ZDHC

ZDHC Dissolved Pulp Guidelines

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NOTES

Any mention of innovations and/or innovative practices within this document are provided as examples and should not be construed as the only ones available. Organisations are responsible for conducting their own research into all possible solutions to determine the best one for them.

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List of terms (Abbreviations)

ADT	In this document, specific chemical and energy consumption, costs and emissions are expressed as 'per 90% air dry pulp → air dry.
Alpha cellulose	A highly refined, insoluble cellulose from which sugars, pectin and other soluble materials have been removed. Also known as chemical cellulose.
Black liquor	Spent Kraft pulping liquor with inorganics and dissolved organics.
Brown liquor	Spent sulphite pulping liquor with inorganics and dissolved organics.
BREF	Best Available Techniques Reference Document.
Causticising	The process in the lime cycle in which hydroxide (white liquor) is regenerated by the reaction $Ca(OH)_2 + CO_3^{-2} \rightarrow CaCO_3$ (s) + 2 OH^-. Green liquor.
CETP	Centralised Effluent Treatment Plant
Chemical Pulp	Fibrous material obtained by removing from the raw material a considerable portion of the non-cellulosic compounds that can be removed by chemical treatment (cooking, delignification, bleaching).
Delignification	Dissolution and removal of lignin from wood chips (cooking: initial, bulk and residual delignification) or from fibres (oxygen stage and bleaching).
DP	Dissolved pulp
ECF	Elemental chlorine-free bleaching sequence containing chlorine dioxide but not elementary chlorine gas.
Forestry	The science and craft of creating, managing, using, conserving and repairing forests, woodlands and associated resources for human and environmental benefits.
Green liquor	Aqueous solution of sodium sulphide and sodium carbonate. Intermediate product in Kraft chemical recovery.
Hardwood	Group of wood species including aspen, beech, birch and eucalyptus. The term hardwood is used in opposition to softwood.

ISO	International Organization for Standardisation
Kraft pulp	Chemical pulp manufactured using sodium sulphide as the primary cooking chemical. Wood chips are digested in an alkaline cooking liquor, an aqueous solution of sodium hydroxide and sodium sulphide (white liquor).
Magnefite	Magnesium-based sulphite pulping process.
Make-up chemicals	Replacement chemicals that are purchased to cover chemical losses of various kinds.
MMCF	Man-made cellulosic fibres
Softwood	Wood from conifers, including pine and spruce. The term softwood is used in opposition to hardwood.
SSL	Spent sulphite liquor. Liquid that is left over from the sulphite pulping process where wood is digested to cellulose pulp with bisulphite under heat and pressure.
TCF	Total chlorine-free bleaching containing Ozone and hydrogen peroxide.
TRS	Total reduced sulphur in flue gas. The sum of the following reduced malodorous sulphur compounds generated in the pulping process: hydrogen sulphide, methyl mercaptan, dimethylsulphide and dimethyl disulphide, expressed as sulphur.
White liquor	Alkaline cooking liquor, an aqueous solution of NaOH and $Na_{-2}S$, for Kraft pulping.
WHO	World Health Organization
ZLD	Zero liquid discharge

Best Available Techniques (BAT) Reference Document for the Production of Pulp, Paper and Board Industrial Emissions Directive 2010/75/EU 2015

Chemical formulae commonly used in this document

CaO	Calcium oxide (lime)
$CaCO_3$	Calcium carbonate
$Ca(OH)_2$	Calcium hydroxide
ClO_2	Chlorine dioxide
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric acid
$Mg(OH)_2$	Magnesium hydroxide
$Mg(HSO_3)_2$	Magnesium bisulphite
NaOH	Sodium hydroxide
Na_2S	Sodium sulphide
NaHS	Sodium hydrosulphide
Na_2CO_3	Sodium carbonate
$NaClO_3$	Sodium chlorate
NOx	The sum of nitrogen oxide (NO) and nitrogen dioxide (NO_2) expressed as NO_2
O_3	Ozone
O_2	Oxygen
SO_2	Sulphur dioxide

Collaborative process and acknowledgements

The fundamental principle of collaboration at ZDHC was followed in the development of this document. A sub-focus group of experts was formed within the MMCF Focus Group to work on conventional wood-based dissolved pulp guidelines by providing inputs on dissolved pulp processes, chemical usage and environmental impacts. The ZDHC Fibres and Materials Competence Centre and Roadmap to Zero (RtZ) Delivery teams co-ordinated with this sub-focus group through a series of calls, e-mails and 1:1 calls to gather and collate inputs on the topics. Inputs were also collated from SAPPI, a major dissolved pulp manufacturer. A Textile Exchange representative was involved in the deliberations of the sub-focus group as part of the collaboration on this topic between ZDHC and Textile Exchange.

Based on the discussions and inputs gathered, a draft document was prepared by ZDHC and reviewed by the sub-focus group members. The suggestions and comments received from them were incorporated into the draft to prepare the guidelines. We acknowledge and thank the contribution of the sub-focus group members and experts for their assistance in developing this document. Please see the end of this document for a complete list of acknowledgements.

Introduction

Dissolved pulp

Dissolved pulps (DP) represent specialty pulps within the chemical pulp segment since they are chemically refined bleached pulps composed of more than 90% pure cellulose (alpha-cellulose), with low contents of hemicellulose, lignin, resin and traces of inorganic impurities like calcium, magnesium, silica and iron. These pulps have special properties, such as a high brightness level, uniform reactivity with chemicals and uniform molecular-weight distribution. Their manufacturing is characterised by the derivatisation and, thus, solubilisation of highly purified cellulose.[1]

Dissolved pulp is so named because it is not made into paper but dissolved in a solvent which makes it completely chemically accessible and removes the remaining fibrous structure. Once dissolved, it can be spun into textile fibres.[2]

Background

Dissolved pulp (DP) is the primary feedstock for producing man-made cellulosic fibres (MMCF) like viscose staple fibres (VSF), modal, viscose filament yarn (VFY), lyocell and acetate with high cellulose content (alpha-cellulose). Dissolved pulp making includes processes to extract cellulose from wood or textile waste as raw material, followed by bleaching to improve the brightness of the pulp, which is then chemically processed to create regenerated cellulosic fibres for various textile applications.

Wood from forests/reclaimed textile waste —> dissolved pulp —> MMCF

- ZDHC has developed the Dissolved Pulp Guidelines V1.0 to enhance the transparency of responsible production in the entire MMCF supply chain, from wood sourcing to man-made cellulosic fibre (MMCF) production.

The document is an initiative by ZDHC to address the use and discharge of chemicals in wood-based dissolved pulp manufacturing*. The guidelines include chemical recovery, wastewater and air emission requirements for wood-based dissolved pulp facilities.

Clean input and efficient process management is crucial in dissolved pulp (DP) manufacturing. They enable high-quality output while minimising environmental impact.

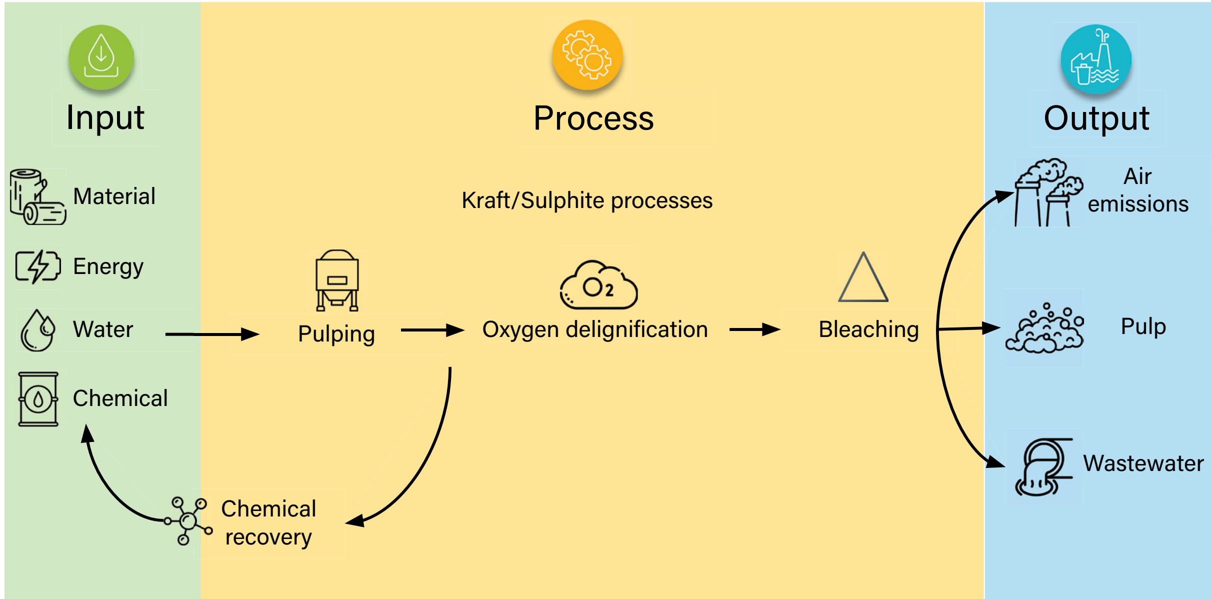


Figure 1: Sustainable chemical management in dissolved pulp (DP) manufacturing

- **Input:** The process begins with the input of sustainably sourced wood (linked to sustainable forestry certifications), which undergoes precise chipping and cooking processes.
- **Process:** Advanced process management techniques, such as oxygen delignification and elemental chlorine-free (ECF) or total chlorine-free (TCF) bleaching, ensure the effective removal of lignin and impurities. Chemical recovery systems play a vital role in this stage, recycling cooking chemicals and reducing waste.
- **Output:** The output is a high-purity pulp, ideal for producing a variety of cellulose-based products, including MMCF, along with emissions of chemicals to wastewater, sludge and air.

* *This document does not cover the process of turning textile waste into dissolved pulp for MMCF.*

Objectives

The ZDHC Dissolved Pulp Guidelines V1.0 addresses integrated expectations for feedstock sourcing, chemical recovery, discharged wastewater and air quality for manufacturing facilities producing dissolved pulp from wood as a feedstock. The guidelines cover:

1) Input Management (Chapter 1)
2) Process Management (Chapter 2)
3) Output Management (Chapter 3)

Scope

In scope

- Wood as feedstock/input for dissolved pulp production
- Pulping processes:
    - Kraft (sulphate)
    - Sulphite
- Bleaching process:
    - Total chlorine-free
    - Elemental chlorine-free

Out of scope

- Reclaimed textile waste as feedstock for DP manufacturing
- Elemental chlorine-based bleaching of pulp (no longer used in the industry)

Connectivity with other ZDHC documents

The ZDHC Dissolved Pulp Guidelines V1.0 is a solution from ZDHC that aims to drive positive change in the dissolved pulp industry toward sustainable chemical management.

This guidelines document should be read in connection with the following:

ZDHC MMCF Guidelines V2.2

ZDHC Wastewater Guidelines V2.2

ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan (SAP) V2.1

ZDHC Sludge Reference Document V1.0

Summary of requirements in the Dissolved Pulp Guidelines V1.0

Scope	Requirements
Input Management	
Kraft/Sulphite processes	▪ Use certified feedstock such as FSC, PEFC, or Canopy certified wood. ▪ Use Blockchain-based traceability or traceability tools for input feedstock. ▪ Keep records of chemical consumption per air-dry tonne of pulp.
Process Management	
Kraft/Sulphite processes	Keep record of chemical recovery ▪ S & Na recovery in Kraft Process ▪ S & Mg recovery in MgO-based Sulphite process ▪ S & Na recovery NaOH-based Sulphite process
Output Management	
Kraft/Sulphite processes	**Wastewater and sludge** ▪ Test wastewater for conventional, heavy metals and MRSL parameters through ZDHC Approved Wastewater Testing Laboratories twice a year (April and October cycles). ▪ Report load-based wastewater parameters COD, TSS, total nitrogen, total phosphorus, AOX per air-dry tonne of pulp (g/ADT) ▪ Conduct Root Cause Analysis (RCA) and a Corrective Action Plan (CAP) for any non-conformities detected. ▪ Report of the major sludge disposal pathway used.
Kraft/Sulphite processes	**Load-based air emissions** Calculate and report load-based air emissions for total suspended particles/dust, SO_2 as S, NOx as NO_2, TRS as S as a yearly average of the calendar year (from 1st January to 31st December).
Kraft/Sulphite processes	**Ambient air emission** Monitor, test and report ambient air emissions of SO_2, NO_2, $PM_{2.5}$, PM_{10} as a yearly average of the calendar year (from 1st January to 31st December).

CHAPTER 1

Input management

High-quality wood chips and specific chemicals are the primary inputs in dissolved pulp manufacturing. These materials undergo chemical processes to break down lignin and hemicellulose from wood, producing a pure cellulose pulp suitable for various applications.

This document focuses on two input management areas:

- Input feedstock sourcing
- Input chemical management

1.1 Requirements for input feedstock sourcing

Wood has been the traditional raw material for dissolved pulp production. About 85% of the dissolved pulp is made from softwood (spruce, pine) or hardwood (beech, eucalyptus, acacia), while about 10% is made from cotton linters. The selection of the type of raw materials, i.e. softwood, hardwood or cotton linter, is important as these would impact the quality of dissolved pulp produced as well as the productivity of the pulp mill.

Pulp facilities should implement a system to meet one or more requirements for input feedstock as below:

1) Conduct a Canopy-style verification audit to assess the risk of sourcing from ancient and endangered forests and other controversial sources.
2) Source inputs certified by the Forest Stewardship Council (FSC) or Programme for the Endorsement of Forest Certification (PEFC).
3) Ensure transparency throughout the value chain through a proper chain of custody system that includes, but is not limited to, Blockchain-based traceability or the use of traceability tools, e.g. FSC Trace.

4) To encourage circularity and reduce reliance on virgin wood, facilities could increase the amount of alternative fibre feedstock they source. This includes, but is not limited to, pre- and post-consumer textile waste and agricultural waste.

To meet this requirement, facilities should:

- Have a written commitment by the facility's top management to increase the percentage of next-generation input feedstock. This commitment should include the type of feedstock used and appropriate targets and timelines to increase the share of next-generation feedstock.
- Take part in the standard certification programme or any other alternative initiative for the use of next-generation feedstock.

Note: *Linter-based dissolved pulp is also used to produce high-purity cellulose derivatives, including cellulose acetate. In recent years, studies have been reported regarding the use of alternative fibre feedstocks such as textile pre- and post-consumer cellulosic waste and non-wood raw materials, including bamboo, bagasse and corn stalk, to produce dissolved pulp.*

The pulp production processes of textile waste and agricultural waste-based feedstock may be covered in the next version update of the guidelines.

1.2 Requirements for input chemical management

DP facilities should meet the average input chemical consumption (including chemicals used for cooking and bleaching) required to produce one air-dry tonne (ADT) of dissolved pulp in the pulp production process, as given in Table 1.

Pulp facilities should implement a system to meet the following requirements for input chemical management.

1) Monitor and record chemicals used in dissolved pulp production, including chemicals used for cooking and bleaching.
2) Calculate the consumption of each chemical per air-dry tonne of pulp to meet the maximum allowable consumption given in Table 1 on an annual basis. This should be calculated annually as an average for the calendar year, from 1st January to 31st December.

Table 1: Input Chemical Maximum Allowable Consumption Ranges for Kraft and Sulphite Pulping Process

Input Chemical	Units	Maximum Allowable Consumption	
		Kraft	Sulphite
NaOH	Kg/ ADT	50	135[a]
Na_2SO_4		20	70
CaO		70	25
MgO		NA	45
H_2O_2		30	40
$NaClO_3$		50	25
H_2SO_4		60	60
O_2[b]		35	80
S[c]		NA	65
SO_2[d]		10	40

All chemical consumption values are expressed as 100% effective chemicals and not as commercial solutions containing various amounts of water.
NA= Not applicable

a) *Sulphite mills may utilise MgO or NaOH as a base. Since NaOH is also used in bleaching processes, sulphite mills that use NaOH for bleaching and as a base for the pulping process tend to have higher NaOH consumption ranges. The value indicated in the table indicates total NaOH usage for cooking and/or bleaching regardless of the recovery percentage in pulping operations.*

b) *Facilities that employ total chlorine-free (TCF) bleaching methods, oxygen (O_2) is used for bleaching and often for the generation of Ozone (O_3) for bleaching.*

c), d) *Sulphite mills use either sulphur (S) or sulphur dioxide (SO_2), while in some cases, facilities may employ a combination of both S and SO_2. For sulphite mills, if only S is used, then the consumption is maximum up to 65 kg/ADT. And when a facility uses only SO_2, the amount of SO_2 would be max at 65*2= 130 kg/ADT.*

CHAPTER 2:

Process management

In the following DP manufacturing chemical processes, sustainable chemical management is key.

1) **Pulping:** This process separates cellulose from lignin and hemicellulose.
2) **Oxygen delignification:** This process significantly reduces the amount of bleaching agents needed and lowers environmental impact.
3) **Bleaching:** These processes, mainly using elemental chlorine-free (ECF) and totally chlorine-free (TCF) methods, enhance pulp brightness while reducing toxic effluents. (Note: Use of chlorine is not allowed under these guidelines)
4) **Chemical recovery systems:** These play a crucial role in recycling and reusing cooking chemicals, thereby decreasing the demand for fresh inputs and mitigating pollution.

Note: *The details of the above processes are provided in Appendix A (Description of processes)*

Requirements for chemical recovery

Pulp facilities should implement chemical recovery processes and initiate the following actions under process management.

- Maintain a detailed record of chemical recovery activities and calculations based on the type of pulping process.
- Meet the chemical recovery requirement, as applicable from Tables 2, 3 and 4.
- Report chemical recovery data as a yearly average of the calendar year (from 1st January to 31st December) on a ZDHC platform to evaluate against the limit values specified below:

Table 2: Sulphur and Sodium Recovery Rates for the Kraft Process

Sulphur Recovery	≥ 60%
Sodium Recovery	≥ 90%

Table 3: Sulphur and Magnesium Recovery Rates for Magnesium Oxide (MgO) Based Sulphite Process

Sulphur Recovery	≥ 60%
Magnesium Recovery	≥ 50%

Table 4: Sulphur and Sodium Recovery Rates for Sodium Hydroxide (NaOH) Based Sulphite Process

Sulphur Recovery	≥ 60%
Sodium Recovery	≥ 60%

2.1 Chemical recovery calculations - Kraft process

In the Kraft process, sodium hydroxide (NaOH) and sodium sulphide (Na_2S) recovery as white liquor and lime recovery (CaO) are important which reduces waste and improves the process efficiency. The detailed recovery process is mentioned in Appendix A. Refer to chemical recovery calculations for the Kraft process as below.

A. Sulphur (S) recovery in the Kraft process

In the Kraft process, sulphur recovery is essential for regenerating sodium sulphide (Na_2S) from black liquor. During the combustion of black liquor in a recovery boiler, sulphur compounds are converted into a smelt containing sodium sulphide, which is reused in the pulping process.[12] The recovery calculation for sulphur is mentioned below.

Overall (S) recovery (%) = 100 - (% S loss)

$$\% \text{ S loss} = \left(\frac{\text{Total S makeup to process (Kg S equivalent/ADT pulp)}}{\text{Total S in chemical cycle (Kg S equivalent/ADT pulp)}} \right) \times 100$$

B. Sodium (Na) recovery in the Kraft process

In the Kraft process, sodium recovery is a critical step where spent pulping chemicals, primarily sodium hydroxide (NaOH) and sodium sulphide (Na_2S), are regenerated from black liquor. The recovery involves processes such as evaporation, combustion and causticising. The recovery calculation is mentioned below.

Overall chemical (Na) recovery (%) = 100 - (% Na loss)

$$\% \text{ Na loss} = \left(\frac{\text{Total Na makeup to process (Kg Na equivalent/ADT pulp)}}{\text{Total Na in chemical cycle (Kg Na equivalent/ADT pulp)}} \right) \times 100$$

2.2 Chemical recovery calculations - Sulphite process

In the sulphite cooking process, sulphur dioxide (SO_2) dissolved in water is used along with magnesium oxide or sodium hydroxide. The chemical recovery process in sulphite pulping is essential for enhancing the sustainability of the process and improving resource utilisation by chemical recycling.

2.2.1 Chemical recovery in MgO-based sulphite process

In magnesium-based sulphite pulping, magnesium oxide from flue gases is recovered in a wet scrubber/electrostatic precipitator to give a magnesium hydroxide slurry. This magnesium hydroxide slurry is then used in another scrubber to absorb sulphur dioxide from the flue gases, producing a magnesium bisulphite solution that is clarified, filtered and used as the pulping liquor.[13]

A. Sulphur (S) recovery in the Sulphite process

Sulphur dioxide from the flue gases is recovered by producing a magnesium bisulphite solution. The recovery calculation for sulphur is mentioned below.

Overall (S) recovery (%) = 100 - (% S loss)

$$\% \text{ S loss} = \left(\frac{\text{Total S makeup to process (Kg S equivalent/ADT pulp)}}{\text{Total S in chemical cycle (Kg S equivalent/ADT pulp)}} \right) \times 100$$

B. Magnesium (Mg) recovery in the MgO-based Sulphite process

Magnesium oxide is recovered from flue gases in a wet scrubber/electrostatic precipitator to give magnesium hydroxide slurry. The magnesium recovery calculation for the magnesium oxide-based sulphite pulping process is below.

Overall chemical (Mg) recovery (%) = 100 - (% Mg loss)

$$\% \text{ Mg loss} = \left(\frac{\text{Total Mg makeup to process (Kg Mg equivalent/ADT pulp)}}{\text{Total Mg in chemical cycle (Kg Mg equivalent/ADT pulp)}} \right) \times 100$$

2.2.2. Chemical recovery in NaOH-based sulphite process

In the sodium-based Sulphite process, sodium base liquor is burned and the inorganic compounds are recovered as molten smelt containing sodium sulphide and sodium carbonate. This smelt may be further processed and used to adsorb SO_2 from the flue gas or sold to a Kraft mill as raw material for producing green liquor. It is not suitable for reuse in sulphite cooking.[13]

A. Sulphur (S) recovery in the Sulphite process
Recovery calculation is the same as mentioned under the MgO-based Sulphite process
B. Sodium (Na) recovery in the NaOH-based Sulphite process
Recovery calculation is the same as mentioned under the Kraft process

CHAPTER 3:

Output management

Output management focuses on ensuring that the environmental impacts of the pulp manufacturing process are monitored and continuously improved. These guidelines cover:

- Wastewater discharge
- Air emissions

(Note: Sludge testing is not applicable for dissolved pulp facilities)

3.1 Wastewater discharge

This section uses the ZDHC Wastewater Guidelines V2.2 as references, but the criteria for testing of conventional parameters, heavy metal and AP/APEO for pulp facilities are mentioned separately below.

3.1.1 Requirements for wastewater

a) Compliance with local regulations:

- Facilities are expected to meet local regulations for wastewater parameters mandated by local legal authorities to ensure that their wastewater discharged to the receiving environment does not compromise the quality of the receiving environment.

Note: *It is not the intent of ZDHC to act as an agency reporting wastewater and sludge discharge data to governments or authorities having jurisdiction. It is expected that suppliers are accountable for reporting their wastewater and sludge discharges, in accordance with applicable laws.*

b) Wastewater testing and reporting

- To test wastewater through ZDHC Approved Wastewater Testing Laboratories twice a year (April and October cycles) for the parameters mentioned in Tables 5-7. And upload the report to the ZDHC platform.
- For any non-conformities detected, facilities undertake a Root Cause Analysis and a Corrective Action Plan. (link to template)
- Calculate load-based wastewater parameters mentioned in Table 8 and report to the ZDHC platform along with the reference data used for calculation. The reported value should be the yearly average.

Note: *Wastewater testing and conformance requirements for dissolved pulp manufacturing facilities do not depend on the volume of wastewater generated as outlined in the ZDHC Wastewater Guidelines V2.2. Even if generated wastewater is less than 15m³ per day, all parameters mentioned under Table 5-7 are applicable to them.*

c) Sludge management

- Meet the local regulations for sludge testing (if any) and disposal.
- Report the major sludge disposal pathway used by them as per the pathways detailed in **ZDHC Sludge Reference Document V1.0.**

3.1.2 Wastewater testing and reporting

The dissolved pulp facility should test wastewater for conventional, heavy metals and ZDHC MRSL parameters (AP/APEOs only) as mentioned under 3.1.2.1 to 3.1.2.3 so that any non-conformities detected can motivate the manufacturer to undertake a Root Cause Analysis and a Corrective Action Plan.

3.1.2.1 ZDHC conventional parameters and anions for wastewater

Conventional parameters have traditionally been used by global legislation to describe and regulate wastewater quality. These parameters, their limit values and standard test methods for analysis are defined in Table 5.

Table 5: ZDHC Conventional Parameters and Anions for Wastewater and Limits

Parameters	Unit	Maximum Allowable Limit	Test Methods			
			International/ Europe	United States	China	India
pH	pH	6 - 9	ISO 10523	USEPA 150.1 SM 4500-H+	HJ1147	IS 3025 (Part 11) Electrometric method only
Temperature-difference[a]	°C	Δ+15	DIN 38 404-4 or equivalent	USEPA 170.1 SM 2550	GB/T 13195	IS 3025 (Part 9)
Take the temperature of the discharged wastewater and the receiving body of water upstream. The temperature of the receiving body is subtracted from the temperature of the discharged wastewater to give the delta temperature difference, which can be a positive or a negative value. The discharge limits only refer to a positive value, which produces an overall increase in the temperature of the receiving body of water. This parameter is measured on-site by the sampler and is applicable only for direct discharge. There may be situations where the sampler is not able to measure the temperature of the receiving body. These situations can be as follows: • The receiving body may be several kilometres away from the point of discharge and the facility is discharging the effluent into the receiving body through a pipeline. • Accessing the location of the receiving body to measure its temperature can be risky in terms of injury to the sampler or damage to equipment. • The effluent is discharged directly into the ground. In all such cases where access to the receiving body is not possible or unsafe, the laboratory should report this parameter as "not applicable".						
Colour: (436nm; 525nm; 620nm)	m-1	7; 5; 3	ISO 7887-B			
Ammonium-nitrogen	mg/L	10	ISO 11732 ISO 7150	USEPA 350.1 USEPA 350.3 SM 4500 NH3 - D, E, F, G, or H	HJ 535	IS 3025 (Part 34) phenate or ammonia selective electrode only
AOX	mg/L	Sample and report only	ISO 9562	US EPA 1650	HJ/T 83-2001	
Biochemical oxygen demand 5-days concentration (BOD_5)	mg/L	50	ISO 5815-1	USEPA 405.1 SM 5210-B	HJ 505	IS 3025 (Part 44) seeded dilution water (BOD5)

Table 5: ZDHC Conventional Parameters and Anions for Wastewater and Limits

Parameters	Unit	Maximum Allowable Limit	Test Methods			
			International/ Europe	United States	China	India
Chemical oxygen demand (COD)	mg/L	350	ISO 6060 ISO 15705	USEPA 410.4 SM 5220-D	HJ 828 GB/T 11914 e	IS 3025 (Part 58) e
Oil and grease	mg/L	10	ISO 9377-2	SM 5520-B/C USEPA 1664 revision B	HJ 637 (total oil and grease)	IS 3025 (Part 39) partition gravimetric or partition Infra-red
Total phenols/ phenol index	mg/L	0.5	ISO 6439	SM 5530-B/C	HJ 503 must meet required reporting limit	IS 3025 (Part 43)
Total chlorine	mg/L	Sample and report only	ISO 7393-2	EPA 330.5 SM4500-Cl-G	HJ 586	
Total dissolved solids (TDS)	mg/L	Sample and report only		SM 2540-C USEPA 160.1	GB/T 5750.4-2006 180oC (180 degree centigrade)	IS 3025 (Part 16) 179°C to 181°C
Total nitrogen	mg/L	30	ISO 11905 - Part 1 ISO 29441	USEPA 351.2 SM 4500P-J SM 4500N-B M 4500N-C	HJ 636	IS 3025 (Part 34) measure and total all forms of nitrogen (ammonia, nitrate, nitrite, organic)
Total phosphorus	mg/L	3	ISO 17294 ISO 11885 ISO 6878	USEPA 365.4 SM 4500P-J USEPA 200.7 USEPA 200.8 USEPA 6010C USEPA 6020A	GB/T 11893	IS 3025 (Part 31) IS 3025 (Part 65)
Total Suspended Solids (TSS)	mg/L	70	ISO 11923	USEPA 160.2 SM 2540D	GB/T 11901	IS 3025 (Part 17) 103°C to 105°C

Table 5: ZDHC Conventional Parameters and Anions for Wastewater and Limits

Parameters	Unit	Maximum Allowable Limit	Test Methods			
			International/ Europe	United States	China	India
Chloride	mg/L	Sample and report only	ISO 10304-1 ISO 15923-1	SM 4110-B SM 4110-C SM 4500-Cl D or E USEPA 300	HJ 84-2016	IS 3025 (Part 32) potentiometric or automated ferricyanide only
Sulphate	mg/L	Sample and report only	ISO 10304-1 ISO 15923-1	SM 4500 SO4, E, F, G SM 4100 B, C USEPA 300 USEPA 9038	HJ 84-2016	IS 3025 (Part 24)

3.1.2.2 ZDHC heavy metals wastewater parameters

Heavy metals are often included in legally mandated standards and are, therefore, listed separately in this section. Table 6 defines these parameters, their limit values and recommended standard test methods for analysis.

Table 6: ZDHC Heavy Metals Wastewater Parameters and Limits

Parameter	Unit	Maximum Allowable Limit	Test Methods			
			International/ Europe	United States	China	India
Arsenic (As)	mg/L	0.05	ISO 17294	USEPA 200.8 USEPA 6010C USEPA 6020A	HJ 700	IS 3025 (Part 65)
Chromium (VI)	mg/L	0.05	ISO 18412	USEPA 218.6	GB 7467	IS 3025 (Part 52) must meet reporting limit
Chromium, total	mg/L	0.20	ISO 17294	USEPA 200.8 USEPA 6010C USEPA 6020A	HJ 700	IS 3025 (Part 65)

Table 6: ZDHC Heavy Metals Wastewater Parameters and Limits

Parameter	Unit	Maximum Allowable Limit	Test Methods			
			International/ Europe	United States	China	India
Cadmium	mg/L	0.10	ISO 17294	USEPA 200.8 USEPA 6010C USEPA 6020A	GB 7475 HJ 700	IS 3025 (Part 65) IS 3025 (Part 41) AAS & ICP Instrumental method
Copper	mg/L	1.00	ISO 17294	USEPA 200.8 USEPA 6010C USEPA 6020A	GB 7475 HJ 700	IS 3025 (Part 65) IS 3025 (Part 42) AAS Instrumental method
Lead	mg/L	0.10	ISO 17294	USEPA 200.8 USEPA 6010C USEPA 6020A	GB 7475 HJ 700	IS 3025 (Part 65) IS 3025 (Part 47) AAS Instrumental method
Nickel	mg/L	0.50	ISO 17294	USEPA 200.8 USEPA 6010C USEPA 6020A	GB 11912 HJ 700	IS 3025 (Part 65) IS 3025 (Part 54) AAS Instrumental method
Zinc	mg/L	5.00	ISO 17294	USEPA 200.8 USEPA 6010C USEPA 6020A	GB 7472 GB 7475 HJ 700	IS 3025 (Part 65) IS 3025 (Part 49) AAS Instrumental method
Mercury	mg/L	0.01	ISO 17294 ISO 11885	EPA 200.8-SIM EPA 6020A-SIM EPA 245.1 EPA 245.7	HJ 597 HJ 694	IS 3025 (Part 48) Cold vapour AAS only IS 3025 (Part 65) [SIM]

3.1.2.3 ZDHC MRSL parameters

The purpose of testing ZDHC MRSL parameters is to check for intentional use of ZDHC MRSL substances and/or high levels of respective contamination in the chemical inputs. Therefore, sampling of ZDHC MRSL wastewater parameters should be done only in untreated wastewater. Only AP/APEOs parameters are applicable for dissolved pulp facilities. Their limit values and recommended standard test methods for analysis of AP and APEO are defined in Table 7.

Table 7: ZDHC MRSL Wastewater Parameters and Limits

Substance	CAS Number	Reporting Limit (ug/L)	Standard Method for Analysis/Testing
Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): including all isomers			
Nonylphenol ethoxylates (NPEO)	Multiple Including 9016-45-9 26027-38-3 37205-87-1 68412-54-4 127087-87-0	5	NP/OP: ISO 18857-2 (modified dichloro-methane extraction) or ASTM D7065 (GC-MS or LC-MS(-MS) OPEO/NPEO (n>2): ASTM D7742, ISO 18857-2
Nonylphenol (NP), mixed isomers	Multiple Including 104-40-5 11066-49-2 25154-52-3 84852-15-3	5	NP/OP: ISO 18857-2 (modified dichloro-methane extraction) or ASTM D7065 (GC-MS or LC-MS(-MS) OPEO/NPEO (n>2): ASTM D7742, ISO 18857-2
Octylphenol ethoxylates (OPEO)	Multiple Including 9002-93-1 9036-19-5 68987-90-6	5	NP/OP: ISO 18857-2 (modified dichloro-methane extraction) or ASTM D7065 (GC-MS or LC-MS(-MS) OPEO/NPEO (n>2): ASTM D7742, ISO 18857-2
Octylphenol (OP), mixed isomers	Multiple Including 140-66-9 1806-26-4 27193-28-8	5	NP/OP: ISO 18857-2 (modified dichloro-methane extraction) or ASTM D7065 (GC-MS or LC-MS(-MS) OPEO/NPEO (n>2): ASTM D7742, ISO 18857-2

3.1.3 Load-based wastewater parameters

To assess the environmental impact and water usage efficiency in dissolved pulp production, facilities should calculate and report the wastewater parameters mentioned under Table 8 as load per air-dry tonne of pulp (g/ADT) instead of solely concentration-based values (mg/L). This approach involves quantifying the total volume of wastewater discharged from the pulp production facility and calculating the load per tonne by correlating the pollutant concentration with the wastewater flow rate.

These parameters should be calculated based on the average water flow sampled over a month from the pulp production process under consideration. The reported value should be the yearly average.

Table 8: Wastewater Parameters - Load per Air-Dry Tonne of Pulp

Parameter	Yearly Average (g/ADT)
Chemical oxygen demand (COD)	Report only
Total suspended solids (TSS)	Report only
Total nitrogen	Report only
Total phosphorus	Report only
Adsorbable organically bound halogens (AOX)	Report only

3.1.4 Wastewater discharge types and sample locations

There are five discharge types under wastewater; these are listed below.

- Direct discharge
- Indirect discharge with pretreatment (with sludge)
- Indirect discharge with pretreatment (without sludge)
- Indirect discharge without pretreatment
- Zero liquid discharge (ZLD)

Additionally, there are two possible sampling locations. These are listed below.

- **Untreated Wastewater ('Raw wastewater')** – Wastewater that is collected prior to any treatment.
- **Discharged wastewater** – Treated wastewater that is discharged to the environment or partially treated or untreated wastewater that is discharged to a Central Effluent Treatment Plant (CETP) for further treatment. (This is not applicable to indirect discharge without pretreatment as well as to zero liquid discharge facilities)

Wastewater sampling locations for dissolved pulp facilities are summarised in Table 9.

Table 9: Wastewater Sampling Locations as per the Discharge Type for Dissolved Pulp Facilities

Wastewater Discharge Type	Wastewater Sampling Location and Test Parameters		
	1. Raw Wastewater (Untreated)	2. Treated Wastewater (Effluent)	
		Conventional Parameter	Heavy Metals
Direct discharge	AP/APEOs	Conventional parameters and anions	As, Total Cr, Cd, Cu, Ni, Cr^{+6}, Pb, Hg, Zn
Indirect discharge with pretreatment (with sludge)	AP/APEOs	NA	As, Cd, Cr^{+6}, Pb, Hg
Indirect discharge with pretreatment (without sludge)	AP/APEOs	NA	As, Cd, Cr^{+6}, Pb, Hg
Indirect discharge without pretreatment	AP/APEOs,As, Cd, Cr^{+6}, Pb, Hg	NA	NA
Zero Liquid Discharge (ZLD)	AP/APEOs	NA	NA

Note: *Pretreatment can be defined as any sort of treatment (flow equalisation, pH adjustment, screening, grit removal, primary treatment such as, but not limited to, coagulation and flocculation and secondary treatment such as, but not limited to anaerobic and aerobic treatment) done before discharging to a Central Effluent Treatment Facility (CETP) to align with local legal and/or CETP regulations and limit values. Pretreatment processes may or may not generate sludge. Without pretreatment effluent goes directly to the CETP without any influence by the facility.*

3.1.5 Sludge management

Facilities must comply with the existing local legal regulations for the treatment and handling of industrial wastewater sludge and should report their major sludge disposal pathway from the below options.

Disposal pathways

The ZDHC Sludge Reference Document details seven disposal pathways for sludge:

- Disposal Pathway A - On-site or Off-site incineration at >1000'C
- Disposal Pathway B - Landfill with significant control measures
- Disposal Pathway C - Building products processed at >1000'C
- Disposal Pathway D - Landfill with limited control measures
- Disposal Pathway E - Off-site incineration and building products processed at <1000'C
- Disposal Pathway F - Landfills with no control measures
- Disposal Pathway G - Land application for a specific purpose in approved areas.

3.2 Air emissions

The complex chemical processes involved in converting raw wood into dissolved pulp contribute to air emissions. These emissions include a variety of pollutants, such as sulphur compounds, nitrogen oxides (NOx), total reduced sulphur (TRS) and particulate matter.

This document specifies the emissions to be monitored from the pulp facility. It covers

- Load-based air emissions
- Ambient air emissions

3.2.1 Requirements for air emissions

a) Compliance with local regulations:

- Have a valid licence to operate.
- Quantify, track and report emissions of all parameters, consistent with applicable local regulations.

Note: *It is not the intent of ZDHC to act as an agency reporting air emissions to governments or authorities having jurisdiction. It is expected that suppliers are accountable for reporting their air emissions, in accordance with applicable laws.*

b) Air emission testing and reporting

For load-based air emissions:

1) Monitor and measure the following parameters:
   - Total suspended particles/dust
   - SO_2 as S
   - NOx as NO_2
   - TRS as S
2) Calculate and report load-based air emissions of these parameters in kilograms per air-dry tonne (kg/ADT) of pulp produced.

Note: *Emissions from recovery boilers and lime kilns of the DP facility are to be monitored.*

For ambient air emissions:

Monitor, measure and report the following ambient air emission parameters outside the facility:

- SO_2
- NO_2
- $PM_{2.5}$
- PM_{10}

DP facilities should report both load-based and ambient air emissions data as a yearly average of the calendar year (from 1st January to 31st December) on a ZDHC platform to evaluate against the limit values specified below.

3.2.2 Limit values for load-based air emissions

Table 10: Air Emission Parameters and Limits for the Kraft Process

Parameter	Type of Mill	Units (Yearly Average)	Max. Allowable Limit
Total suspended particles/ Dust	Kraft	kg/ADT	0.5
SO_2 as S	Kraft	kg/ADT	0.4
NOx as NO_2	Kraft	kg/ADT	1.5 for hardwood pulp 2.0 for softwood pulp
TRS as S	Kraft	kg/ADT	0.2

Table 11: Air Emission Parameters and Limits for the Sulphite Process

Parameter	Type of Mill	Units(Yearly Average)	Max. Allowable Limit
Total suspended particles/ Dust	Sulphite	kg/ADT	0.15
SO_2 as S	Sulphite	kg/ADT	1.00
NOx as NO_2	Sulphite	kg/ADT	2.00
TRS as S	Sulphite	kg/ADT	NA

Reference: Environmental, Health, and Safety Guidelines PULP AND PAPER MILLS, World Bank Group, Dec 2007

Note: *Yearly average: The average of all daily averages taken within a calendar year, weighted according to daily production and expressed as mass of emitted substances per unit of mass of products/materials generated or processed.*

ADT= Air-dry tonne (of pulp) expressed as 90% dryness

The daily average of air emissions should be used to calculate the yearly average. The emissions to air refer to the following standard conditions: dry gas, temperature of 273.15 K, pressure of 101.3 kPa, and 6% O_2.

3.2.3 Limit values for ambient air emission

Table 12: Ambient Air Emission Parameters and Limits in the Surrounding Environment (Outside the Facility)

Parameter	Type of Mill	Units (Yearly Average)	Max. Allowable Limit
SO_2	Sulphite/ Kraft	ug/m^3	50
NO_2	Sulphite / Kraft	ug/m^3	40
$PM_{2.5}$	Sulphite / Kraft	ug/m^3	20
PM_{10}	Sulphite / Kraft	ug/m^3	30

Note: *Ambient air limit values refer to the level of air quality with an adequate margin of safety to protect public health.*

The assessment area is proposed to begin at the facility's fence and extend within a circumference around the emission centre, with a radius of one kilometre or less from the source.

Limits are based on WHO-recommended ambient air quality norms (Ref: World Health Organization, Air quality guidelines for Europe. 2nd Edition, 2000)

3.2.4 Air emission monitoring and reporting

A. Load-based air emission monitoring and reporting:

Facilities can employ continuous emission monitoring systems (CEMS) and/or periodic stack testing to measure load-based air emissions.

Monitoring

Dissolved pulp facilities can use the following approaches for data collection and reporting. The ultimate objective is to allow DP manufacturing facilities to share their air emissions results systematically and efficiently:

- **Automated data logging:** Continuous data collection from CEMS and other monitoring systems.

- **Real-time monitoring:** Regular manual sampling and testing by an ISO 17025 accredited laboratory is recommended. Standard test methods shall be chosen for the manufacturing region. In the absence of local or regional test methods, internationally recognised test methods, often recommended by governmental organisations, such as the ISO, EPA or GB, ASTM shall be used. The equipment used should be fully operational and undergo regular calibration to maintain accuracy and reliability. Additionally, it must be operated by skilled personnel to ensure proper handling and optimal performance.
- **Compliance reporting:** Regular reports to regulatory bodies, ensuring adherence to permissible emission limits.

Note: *Samples shall not be taken when the production process is not running or the air emissions are not representative of normal operations.*

<u>Reporting</u>

- Real-time monitored data on air pollutant concentration should be used and correlated with the production output to calculate the emission load per air-dry tonne of pulp.
- Reported values should be the estimated yearly average for the calendar year.
- The testing cycle runs from 1st January to 31st December within the same calendar year.

<u>Calculation for load-based air emissions</u>

- Emission Rate (kg/hr): The measured emission concentration (mg/m^3) is multiplied by the flow rate (m^3/hr).
- Production Rate (ADT/hr): The quantity of products produced over time.
- Load-Based Emission (kg/ADT): The emission rate is divided by the production rate.

$$\text{Load-based emissions} = \frac{\text{Emission rate (Kg/hr)}}{\text{Production rate (ADT/hr)}}$$

B. Ambient air emission monitoring and reporting:

<u>Monitoring</u>

One of the following monitoring methods can be employed to measure ambient air emissions in the surrounding area of the production facility.

- **Fixed or mobile air quality monitoring stations:** Fixed or mobile air quality monitoring stations placed around the facility and in surrounding areas can be used to assess the impact of emissions from the pulp mill on the local environment.
- **Real-time monitoring:** Regular manual sampling and testing by an ISO 17025 accredited laboratory is recommended. Standard test methods shall be chosen for the manufacturing region. In the absence of local or regional test methods, internationally recognised test methods, often recommended by governmental organisations, such as the ISO, EPA or GB, ASTM shall be used. The equipment used should be fully operational and undergo regular calibration to maintain accuracy and reliability. Additionally, it must be operated by skilled personnel to ensure proper handling and optimal performance.
- **Air dispersion modelling:** This can be used to assess ambient air emissions. Based on emission data, meteorological conditions and topographical features, it uses mathematical simulations to predict how pollutants disperse in the atmosphere.
- **Authorised data:** Data collected from the local governing body/regulatory authorities

Note: *Samples shall not be taken when the production process is not running or the air emissions are not representative of normal operations (e.g. dust storms).*

<u>Reporting</u>

- Reported values should be the estimated yearly average for the calendar year.
- The testing cycle for ambient air emissions runs from 1st January to 31st December within the same calendar year.

APPENDIX A
(Description of processes)

In dissolved pulp manufacturing, the key chemical processes include:

1) **Pulping:** This process separates cellulose from lignin and hemicellulose.
2) **Oxygen delignification:** This step significantly reduces the amount of bleaching agents required and minimises environmental impact.
3) **Bleaching:** Utilising elemental chlorine-free (ECF) and total chlorine-free (TCF) methods enhances pulp brightness while reducing toxic effluents. (Note: The use of chlorine is prohibited under these guidelines).
4) **Chemical recovery systems:** These systems are essential for recycling and reusing cooking chemicals, reducing the need for fresh inputs and mitigating pollution.

1. Pulping processes

Wood-based dissolved pulps typically are manufactured via two processes:

d) Kraft process
e) Sulphite process

Both processes involve “cooking” the wood in an aqueous chemical solution (i.e. pulping liquor) at elevated temperatures to chemically separate the cellulose fibres from the wood.

The Kraft and Sulphite processes are both chemical pulping methods, but they differ in the type of chemicals used and the resulting pulp characteristics. The Sulphite process is acidic, while the Kraft process is alkaline. The Sulphite process produces pulp with an alpha-cellulose content of 90–92%, whereas the Kraft process typically produces pulp with an alpha-cellulose content of 94–96%. After cooking, the pulp is washed and

screened to separate residual substances and to purify the pulp for screening, oxygen delignification and bleaching.[2, 4]

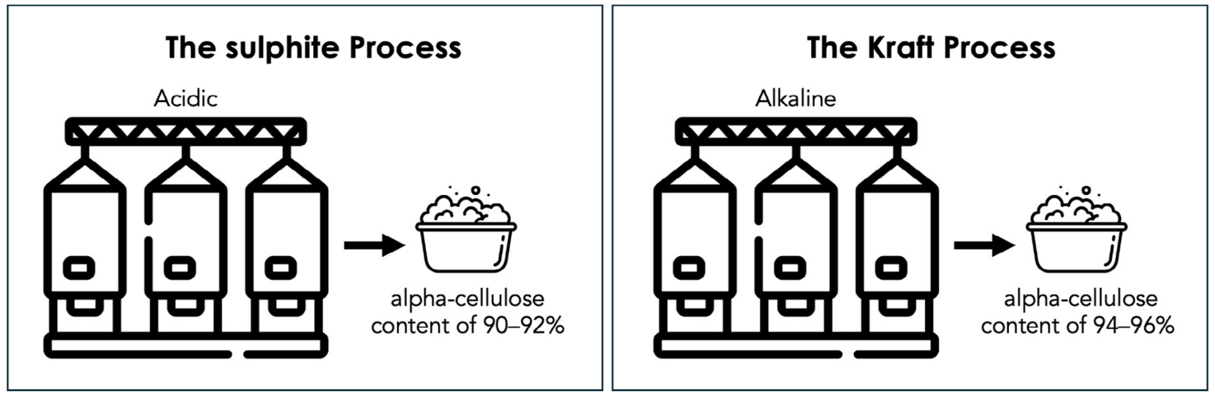


Figure 2: Kraft and Sulphite Pulping Process

1.1 Kraft (sulphate) pulping process

In the Kraft (sulphate) pulping process, wood chips are cooked with an aqueous solution of sodium hydroxide (NaOH) and sodium sulphide (Na_2S) under pressure to separate cellulose fibres from lignin. The resulting pulp is washed to remove spent cooking liquor, known as black liquor.

The black liquor (lignin-rich) produced from Kraft pulp production contains 95-98% of digested chemicals. These chemicals should be recovered before disposal to reduce air emissions and water pollution.

The Kraft process is known for its efficiency in recycling pulping chemicals, co-generating steam and power and producing strong pulp. The chemicals in the black liquor are recovered and reused, creating a closed-loop system that maximises chemical recovery and reduces environmental impact.[5] The chemical recovery cycle is explained in separate sections (Section 2.4).

1.2 Sulphite pulping process

The Sulphite pulping process involves chemical pulping of wood using a solution of sulphur dioxide (SO_2) adsorbed in a base solution. This method breaks down lignin in wood to extract cellulose fibres, producing pulp but with less colour. The process includes digestion under high pressure and temperature, washing, bleaching and chemical recovery.

Sulphite pulping has advantages such as a higher pulp yield and reduced environmental impact compared to other pulping methods.

The Sulphite pulping process employs various cooking bases, like calcium, magnesium, sodium and ammonia; it also offers a wide range of operating pH levels, with conditions ranging from highly acidic to highly alkaline. Some sulphite mills utilise MgO as a base, while others may employ NaOH. Since NaOH is also utilised in bleaching processes, sulphite mills that use NaOH for both bleaching and pulping bases tend to have higher NaOH consumption ratios.[6]

The Sulphite pulping process typically involves the following steps:

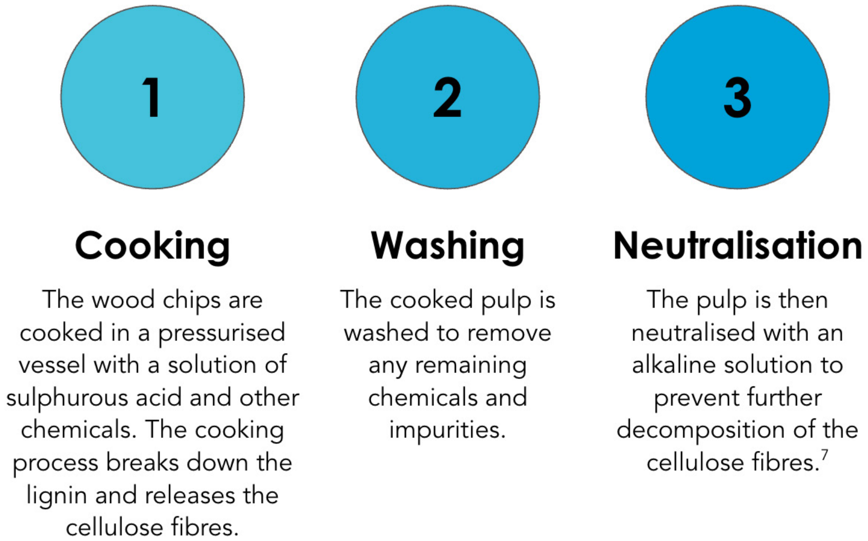
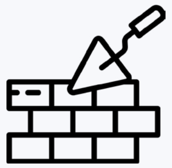
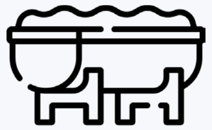
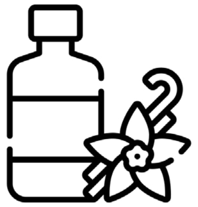
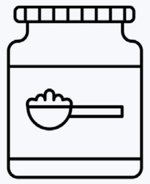


Figure 3: Key Steps in the Sulphite Pulping Process

During cooking, hemicellulose and lignin are released into the cooking liquor. The spent sulphite liquor (SSL) can be sent directly to the chemical and energy recovery units or separated and utilised to produce other products. Pulp mills that convert most of the spent sulphite liquor into various by-products are called 'biorefineries.'

Table 13: By-Products in Biorefineries[8, 14]

	Lignosulph-onates	About 70% of SSLs serve as additives in various industries. They act as binding agents in feed pellets, mineral briquettes and dust abatement agents on roads. Chemically treated lignosulphonates are effective dispersants for water reduction in concrete, brick production, ceramic manufacturing and dye pigment production.
	Ethanol	A part of the hemicellulose generated from softwood can be fermented and distilled into ethanol. In the fermentation process, ethanol and carbon dioxide are produced. The ethanol is distilled to meet the required strength and quality. The carbon dioxide produced can be collected and sent to a carbon dioxide recovery plant.
	Fodder yeast	Hemicellulose is a raw material for producing fodder yeast through a clean fermentation process, which is commonly used in livestock and pet food production.
	Vanillin	Lignosulphonates are also used as a raw material for manufacturing vanillin. The process starts with a catalytic, high-pressure cracking of the lignosulphonate, followed by several purification steps. Vanillin is one of the most common flavours and fragrances used, with many applications.
	Soda	May occur as a by-product when hemicellulose extraction is carried out in a hot alkali extraction stage using NaOH.
	Acetic acid and furfural	Can also be extracted from the SSL.

2. Oxygen delignification before bleaching

After pulping, chemical pulps still have residual lignin content (<5%) and require delignification and bleaching to remove it. The oxygen delignification process aims to delignify the pulp significantly and act as a bridging step between cooking and bleaching. It uses elevated temperatures, oxygen and a base to increase pH in alkaline conditions. Removing a substantial amount of lignin before the bleaching stages significantly reduces the need for chlorine-based or other bleaching chemicals, leading to reduced chlorinated organic compounds (dioxins and furans) generation, thereby reducing the environmental footprint of the pulp production process. Oxygen delignification helps produce a higher quality pulp with better brightness and strength properties, as it selectively targets and removes lignin without excessively damaging the cellulose fibres.[14, 17]

3. Bleaching processes

Pulp bleaching methods can be conventional elemental chlorine-based, elemental chlorine-free (ECF) or total chlorine-free (TCF). However most of the dissolved pulp mills are currently using either ECF or TCF bleaching. In pulp manufacturing, bleaching sequences apply various bleaching agents in different orders and combinations. The bleaching stages are nominated using symbolic shorthand according to the bleaching agent that is applied: oxygen (O), hydrogen peroxide (P) or combinations (OP) and chlorine dioxide (D).[9, 10]

Table 14: ECF and TCF Bleaching Processes

Elemental Chlorine-Free (ECF)[10]	Total Chlorine-Free (TCF)[11]
Chlorine dioxide (ClO_2) and other agents, such as hydrogen peroxide, are used to reduce the use of elemental chlorine gas. Predominant method in the dissolved pulp industry.	It uses hydrogen peroxide (H_2O_2) and/or ozone (O_3) as the primary bleaching agents as an alternative to traditional chlorine-based processes. Generates less toxic waste compared to chlorine-based bleaching. Generally, Ozone bleaching is performed to remove colour and enhance brightness, followed by hydrogen peroxide bleaching to improve brightness and whiteness and chelation further to remove residual metal ions.

4. Chemical recovery

Chemical recovery in dissolved pulp manufacturing is crucial for environmental and economic sustainability. It allows for the efficient reuse of valuable chemicals, significantly reducing the need for fresh inputs and minimising waste generation. Recovery processes reduce harmful emissions and effluents, contributing to a cleaner, more sustainable manufacturing operation.

4.1 Chemical recovery in Kraft (sulphate) pulping process

In the Kraft process, sodium hydroxide (NaOH) and sodium sulphide (Na_2S) recovery as white liquor and lime recovery (CaO) are important which reduces waste and improves the process efficiency.

The generation of sodium sulphide (Na_2S) as a cooking chemical is crucial for the recovery process, although it does not directly participate in the delignification reactions. Sodium sulphide reacts with water (i.e. in the white liquor) and generates sodium hydrosulphide (NaSH). Sodium hydrosulphide (NaSH) and sodium hydroxide (NaOH) are the active chemicals that degrade and dissolve lignin during Kraft pulping.[5]

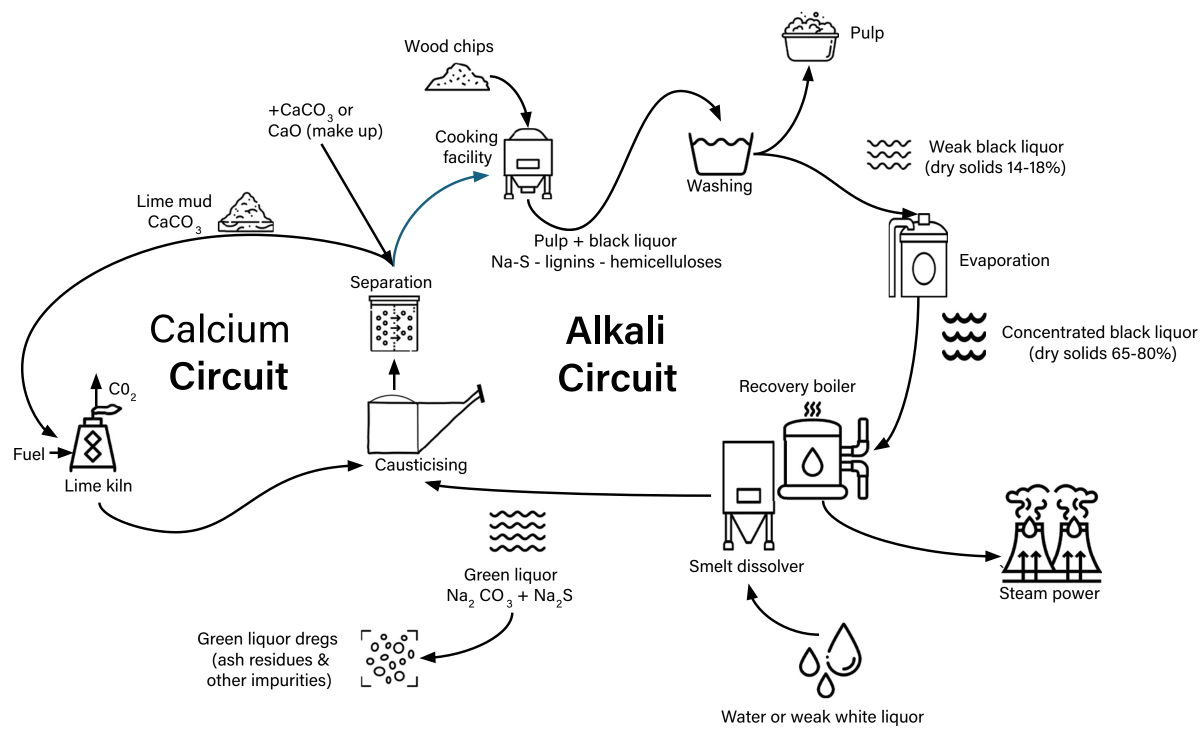


Figure 4: Chemical recovery in Kraft (sulphate) pulping process [5]

Steps in Recovery Process[5]

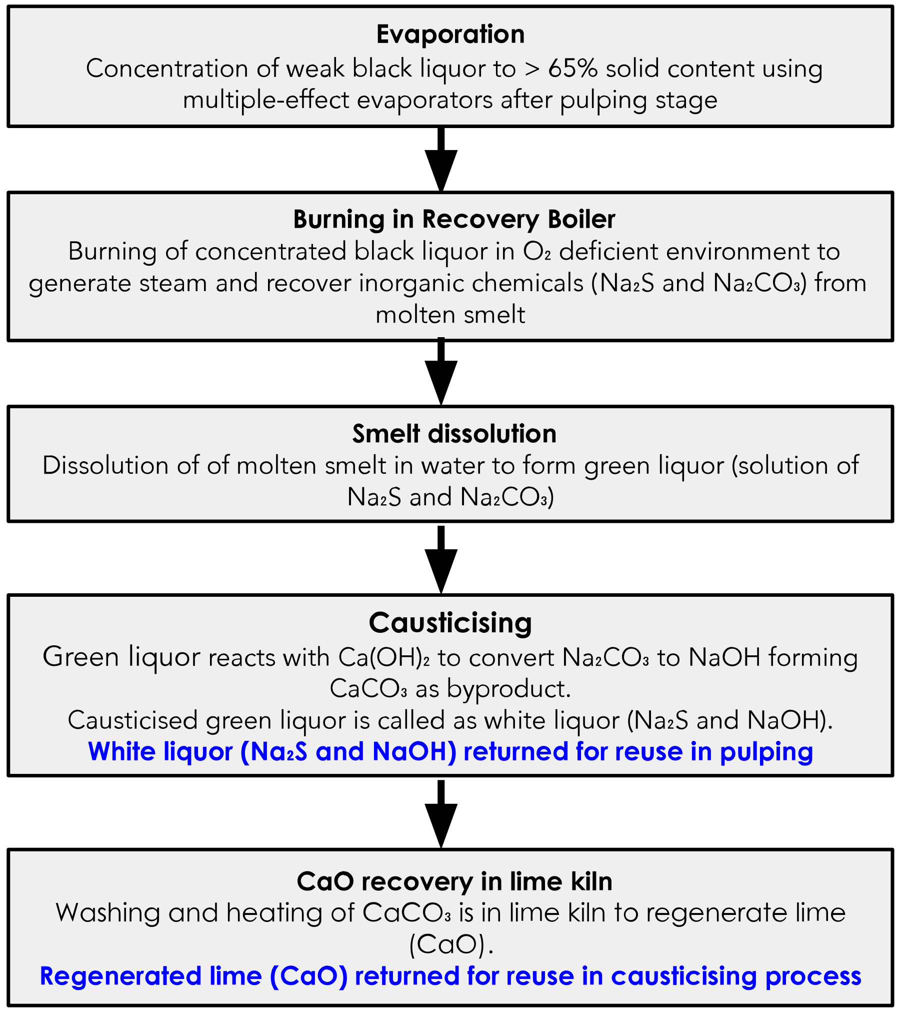


Figure 5: Kraft process – key steps in chemical recovery processes

4.2 Chemical recovery in the sulphite pulping process

In the sulphite cooking process, sulphur dioxide (SO_2) dissolved in water is used with a base like calcium, magnesium, sodium or ammonia. Calcium as a base, which used to be common as it was inexpensive, is now outdated because the cooking chemicals cannot be recovered. Most mills use magnesium or sodium sulphite pulping and both of these chemicals are helpful for chemical recovery. The lignosulphonates produced during cooking can also make different chemical products. Therefore, the current document emphasis is on chemical recovery from magnesium or sodium-based sulphite pulping process.[13]

The chemical recovery process in sulphite pulping (Figure 6) is essential for enhancing the sustainability of the process and improving resource utilisation by chemical recycling.

4.2.1 Chemical recovery in magnesium oxide (MgO) based sulphite process

The recovery process used in magnesium-based sulphite pulping, the "Magnefite" process, is well developed. Magnesium oxide from flue gases is recovered in a wet scrubber/electrostatic precipitator to give magnesium hydroxide slurry. This magnesium hydroxide slurry is then used in another scrubber to absorb sulphur dioxide from the flue gases, producing a magnesium bisulphite solution that is clarified, filtered and used as the pulping liquor.[13]

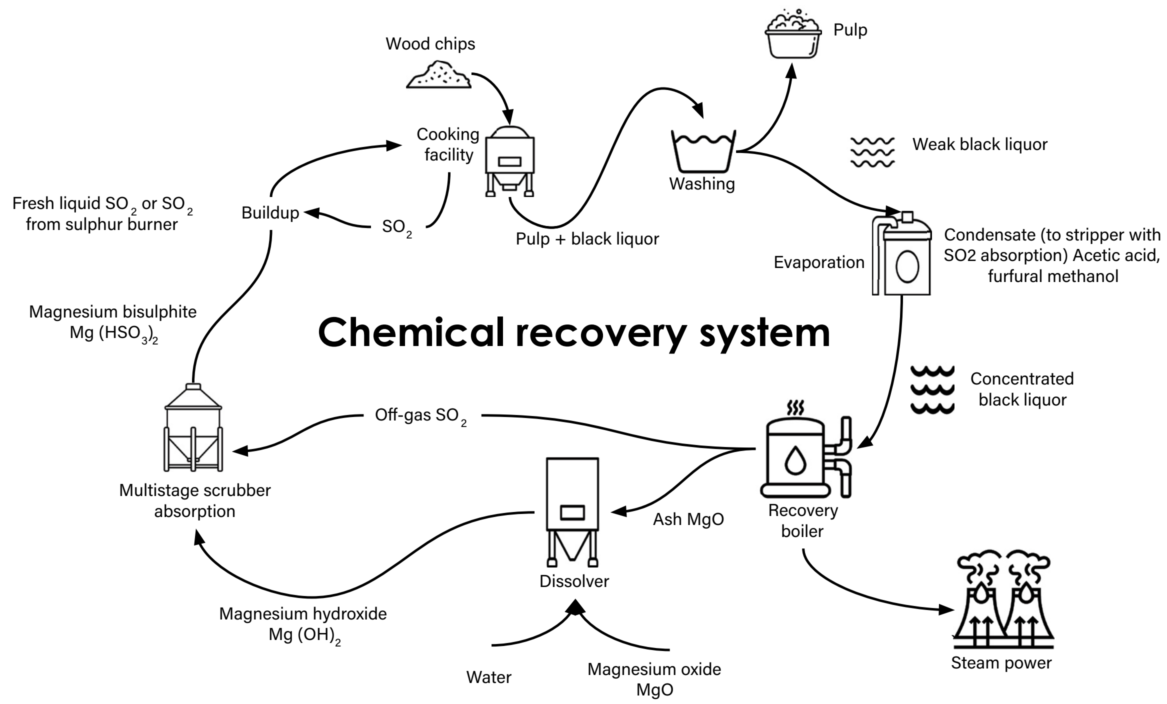


Figure 6: Chemical recovery in magnesium-based sulphite pulping process[14]

Steps in the recovery process

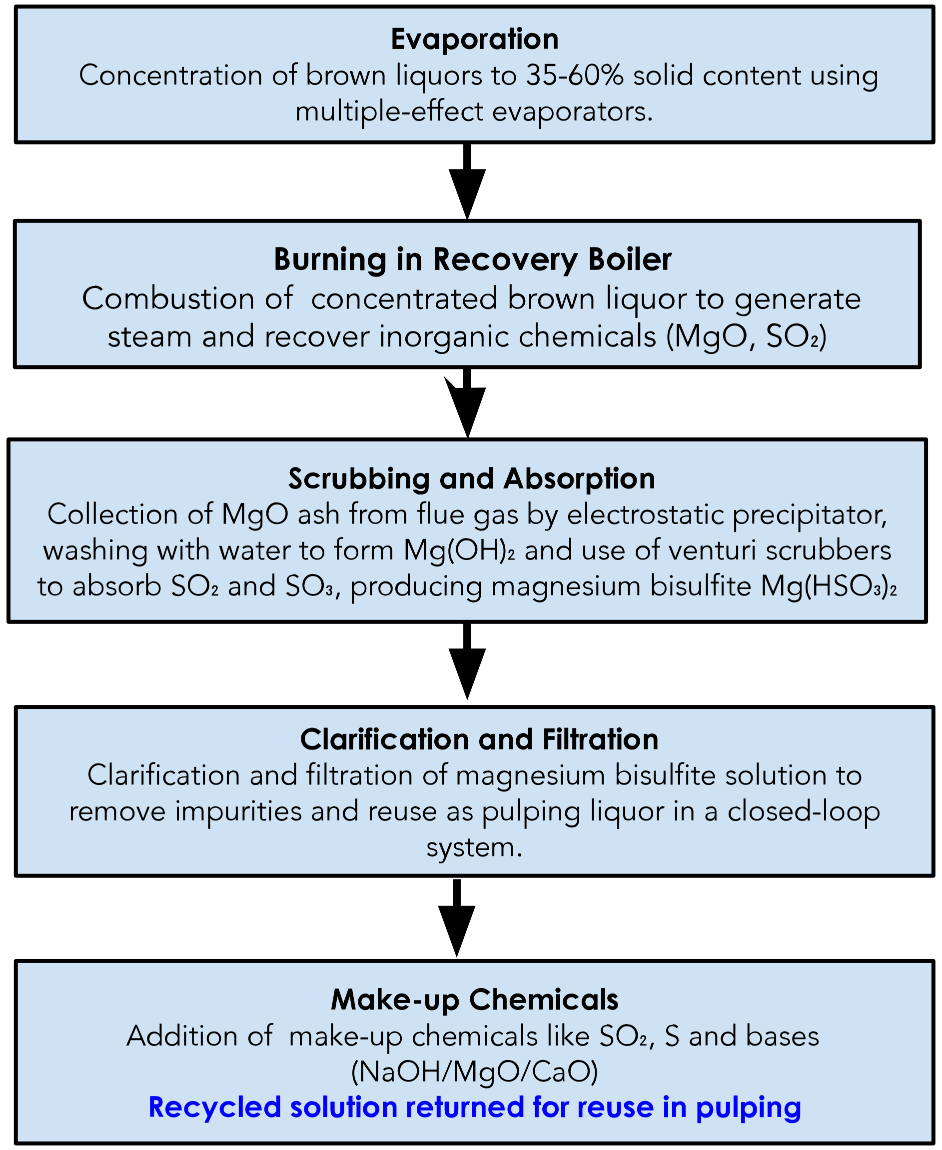


Figure 7: MgO-based sulphite process – Key steps in chemical recovery processes

4.2.2 Chemical recovery in sodium hydroxide (NaOH) based sulphite process

When sodium-based liquor is burned, the inorganic compounds are recovered as molten smelt containing sodium sulphide and sodium carbonate. This smelt may be further processed and used to adsorb SO_2 from the flue gas or sold to a Kraft mill as raw material for producing green liquor. It is not suitable for reuse in sulphite cooking.[13]

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