, when examining whether a kraft mill is possible to become sulfur self-sufficient, the focus should be on these above-mentioned sources of sulfur. The Na/S balances of hypothetical pulp mills show that most of the input sulfur in the process comes from by-products of other processes. For Mill 1, more than 95% of sulfur comes from by-products, while for Mill 2, approximately 68% comes from by-products. The total amount of sulfur inputs for Mill 1 is 8,77 kg/ADt and for Mill 2 0,37 kg/ADt. The impact of other sulfur inputs on the total Na/S balance is marginal, especially for Mill 1, as less than 5% comes from sources other than process by-products.

For Mill 2, the amount is slightly higher, as about 32% of the sulfur comes from somewhere other than the by-products of the processes. However, these numbers indicate that for both mills, more than half of the sulfur comes from sulfur-containing by-products of the processes.

Sulfate emissions to water bodies reduced at Mill 1 are calculated to be over 100% less and at Mill 2 approximately 50% less compared to the sulfate limit value set for the Kemi pulp mill in discharged wastewater (36,000 t/a). It can be seen that AD can significantly reduce the sulfate load of the mill's wastewater. Anaerobic digestion can therefore be used to significantly reduce the sulfate load of discharged wastewater. Of course, it should be noted that the calculation performed are theoretical, which creates unreliability in the results. In a real continuous process, the values are more likely to differ from these calculated values, although the results can be considered indicative.

With the results from the calculations, it can be noticed that, at least in theory, the mass percentage of ash in the solution can be reduced, and then the entire bleaching effluent can be directed to anaerobic digestion. For Mill 1 and Mill 2 the only limiting factor for the amount of ash directed to AD seems to be the sulfur content. For this case, the maximum amount of ESP that can be directed to AD is approximately 7% and for ARC purge approximately 10% compared to the total amount of these residuals generated. The changes in the mass percentages have not been tested in practice. Therefore, it is not known how the SRBs would react to this change that the amount of effluent increases 100-fold and the amount of ash decreases 100-fold. The percentual amount of ash decreases from 1% to approximately 0.1% and the amount of effluent increases from 99% to approximately 99.9%. The effects this has on the sulfate reduction rate and thus on the process itself should be investigated through practical experiments.

When analysing the calculated volume flows for Mill 1, Mill 2, and the volume flows calculated based on the laboratory experiment, it can be seen that if the ratio of mass percentages is 1% and 99%, approximately 7 m<sup>3</sup>/ADt from 8 m<sup>3</sup>/ADt of the bleaching effluent remains unused. The volume flows based on laboratory experiment results are approximately maximum of 1 m<sup>3</sup>/ADt while the flow for Mill 1 and Mill 2 is approximately 8,0 m<sup>3</sup>/ADt. This is because the sulfur in ESP ash and ARC purge determines how much ash and purge can be used, which in turn determines the amount of solution when the mass percentages are known. In comparison, if the optimal mass percentages for ash and effluent are determined first, it

can be noticed that the entire bleaching effluent can be used and thus more sulfur for AD and less sulfate with wastewater into water bodies. The avoided sulfate emissions for bleaching effluent and ash, calculated using the volume flows based on the laboratory experiment, are between 11,7 and 15,7 kg/ADt which equal to approximately 11,2% less sulfate emissions compared to total amount of sulfates from bleaching effluent and ash generated. The sulfate emissions for hypothetical mills would be reduced by approximately 48,0% compared to total amount of sulfates in bleaching effluent and ash. Therefore, the amount of sulfur recovered from the solution based on laboratory experiment are between 3,9 and 5,2 kg/ADt which equal to 11,2% sulfur recovered from the total amount. For hypothetical mills the amount of sulfur recovered from effluent and ash is approximately 48% of the sulfur in bleaching effluent and ash. As can be seen, the amount of sulfate emissions reduced is multiple for hypothetical mills compared to the amounts based on laboratory experiment. The total amount of sulfur recovered with AD for Mill 1 is 47,5% and for Mill 2 48,0% while the amount based on the laboratory experiment is approximately 11,2%. Although the composition of the samples is not exactly the same, it can be assumed that the samples are comparable, since the solution from hypothetical mills contains more than 99% of the bleaching effluent. As a further study, it could be investigated whether kraft mills would have other potential side streams/waste streams that could be treated with anaerobic digestion and thus recover more sulfur.

The thesis has focused on the kraft mill's Na/S balance, but as can be seen from the results, with AD only sulfur is recovered. In this case, sodium from ESP ash and ARC purge is still not recovered and is disposed. The disposed amount of sodium alongside AD residuals is 32,2% of ESP ash directed to AD 27,4% of ARC purge directed to AD. Sodium is an important element in kraft pulping, as it is found in cooking chemicals, for example, and is used in the manufacture of chlorine dioxide. In the future, sodium recovery and related technologies should be studied in order to improve the recovery of chemicals and important elements in kraft mills. If sodium could also be recovered from waste streams, it could potentially be possible to achieve savings in chemical costs. One possibility is also to investigate the possible ways to recover sodium from sludge generated in AD. As AD is not able to recover sodium, this sludge could possibly be a viable source of sodium.

## 7 Conclusions

Sulfur self-sufficiency at kraft mills is possible, at least in theory. With anaerobic digestion, sulfate can be reduced from kraft mill side streams to hydrogen sulfide, which in turn can be used to produce sulfuric acid with SulfoLoop. This sulfuric acid can be used, among other things, in tall oil plant, in ash leaching, in pH adjustment at the bleach plant, and in the production of chlorine dioxide. Sulfuric acid produced with SulfoLoop could replace conventional sulfuric acid produced with fossil-based sulfur, so this could also be a more sustainable alternative to the conventional sulfuric acid. If sulfuric acid is produced in SulfoLoop more than the mill's own consumption, it could also possibly be sold externally and thus gain more economic benefits from it. Based on the discussion section, it can be stated that if fossil-based sulfur in sulphuric acid can be replaced by sulfur recovered from the side streams of the process, such as bleaching filtrate, ESP ash and ARC purge, the plant can be said to be sulfur self-sufficient.

The efficiency and outcome of AD are influenced by several key parameters such as sulfate concentration, COD/SO<sub>4</sub> ratio, organic acid content, and process conditions. Higher sulfate concentrations before AD can improve the sulfate reduction rate, as was noted for sample 4, which showed the best performance despite not having the best COD/SO<sub>4</sub> ratio among the samples. While a lower COD/SO<sub>4</sub> ratio is typically more desired for sulfate reduction, the results from laboratory experiment indicate that sulfate concentration might have a more significant role in determining the reduction rate. Higher concentrations of lactic acids, acetic acids, and propionic acids showed enhancing effects on sulfate reduction rates as was seen for samples 3 and 4. From microbial activity point of view, the maintenance of optimal process conditions is critical as changes in pH and temperature might inhibit the process.

It can be stated that AD is an effective way to reduce sulfate emissions to water bodies, if the entire bleaching filtrate can be directed to the anaerobic digestion plant. It was noticed that sulfate emissions to water bodies could be reduced by over 100% at Mill 1 and approximately 50% at Mill 2, which is a substantial improvement compared to regulatory discharge limits. The laboratory experiment results indicate that AD can recover sulfur from bleaching effluents, which would otherwise be discharged into water bodies. The results showed that complete reduction of sulfate as hydrogen sulfide is possible if certain process conditions,

such as the amount of organic matter, and ratio of COD and sulfate, are kept in optimal level. In case there is a lack of organic carbon or nutrients, an addition of these listed is possible.

The sulfur content in ESP ash and ARC purge acts as a limiting factor in how much of these residuals can be directed to anaerobic digestion. This amount of sulfur should not be exceeded or lowered, otherwise an imbalance would be created in the mill's Na/S balance. Consequently, the plant could incur sulfur losses, among other things. The sufficiency of ESP ash and ARC purge should not be a limiting factor. The need for ESP ash from the total amount of ash generated is approximately 7% for Mill 1 and for ARC purge about 10% for Mill 2. In terms of the sufficiency of ash, its amount in the mixture could be increased, but the sulfur content of the ash is a limiting factor in this situation as well.

The comparison of Na/S balances with and without anaerobic digestion indicates that the implementation of AD does not directly impact the Na/S balance of a mill. The balance remains constant because the sodium and sulfur previously in the ash dump or ARC purge are now directed to anaerobic digestion. It was noted that the consumption of makeup chemicals also remains constant. For Mill 1, ash dumping is mandatory due to excess amount of sulfur in the process and for Mill 2, disposal of ARC purge is mandatory due to excess chlorine in the process. With AD valuable element sulfur can be recovered and further converted into sulfuric acid. While sodium remains in the residuals generated in AD, sulfur from bleaching effluent previously discharged into water bodies is now recovered, impacting the overall process. The recovered sulfur can be converted into sulfuric acid with SulfoLoop, improving resource efficiency.

For Mill 1, which is the ECF plant using softwood, over 95% of the sulfur input originates from by-products of other processes. The same number for Mill 2, a TCF plant using eucalyptus, is approximately 68%. When comparing the total amount of sulfur input for the two mills, it can be noted that for the ECF plant the input is multiple compared to the input of the TCF plant. For ECF plant the most relevant by-products that bring sulfur into the process are sludge from ClO<sub>2</sub> plant and residual from tall oil plant. The amount of sulfur from ClO<sub>2</sub> plant sludge is already larger than the total sulfur input for TCF mill. With that comparison it can be concluded that the chosen bleaching method highly impacts to the sulfur inputs of a mill but there are no great impacts to the amount of sulfur directed to AD.

In the laboratory experiment, the mass percentages in the solution differ from the one calculated for hypothetical mills. In this case, most of the bleaching effluent remains unused due to the sulfur content in ESP ash and ARC purge limiting the amount of ash that can be directed to AD. However, if the mass percentages are adjusted to approximately 0,1% ash and approximately 99,9% effluent, the entire bleaching effluent can be utilized which leads to significant reductions in sulfate emissions as noted in the discussion part. With modifying the mass percentages, more sulfate can be directed to anaerobic digestion, more sulfur is generated and finally more sulfuric acid is produced. Therefore, the optimal mass percentages should be determined on a case-by-case basis taking into account the masses of residuals utilized.

## 8 Summary

Pulp and paper (P&P) industry faces climate change challenges that drive improvements in freshwater consumption and chemical recovery. The increasing demand for sulfur, alongside diminishing fossil-based sulfur supplies, emphasizes the need for innovative recovery methods such as anaerobic digestion (AD). Additionally, freshwater scarcity pressures the P&P industry to enhance water consumption habits, such as improving chemical recovery in kraft mills to enable water circulation in the mill.

In this thesis, the focus was on determining whether anaerobic digestion is a suitable method to reduce sulfate as sulfide from different sulfate containing waste streams in a kraft mill. The research questions of the study were: In which type of conditions can a kraft mill become sulfur self-sufficient? How does the addition of anaerobic digestions impact to the sulfur self-sufficiency?; What are the main parameters that affect anaerobic digestion? How do these parameters affect the efficiency and the outcome of the process?; How effectively can anaerobic digestion reduce sulfur emissions and recover useful by-products while simultaneously maintaining the Na/S balance of a kraft mill?. These questions were studied through analyzing laboratory experiment results, determining optimal ratio of bleaching effluent and ash of the solution treated with AD, avoided load of sulfate in discharged wastewater and comparing Na/S balances of two hypothetical kraft mills before and after the addition of AD.

Laboratory experiment results showed promising results for AD as an efficient sulfate reducing method. By the addition of SulfoLoop and AD a kraft mill can become sulfur self-sufficient as it was noted that the main input of sulfur to the process is alongside sulfuric acid. The efficiency of AD is influenced by sulfate concentration, COD/SO<sub>4</sub> ratio, and organic acid content based on the laboratory experiment. AD has the potential to significantly reduce sulfate emissions to water bodies, with estimated reductions of 48%. While anaerobic digestion does not directly affect to the Na/S balance of a kraft mill, it allows recovery of sulfur that would otherwise be discharged into water bodies. Sodium recovery is not possible with AD so alternative option should be investigated for this recovery. Adjusting the mass percentages in the solution, sulfur recovery is optimized, sulfate emissions minimized and sulfur to sulfuric acid production maximized.



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