

# ZDHC Man-made Cellulosic Fibre (MMCF) Guidelines

Version 2.2

August 2023

## NOTES

The ZDHC Foundation's ZDHC Man-Made Cellulosic Fibres (MMCF) Guidelines is not intended to replace brand-specific requirements for chemical management but to be supportive or complimentary to such requirements.

The information in this ZDHC Man-Made Cellulosic Fibres (MMCF) Guidelines is provided for information only and does not guarantee the following:

- a. Compliance with, or take the place of, legal or regulatory requirements. Examples might include: stricter legal, local or regional regulatory requirements on the use, storage and transport of chemical products; or other requirements relating to the handling and disposal of chemical products, which shall supersede any requirements as set forth in this document.
- b. Compliance with, or conformance to, any national or international environmental or workplace safety requirements, including, but not limited to, relevant regulations and/or standards.
- c. Nor do the ZDHC Man-Made Cellulosic Fibres (MMCF) Guidelines replace any national or international environmental or workplace safety requirements including, but not limited to, regulations and/ or standards.

The ZDHC Man-Made Cellulosic Fibres (MMCF) Guidelines is not intended nor can be used as a statement of legal requirements.

ZDHC refers to the UN GHS (Globally Harmonized System of Classification and Labelling of Chemicals) as the internationally recognised standard for hazardous material classification and labelling. All the other National/Regional existing schemes, derived from the implementation of the GHS, have to be considered included in the list of the accepted ZDHC standards for this purpose. To simplify the ZDHC Man-Made Cellulosic Fibres (MMCF) Guidelines comprehension, ZDHC uses GHS throughout as its reference for Hazard Statements and Pictograms in SDS and labels in order to avoid local variables.

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- c. For any results obtained or not obtained from the use of the ZDHC Man-Made Cellulosic Fibres (MMCF) Guidelines.

## **Revision History**

Version	Changes	Time of
Number		Publication
Version 2.2	<ul> <li>Revision to the Progressive limit value for copper and ammonia recovery for cupro fibre</li> <li>Revision to the raw material consumption value for ace-tops for acetate fibre</li> </ul>	August 2023
	<ul> <li>tone for acetate fibre</li> <li>Alignment of wastewater test methods for some parameters to the ZDHC Wastewater Guidelines V2.1</li> <li>APEO wastewater limit value changed from Foundational/ Progressive/Aspirational categories into a single category of 5 ug/litre</li> <li>Removal of 'Sum of Hydrocarbon' parameter</li> <li>Requirements for sludge changed to: MMCF manufacturing facilities should meet local legal regulations. If no such regulation exists, facilities to refer and implement ZDHC requirements for sludge disposal and testing as mentioned under ZDHC Wastewater Guidelines V2.1 and ZDHC Sludge Reference Document V1.0</li> <li>Addition of wastewater discharge types, sample locations and test parameters for MMCF facilities</li> </ul>	
	<ul> <li>Addition of acetone air emission limit values at Foundational/Progressive/Aspirational level for acetate fibre manufacture</li> <li>Revision of ambient air emissions limit value for CS<sub>2</sub>, H<sub>2</sub>S and NH<sub>3</sub> from Foundational/ Progressive/Aspirational to a single limit.</li> <li>Separate tables have been added for air emissions by mass balance calculation and ambient air emissions by direct testing.</li> <li>CS<sub>2</sub> &amp; H<sub>2</sub>S ambient air emission limits are referred from the World Health Organization, Air quality guidelines for Europe. 2nd Edition, 2000 and reference has been added ed</li> </ul>	

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Version 2.1	<ul> <li>Revision in the copper and ammonia recovery (cupro fibre) calculation</li> <li>Correction in test method for Zn, sulphide, CS<sub>2</sub> (specific parameter) due to typographical error</li> </ul>	February 2023
Version 2.0	<ul> <li>Scope expansion to include viscose filament yarn, lyocell, cuprammonium rayon (cupro) and cellulose acetate (acetate)</li> </ul>	January 2023
	<ul> <li>Guidelines and requirements defined for chemical recovery, wastewater and sludge discharge and air emissions discharge for the fibres included in the expanded scope</li> </ul>	
	<ul> <li>Testing of toxicity of wastewater (which was optional in MMCF Wastewater Guidelines V1.0 for viscose and modal staple fibres) is deleted from the requirements in MMCF Wastewater Guidelines V2.0 for viscose staple fibre and modal staple fibres.</li> </ul>	

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# Definitions

Visit the ZDHC Glossary to search for explanations on terminology used across this document and the ZDHC Foundation

# **Abbreviations**

CETP	Centralised effluent treat
CIL	Chemical Inventory List
VSF	Viscose staple fibre
VFY	Viscose filament yarn
cupro	Cuprammonium rayon
EN	European norm
ETP	Effluent treatment plant
EU BAT BREF POL	EU BAT BREF Reference
	in the Production of Poly

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atment plant

### Document on Best Available Techniques lymers (August 2007)

GB	Guojia Biaozhun (Chinese required national standard)
GB/T	Guojia Biaozhun/Tuījiàn, (Chinese recommended national
	standard)
HJ/T	Chinese recommended environmental protection standard
	(Chinese industry standard)
IPE	Institute of Public and Environmental Affairs – Chinese non-
	governmental organisation
ISO	International Organization for Standardisation
LC	Liquid chromatography
MMCF	Man-Made Cellulosic Fibres
N/A	Not available or not applicable
NMMO	N-methyl-morpholine-n-oxide
PTE	Potential to emit
RL	Reporting limit
USEPA	United States Environmental Protection Agency
<b>WHO</b>	World Health Organization
WWTP	Wastewater treatment Plant
ZDHC MRSL	ZDHC Manufacturing Restricted Substances List
ZLD	Zero liquid discharge

# Collaborative process and acknowledgements

The fundamental principle of collaboration at ZDHC was followed in the development of this document. The ZDHC Fibres & Materials Competence Centre and Roadmap to Zero (RtZ) Delivery teams reached out to the former MMCF Task Team, formed in 2018 consisting of Signatory Brands, Collaborators and industry affiliates. ZDHC co-ordinated with this task team from April 2023 through a series of calls, e-mails and 1:1 calls to gather and collate inputs on the updates. A draft guidelines document was then prepared by the Fibres & Materials Competence Centre and reviewed by the task team members. The suggestions and comments received from them were incorporated into the draft, which was then sent for their final review.

ZDHC MMCF Guidelines Version 2.2 | August 2023 We acknowledge and thank the contribution of the task team members for their assistance in the development of this document. For a full list of acknowledgements, please see the end of this document.

# Summary of Requirements in MMCF Guidelines V2.2

Guidelines	Requirements	Monitoring Mechanism
N	IMCF Responsible Fibre Production Guidelines	/2.2
Viscose staple fibre	<ol> <li>% sulphur recovered and fed back into process</li> <li>Sodium sulphate recovery (%)</li> <li>Wastewater environmental impact of some parameters as load-based values (g/tonne of fibre)</li> <li>Share raw material consumption data</li> </ol>	
Lyocell	<ol> <li>NMMO recovery (%)</li> <li>Wastewater environmental impact of some parameters as load-based values (g/tonne of fibre)</li> <li>Share raw material consumption data</li> </ol>	<ol> <li>Self-evaluation</li> <li>monitoring</li> <li>ZDHC Supplier</li> <li>Platform – MMCF</li> <li>Module (proposed)</li> </ol>
Viscose filament yarn	<ol> <li>Sodium sulphate recovery (%)</li> <li>Wastewater environmental impact of some parameters as load-based values (g/tonne of fibre)</li> <li>Share raw material consumption data</li> </ol>	
Cupro	<ol> <li>Copper, ammonia recovery (%)</li> <li>Share raw material consumption data</li> </ol>	

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Guidelines	Requirements	Monitoring Mechanism
MMCF	Responsible Fibre Production Guidelines V2.2 (	continued)
Acetate	<ol> <li>Acetone recovery (%)</li> <li>Wastewater environmental impact of some parameters as load based values (g/tonne of fibre)</li> <li>Share raw material consumption data</li> </ol>	<ol> <li>Self-evaluation &amp; monitoring</li> <li>ZDHC Supplier</li> <li>Platform – MMCF</li> <li>Module (proposed)</li> </ol>
	MMCF Wastewater Guidelines V2.2	
Viscose staple fibre Lyocell	<ol> <li>Conventional parameters: pH, temperature, colour, COD, BOD, oil and grease, Total-N, AmmoN, TSS, Total-P, AOX, phenol</li> <li>Additional: total Cr, Cd, Cu, Ni, Cr<sup>+6</sup>, Pb, Hg, APEOs</li> <li>Specific: Zn, sulphide, CS<sub>2</sub></li> <li>Conventional parameters: pH, temperature, colour, COD, BOD, oil and grease, Total-N,</li> </ol>	1. Two cycles of testing (April and October) through ZDHC Approved Solution Providers (wastewater
	AmmoN, TSS, Total-P, AOX, phenol 2. Additional: total Cr, Cd, Cu, Ni, Cr <sup>+6</sup> , Pb, Hg and APEOs	laboratories), with test reports upload- ed on the ZDHC Gateway
Viscose filament yarn	<ol> <li>Conventional parameters: pH, temperature, colour, COD, BOD, oil and grease, Total-N, AmmoN, TSS, Total-P, AOX, phenol</li> <li>Additional: total Cr, Cd, Cu, Ni, Cr<sup>+6</sup>, Pb, Hg, APEOs</li> <li>Specific: Zn, sulphide, CS<sub>2</sub></li> </ol>	2. ZDHC Supplier Platform – MMCF Module (proposed)

Guidelines	Requirements	Monitoring Mechanism
	MMCF Wastewater Guidelines V2.2 (continue	d)
Cupro	<ol> <li>Conventional parameters: pH, temperature, colour, COD, BOD, oil and grease, Total-N, AmmoN, TSS, Total-P, AOX, phenol</li> <li>Additional: total Cr, Cd, Cu, Ni, Cr<sup>+6</sup>, Pb, Hg, APEOs</li> </ol>	1. Two cycles of testing (April and October) through ZDHC Approved Solution Providers (wastewater laboratories), with
Acetate	<ol> <li>Conventional parameters: pH, temperature, colour, COD, BOD, oil and grease, Total-N, AmmoN, TSS, Total-P, AOX, phenol</li> <li>Additional: Total Cr, Cu, Ni, Cr<sup>+6</sup>, Pb, Hg, APEOs</li> <li>Specific: Zn</li> </ol>	<ul> <li>laboratories), with</li> <li>test reports upload</li> <li>ed on the ZDHC</li> <li>Gateway</li> <li>2. ZDHC Supplier</li> <li>Platform – MMCF</li> <li>Module (proposed)</li> </ul>
	MMCF Air Emissions Guidelines V2.2	
Viscose staple fibre	<ol> <li>Sulphur air emissions through mass balance calculation</li> <li>Ambient air emission parameters CS<sub>2</sub> and H<sub>2</sub>S to be tested through appropriate ISO 17025 certified lab or using air dispersion modelling</li> </ol>	1.Self-evaluation and monitoring
Lyocell	Not applicable. (Because NMMO is easily dissolved in water and is not volatile, air emissions in the lyocell process is minimal. The waste air out of the spinning process contains a small amount of NMMO which can be recovered by scrubbers at the vent.)	2.ZDHC Supplier Platform – MMCF Module (proposed)

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Guidelines	Requirements	Monitoring Mechanism	
	MMCF Air Emissions Guidelines V2.2 (continued)		
Viscose filament	1. Ambient air emission parameters CS <sub>2</sub> and		
yarn	$\rm H_2S$ to be tested through appropriate		
	ISO 17025 certified lab or using air	1.Self-evaluation	
	dispersion modelling	and monitoring	
Cupro	1. Ambient air emission parameters $NH_3$ to be		
	tested through appropriate ISO 17025	2.Supplier	
	certified lab or using air dispersion	Platform – MMCF	
	modelling	Module (proposed)	
Acetate	1. Acetone air emissions through mass balance		
	calculation		

For note taking:

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## Introduction

## Background

ZDHC is a global multi-stakeholder organisation/initiative that oversees the implementation of its Roadmap to Zero Programme with a Committed Community of over 320 organisations from the textile, apparel, leather and footwear industry.

Our vision is to create a world where better chemistry leads to the protection of life, land, air, and water, and our signatories are vital in driving collective progress.

The Roadmap to Zero Programme, by ZDHC, leads the fashion industry to eliminate harmful chemicals from its global value chain by building the foundation for more sustainable manufacturing to protect workers, consumers and our planet's ecosystems.

To address the use and discharge of hazardous chemicals in man-made cellulosic fibre (MMCF) manufacturing, ZDHC published the ZDHC MMCF Guidelines V1.0 in April 2020. These guidelines were focussed on the viscose staple fibre manufacturing sector. It was felt that the scope of these guidelines should be expanded to other fibre categories in the MMCF sector, such as lyocell, viscose filament yarn (VFY), cuprammonium rayon (cupro) and cellulose acetate (acetate). A collaborative and aligned approach to these fibres would generate cleaner outputs from production while including a circular approach to their processes. At the same time, due to the publication of the ZDHC Wastewater Guidelines V2.1 and the Sludge Reference Document V1.0, it was imperative to align the Wastewater Guidelines for viscose staple fibre in the V1.0 document with these new requirements.

A task team drawn from ZDHC Signatories was set up to study the above and update the guidelines to the ZDHC MMCF Guidelines V2.2 for the scope expansion.

## Objective

The ZDHC MMCF Guidelines V2.2 addresses integrated expectations for discharged wastewater quality, air emissions and chemical recovery for manufacturing facilities producing man-made cellulosic fibres.

The complete set includes:

- ZDHC MMCF Responsible Fibre Production Guidelines V2.2 (Chapter 1)
- ZDHC MMCF Wastewater Guidelines V2.2 (Chapter 2)
- ZDHC MMCF Air Emissions Guidelines V2.2 (Chapter 3)

The three sections (above) of the ZDHC MMCF Guidelines V2.2 should be implemented as one. Outputs from the production process of fibres cannot be seen as stand-alone outputs and these three chapters provide guidance for an aligned industry approach. With this set of guidelines, ZDHC appeals to its Committed Community and the entire MMCF industry to improve the quality of discharged industrial wastewater and production-related air emissions. ZDHC also expects to support the transition of the production of MMCF towards a circular approach by proposing recovery rates for substances such as sulphur, sodium sulphate, NMMO, ammonia, copper and acetone.

ZDHC hopes to define milestones through a roadmap for fibre manufacturing facilities advancing towards the production described in the EU BAT BREF Reference Document on Best Available Techniques for the Production of Polymers (EU BREF POL). Aiming to prevent and control pollution arising from production, which will lead to a high level of environmental protection.\*

This document does not include requirements for the process of converting wood to dissolving pulp for MMCF fibres. The work to add this process to the guidelines' scope will be taken up in the MMCF V3.0 update.

As manufacturing facilities are not identical in terms of capabilities, knowledge, strategic priorities or resources, this document provides a three-level approach for the limit values and recovery rates of the proposed parameters. To promote continuous improvement the

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<sup>\* (</sup>European Commission - IPPC Bureau 2007) https://ec.europa.eu/commission/presscorner/detail/fr/MEMO\_07\_441

levels get more stringent as they move from Foundational, Progressive to Aspirational. We encourage suppliers to strive for continuous improvement on their impact on the environment and human health. Manufacturing facilities shall proactively develop and manage a data-driven, continuous improvement plan to achieve the requirements of each level.

To learn more about the continuous improvement roadmap, see <u>ZDHC MMCF Guidelines</u> <u>Implementation Plan V2.2</u>.

## Connectivity

The ZDHC MMCF Guidelines V2.2 is part of a series of guidelines and solutions from ZDHC to drive positive change in the industry towards sustainable chemical management. MMCF fibre and filament manufacturing facilities are expected to comply with the solutions applicable to them, considering the type of processes conducted in the facility. The following documents must be taken into account:

ZDHC MMCF Responsible Fibre Production Guidelines V2.2 To be interpreted also with:

ZDHC Wastewater Guidelines V2.1

#### ZDHC MMCF Wastewater Guidelines V2.2

To be interpreted also with:

- ZDHC Wastewater Guidelines V2.1
- ZDHC Sludge Reference Document V1.0
- ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan (SAP) V2.1

#### ZDHC MMCF Air Emissions Guidelines V2.2

To be interpreted also with:

ZDHC Air Emission Guidelines V1.0 (under development)

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## Chapter 1: ZDHC MMCF Responsible Fibre Production Guidelines V2.2

The objective of the Responsible Fibre Production Guidelines is to address the expectations for:

- Process chemical recovery rates
- Wastewater environmental impact in t produced
- Best practices in production of MMCF

## 1.0 Scope

The feedstock in scope for production includes, but is not limited to, wood and bamboo, and covers outputs proceeding from the dissolving of fibre and filament for the following MMCF fibres:

- Viscose staple fibres (VSF)
- Modal staple fibres
- Viscose filament yarn (VFY)
- Lyocell
- Cuprammonium rayon (cupro)
- Cellulose acetate (acetate)

## 2.0 Best practices for fibre feedstock

The selection of feedstock for the production of MMCF can have a great impact on the environment. The growth in market share of these fibres shows there is a need to establish clear policies related to raw material inputs. The following subsections contain recommended best practices that should be implemented by organisations.

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· Wastewater environmental impact in terms of load per tonne of fibre or filament

## 2.1 Raw material sourcing

- a. Organisations shall have a responsible raw material policy defining the sourcing of wood, pulp, and pulp fibre, eliminating sourcing from ancient and endangered forests, endangered species habitats and other controversial sources. To support this policy, organisations should:
  - i. Conduct a Canopy style verification audit to assess the risk of sourcing from ancient and endangered forests and other controversial sources.
  - ii. Include a preference for Forest Stewardship Council (FSC) or Programme for the Endorsement of Forest Certification (PEFC) certified inputs.
- b. To ensure transparency throughout the value chain, organisations should have a proper chain of custody system that includes, but is not limited to, blockchain-based traceability or use of Unique Trace.

## 2.2 Circularity and recycled feedstock

To reduce the environmental impact of MMCF production it is imperative to incentivise new developments that lead to the creation of a product fit for purpose within a circular economy.

Brands and manufacturing facilities should work to reduce the input of virgin raw materials by increasing the amount of alternative fibre feedstock. This includes, but is not limited to, pre and post-consumer fibre waste and agricultural waste.

- a. Organisations should have a sourcing strategy that includes commitments to increase the percentage of raw material originated from next generation feedstock.ª This strategy should clearly define the feedstock used, as well as appropriate targets and timelines for adopting materials originated from next generation feedstock.
- b. To support the use of recycled feedstock, organisations should take part in the Textile Exchange Recycled Claim Standard certification programme at a minimum.

## 3.0 Responsible production of MMCF

Another aspect to consider when planning the move to a circular economy approach is the recovery of chemicals used or produced as a by-product during the fibre production process.

Manufacturing facilities should strive for continuous improvement in the management of hazardous substances within their value chain. For this reason, policies around the production of these fibres should not only include alternative non-virgin feedstock sources but also address the recovery of chemicals and by-products related to the MMCF production process.

## 3.1 Viscose and modal (staple fibres)

#### **Chemical recovery**

During the viscose and modal (staple fibre) production process, sulphur compounds from the spin bath and by-products, sodium sulphate, should be recovered and either returned to the onsite production processes or sold as by-products. Control technologies and recovery treatments should be applied to achieve the recommended recovery percentage of these chemicals (sulphur and sodium sulphate) as listed in this document.

#### Sulphur recovery - treatment methods and control technologies

The sulphur recovery treatment methods mainly include:

- CS<sub>2</sub> recovery from spinning off-gases by a condensation route.
- CS<sub>2</sub> recovery by activated carbon adsorption from exhaust gases of spinning and spin bath, coupled with either of the following upstream processes to remove H<sub>2</sub>S:
  - a. Recovery as sulphur by catalytic redox process.
  - b. Recovery as NaHS+Na<sub>2</sub>S is produced by caustic scrubbing.
- Conversion of both CS<sub>2</sub> & H<sub>2</sub>S to sulphuric acid by a catalytic process.

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a ZDHC refers to next generation feedstock as the one originated from alternative and recycled feedstock

There are various sulphur recovery technologies available within viscose and modal production. The control technology applied at the point of fibre production depends on many conditions, including:

- · Year of establishment of the plant and the technology used
- National regulations
- Best available technologies

Recovery technologies within viscose and modal (staple fibres) production are specified in the Best Available Techniques for Polymer Production applicable to viscose and modal staple fibres (EU BAT BREF POL). In addition, there are several other technologies that have been applied in viscose processes in recent years to improve its natural resource efficiency.

#### **Recovery rates**

Table 1: Correlation of sulphur air emissions (kg/tonne of fibre) and the corresponding % sulphur recovery rates calculated based on the CS<sub>2</sub> charged in feed

ZDHC Levels	Sulphur air emissions (kg/tonne of fibre) <sup>a,c</sup>	Corresponding % sulphur recovery <sup>b,c</sup>
Foundational	35	85%
Progressive 20		92%
Aspirational	12	95%

<sup>a</sup> Same limit values are mentioned under ZDHC MMCF Air Emissions Guidelines (Chapter 3: Appendix B, Table 2.A- Air emissions).

<sup>b</sup> Based on mass balance calculation explained under the ZDHC MMCF Air Emissions Guidelines (Chapter 3: Appendix B, Table 2.C- Mass balance of sulphur or acetone flows).

<sup>c</sup> Sulphur air emissions (kg/tonne of fibre) and corresponding % sulphur recovery values mentioned in the table are calculated considering CS<sub>2</sub> addition per unit product of 280kg/tonne by using sulphur mass balance method.

Note- CS, charged in the feed for viscose production is recovered either as CS<sub>2</sub> or other sulphur containing chemicals by various technologies (O1-O6). Therefore to simplify the mass balance recovery calculation, both CS<sub>2</sub> added and CS<sub>2</sub> recovered are converted into sulphur and therefore chemical recovery is reported as % sulphur recovery and not as CS2 recovery.

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Table 2: Sodium sulphate recovery rates (VSF)

ZDHC Levels	Sodium sulphate recovery (%)
Foundational	50
Progressive	60
Aspirational <sup>d</sup>	70

Calculation of sodium sulphate recovery<sup>e</sup>

Sodium sulphate		quantity of sodium sulp
recovery (%)	=	viscose or

## 3.2. Viscose filament yarn (VFY)

#### **Chemical recovery**

There is no proven technology for CS, recovery from waste gases generated in viscose filament yarn manufacturing, either in spool spun yarn (SSY), continuous spun yarn (CSY) or pot spun yarn (PSY). Theoretically, recovery is feasible in SSY via technical treatment, and some facilities are equipped with related equipment, but the proportion of CS<sub>2</sub> generated is not high. This means that all CS<sub>2</sub> inputs need to be treated or discharged rather than recycled in VFY production.

Table 3: Sodium sulphate recovery rates (VFY)

ZDHC Levels	Sodium sulphate recovery (%)
Foundational	60
Progressive	65
Aspirational	70

<sup>d</sup> A higher rate of recovery for Aspirational Level is theoretically achievable, but such higher levels will require increased input of energy and steam, which can lead to increased GHG emissions, creating additional environmental pollution. <sup>e</sup> To support the reporting of this parameter, facilities should provide information about by-products produced including, but not limited to, sodium sulphate, H<sub>2</sub>SO<sub>4</sub>, barium sulphate, etc. on MMCF Module (ZDHC Supplier Platform)

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phate produced as by-product (tonne) x 100

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modal fibres produced (tonne)
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#### Calculation of sodium sulphate recovery<sup>e</sup>

Sodium sulphate	quantity of sodium sulphate produced as by-product (tonne) x			
recovery (%) =	VFY produced (tonne)			

100

## 3.3 Lyocell

#### **Chemical recovery**

The core part of the lyocell process is the direct dissolution of cellulose through NMMO (N-methyl-morpholine-n-oxide). The solvent, NMMO, is able to dissolve cellulose physically without any chemical pretreatment. The important environmental issue in lyocell production is the recovery of NMMO. During the production of lyocell, after washing out residual NMMO, spin finish is applied and the fibre is dried and packed.

#### NMMO recovery – treatment methods and control technologies

NMMO is recovered through a multi-stage cleaning process, including filtration, purification (ionic exchange) and evaporation.

NMMO (in certain concentrations) can be recovered at a very high recovery rate. Meanwhile, water that is regained during the evaporation step is recycled back into the washing section of the fibre line.

Table 4: NMMO recovery rates

ZDHC Levels	NMMO recovery (%)
Foundational	99.5
Progressive	99.7
Aspirational	99.8

<sup>e</sup> To support the reporting of this parameter, facilities should provide information about by-products produced including, but not limited to, sodium sulphate, H<sub>2</sub>SO<sub>4</sub>, barium sulphate, etc.on MMCF Module (ZDHC Supplier Platform)

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#### Calculation of NMMO recovery

- Recovery rate of NMMO (%) = [1- (NMMO loss / NMMO consumption)] x100
- remaining on waste
- NMMO consumption = NMMO fresh input + NMMO recovered and recycled

Alternatively, this could also be calculated only through mass balance:

Recovery rate of NMMO = (1- (NMMO net input / NMMO consumption)) %

Because in the process NMMO is present in different concentrations, for the calculation all concentrations must be converted to a %.

## 3.4 Cupro

#### **Chemical recovery**

During cupro production, copper and ammonia are used as cellulose solvents and are recovered by a closed-loop process. Copper and ammonia discharged in wastewater are recovered using various wastewater treatment technologies. In addition, some ammonia escapes into the atmosphere as a gas and is recovered by scrubbing techniques and then transferred to the wastewater.

Copper and ammonia recovery – treatment methods and control technologies During the production of cupro, copper and ammonia in the wastewater are recovered by

a multi-stage process.

- Copper is recovered mainly by sedimentation separation and ion exchange
- Ammonia is recovered mainly by distillation and ion exchange

Ammonia gas that escapes is captured by a wet scrubber and the captured ammonia is recovered through the wastewater treatment process described above.

The recovered chemicals are reused in the spinning dope production process. ZDHC MMCF Guidelines

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NMMO loss = NMMO in wastewater to WWTP + NMMO remaining on product + NMMO

Table 5: Copper and ammonia recovery rates

ZDHC Levels	Ammonia recovery (%)	Copper recovery (%)
Foundational	40	98.0
Progressive 42		99.0
Aspirational	44	99.5

Calculation of ammonia and copper recovery is done as mentioned below.

Copper Recovery (%) = Total copper used - Copper fresh input x100 Total copper used

#### Notes:

Since ammonia is recovered as an aqueous solution, the total amount of ammonia recovered can be directly determined.

Copper, on the other hand, is recovered as slurry, making it difficult to directly determine the total amount of copper recovered.

However, the total used copper can be determined from the total amount of produced spinning dope and its concentration. Therefore, the recovered copper can be determined by subtracting fresh input from the total used copper.

## 3.5 Acetate

#### **Chemical recovery**

During the production of acetate fibre, acetone solvent (which is non-toxic but can cause serious eye irritation, drowsiness and dizziness) is recovered by a closed-loop process. Scrubbers can be used to recover acetone during all the production processes even though acetone is a very highly volatile solvent and easily escapes to the environment.

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#### Acetone recovery – treatment methods and control technologies

- solvent in the process.
- cling and regenerating back into the system.

Table 6: Acetone recovery rates

ZDHC Levels	Acetone recovery <sup>f</sup> (%)
Foundational	93
Progressive	95
Aspirational	98

Calculation of acetone recovery is done by mass balance.

Recovery (%) of acetone = (total acetone used) - (fresh acetone input) x 100 (total acetone used)

Where fresh acetone input = (opening stock as per inventory + purchase) - closing stock

### 3.6 Sodium Sulphate, NMMO, ammonia, copper and acetone recoveries

This document recognises that there are several technologies available for the recovery of sulphate during the MMCF production process. It is important to clarify that while this document focuses on the recovery of sodium sulphate salt, there are other recovery technologies available. It is the intention of ZDHC to review such technologies available in the market and add to the updates of this document.

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• The distillation process of acetone-water mixture and the re-use of the regenerated

• Capturing any possible escaped acetone vapours through charcoal filters and recy-

<sup>f</sup>Acetone recovery is based on mass balance calculation explained under the ZDHC MMCF Air Emissions Guidelines (Chapter

<sup>3:</sup> Appendix B-Table 2.C Mass balance of sulphur or acetone flows)

The reporting frequency for the average recovery rate shall be based on an annual self-assessment. The reporting cycle shall be for a calendar year (Jan - Dec) with the reporting deadline of 31st December each calendar year.

Table 7: Recovery rates for sulphate, NMMO, ammonia, copper and acetone

ZDHC Levels	Unit	Sulphate	Sulphate	NMMO	Ammonia	Copper	Acetone
		recovery	recovery	recovery	recovery	recovery	recovery
		(VSF) <sup>9</sup>	(VFY) <sup>9</sup>	(lyocell)	(cupro)	(cupro)	(acetate)
Foundational		50	60	99.5	40	98	93
Progressive	%	60	65	99.7	42	99.0	95
Aspirational		70	70	99.8	44	99.5	98

## 3.7 Best practices for raw materials consumption

The parameters listed below are defined as the amount of raw material or natural resource input required to produce one tonne of fibre or filament, be it the raw material average input for viscose, modal fibre or filament, lyocell, cupro and acetate production process. To understand more about the production process, it is important to have a complete overview of the raw material average input consumption. To share this information, manufacturing facilities should calculate their consumption on an annual base average of fibre production per site. The minimum average accepted is no shorter than one month.

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Table 8: Recommended raw material consumption for viscose, modal (staple fibre or filament), lyocell, cupro and acetate per tonne of fibre or filament<sup>a,b</sup>

		Recommended consumption					
Parameter	Unit	Viscose or Modal Staple Fibre	VFYª	Lyocell	Cupro°	Acetate	
CS <sub>2</sub>		80-100	250-300	N/A	N/A	N/A	
NMMO (100%)		N/A	N/A	12-30	N/A	N/A	
Ammonia		N/A	N/A	N/A	250-500	N/A	
Copper Sulphide	kg/ tonne of fibre or	N/A	N/A	N/A	5-30	N/A	
Zn	filament	2-10	10-20	N/A	N/A	N/A	
Spin finish		3-5.3	10-25	3-5.3	12-25	3-5.3	
NaOClc		0-70	0-50	0-90	5-40	N/A	
Acetone		N/A	N/A	N/A	N/A	2-3	

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<sup>a</sup> The applicability of this table for modal staple fibre production shall only be for sites with mixed production of viscose and

<sup>b</sup> Correlating consumption values to recovery rates will require extensive data collection and analysis to make decisions with

<sup>d</sup> CS<sub>2</sub> consumption figures are based on the weighted average of different technologies and are limited to standalone VFY

<sup>&</sup>lt;sup>g</sup> During viscose staple fibre and viscose filament yarn production, sodium sulphate is recovered as a by-product from the spin bath.

modal fibres. This table does not apply to facilities with production of modal without viscose production. While ZDHC recognises the importance of energy and water consumption during the production process, the inclusion of these parameters in this document will require further data collection and analysis.

a science-based approach and will remain a topic for the next revision. (For example, caustic consumption correlates with sodium sulphate recovery.)

<sup>&</sup>lt;sup>c</sup> NaOCl consumption is reported on an "as such" basis and not on the available chlorine basis.

sites.

<sup>&</sup>lt;sup>e</sup> Consumption calculations for cupro includes the linter purification process up to the spinning process.

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Concentration in mg/L x		Water flow per day in m <sup>3</sup>
(B)		(C)
B = Concentration of the	B = Concentration of the	
parameter obtained from	parameter obtained from the	
testing result done for the		the sample for the
ZDHC MMCF Wastewater	ZDHC MMCF Wastewater	
Guidelines V2.2.	Guidelines V2.2.	
		collected.
	(B) B = Concentration of the parameter obtained from t testing result done for the ZDHC MMCF Wastewater	(B) B = Concentration of the parameter obtained from the testing result done for the ZDHC MMCF Wastewater

Table 10: Example of sampled average load per tonne of fibre or filament

Reporting cycle and year	Parameter	Sampling month for reporting ZDHC MMCF Guidelines V2.2	Test result (concentration value)	Water flow volume – sampled average	Load per tonne of fibre or filament (g/ tonne of fibre)
1-2023	COD-Sea	January 2023	150mg/L	January 2023 = 60 m³ /day	150 x 60 = 9,000
2-2023	COD-Sea	June 2023	130 mg/L	June 2023 = 60 m³/day	130 x 60 = 7,800

Table	8:	Recommended	raw	material	consumption	for	viscose,	modal	(staple	fibre	or
filamer	nt),	lyocell, cupro a	nd ad	cetate pe	r tonne of fibre	or	filament <sup>a,</sup>	<sup>ь</sup> (contin	iued)		

			Recomme	ended consu	mption	
Parameter	Unit	Viscose or Modal Staple Fibre	VFY⁴	Lyocell	Cupro <sup>e</sup>	Acetate
Acetic acid		N/A	N/A	N/A	N/A	1-4
Acetic anhydride	t/tonne of fibre	N/A	N/A	N/A	N/A	0.5-3
Caustic	or	0.45-0.6	0.6-0.8	N/A	0.25-0.5	N/A
H <sub>2</sub> SO <sub>4</sub>	filament	0.65-1.03	0.9-1.1	N/A	1.5-2	0.03-0.09
Pulp		1.010-1.065	1-1.2	1.01-1.065	1-1.1	1.01-1.065

## 3.8 Environmental impact: wastewater parameters - load per tonne of fibre or filament

To understand the environmental impact and efficiency of water usage in the production of viscose or modal staple fibres or filament, lyocell and acetate, it is necessary to measure the wastewater parameters listed below in terms of load-based values (g/tonne of fibre produced) rather than only concentration-based (mg/L of discharged wastewater). This requires measuring the amount of discharged wastewater from the fibre or filament production process, and calculating the load per tonne of fibre or filament by linking the pollutant concentration with the wastewater flow rate.

Calculation of the parameters shall be done using the sampled average across one month of water flow from the fibre or filament production process considered for the calculation. The concentration (mg/L) used for this calculation shall be taken from the ZDHC MMCF Wastewater Guidelines V2.2 reporting cycles. The selected month used to create the sampled average water flow shall be the same as the sampling month of the reporting parameter.

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The lower the load, the more progressive the facility is.

Table 9: Calculation of the parameter to be reported in load per tonne of fibre or filament

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Table 11:	Wastewater	parameters	to be	assessed	in I	load per	tonne	of fibre	or	filament
(sampled a	average)									

									Limits							
	Unit –		F	oundational				-	Progressive	-			_	Aspirational		
	Unit	VSF	VSF/ Lycocell	Lyocell	VFY	Acetate	VSF	VSF/ Lycocell	Lyocell	VFY	Acetate	VSF	VSF/ Lycocell	Lyocell	VFY	Acetate
COD <sup>#</sup> – to sea			9000		24000	9000		6000		18000	6000		3600		12000	3600
COD <sup>#</sup> – to other bodies of water	Load* in g/ tonne of fibre/fil- ament		7200		14400	7200		6000		12000	6000		3600		9600	3600
BOD – 5 day	unient		1800		7200	1800		900		4800	900		300		2400	300
Zn		1	50	N/A	600	150	6	60	N/A	360	60	3	0	N/A	240	30

To support the reporting of this document, facilities should provide the following information:

- Fibre production of the month in which wastewater sampling is done by a ZDHC Approved MMCF Wastewater Solution Provider.
- Wastewater test results, from a ZDHC Approved MMCF Wastewater Solution Provider, of the required parameters within the corresponding testing cycle.
- Wastewater flow rate during the month when sampling for the testing of the above parameters is conducted.

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<sup>\*</sup> Load calculated for a 60m<sup>3</sup> per day water flow average.

<sup>&</sup>lt;sup>#</sup>For any MMCF facility COD values will be either for discharge to sea or discharge to other water bodies.

Note: load per tonne has been excluded for cupro. Since cupro is an integrated production process from linter purification to spinning, the BOD and COD load per tonne of fibre significantly exceed the limit values listed here.

## Chapter 2: ZDHC MMCF Wastewater Guidelines V2.0

The MMCF Wastewater Guidelines addresses the expectations for wastewater discharge parameters and limit values (concentration based) related to the production of man-made cellulosic fibres.

It includes the parameters, analytical test methods and sampling procedures for wastewater testing. This enables brands and manufacturing facilities to share their test results in a systematic and efficient manner via the ZDHC Gateway.

The expected outcomes of using this document are:

- To ensure wastewater discharge does not have an adverse impact on nearby communities and the environment.
- To provide a unified monitoring and testing programme for manufacturing facilities to systematically and efficiently share discharge and emissions data with brands and other interested parties.
- To increase operational efficiencies by defining a standard cadence for wastewater and reporting requirements which applies to all organisations that adopt this document.
- To define limit values for conventional and additional parameters, including APEOs, in the wastewater, so that any non-conformities detected can motivate the manufacturer to undertake root-cause analysis and a Corrective Action Plan.

## 1.0 Scope

This document applies to the process related to discharged wastewater and sludge associated with the production of man-made cellulosic fibres from different feedstock sources such as, but not limited to, wood and bamboo.

The fibres within the scope are:

- Viscose staple fibres
- Modal staple fibres
- Viscose filament yarn

- Lyocell
- Cupro
- Acetate

ZDHC MMCF Guidelines Version 2.2 | August 2023 Testing and reporting of the listed parameters in this document by MMCF manufacturers should be conducted in correlation with the <u>ZDHC Wastewater Guidelines V2.1</u>. Higher limit values can be reported at vertically integrated facilities, where wastewater from the fibre or filament production process is mixed with wastewater from the dissolving pulp process. The reported data will be collected and analysed to help define limit values for such facilities and add dissolving pulp for MMCF to the scope of this document.

Facilities with vertically integrated production that also includes dyeing or finishing processes for yarn or fabrics should apply the most current ZDHC MRSL and test the wastewater for all the ZDHC MRSL parameters listed in the <u>ZDHC Wastewater Guidelines V2.1</u>.

## 2.0 Requirements

## 2.1 Minimum requirements

The minimum requirements of this document are to comply with local legal regulations for wastewater and sludge.

## 2.2 General principles for sampling and reporting

The general principles for sampling and reporting of this document are directly linked to the latest published version of the ZDHC Wastewater Guidelines V2.1. To learn more <u>click</u> <u>here</u> and for ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan V2.1 <u>click here</u>.

Details to be specifically referenced in the ZDHC Wastewater Guidelines V2.1 1. Types of discharge (direct, indirect with or without pre-treatment, zero liquid

- Types of discharge (direct, indirect discharge)
- 2. Sampling points based on the type of discharge
- 3. Testing cycles and reporting frequency in the ZDHC Gateway

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discharge in the ZDHC Gateway Based on ZDHC Wastewater Guidelines V2.1, the wastewater discharge types and sample locations for MMCF facilities are summarised in the table below. Table 12: Wastewater discharge types, sample locations and test parameters for MMCF facilities

Sr No.	Wastewater dis-		Wastewater	sampling location a	and test parameters	
	charge type	1. Raw Wastewater	2. Treated Wastwater (Effluent)			3. Sludge
		(untreated)	Conventional Parameters	Heavy Metals	Specific	
1	Direct discharge	APEOs (MRSL wastewater	pH, temperature difference, colour, COD,	Total Cr, Cd, Cu,	Zn, sulphide, CS <sub>2</sub>	As per local lega
		parameter)	BOD, oil and grease, total nitrogen,	Ni, Cr <sup>+6</sup> , Pb, Hg		exists, manufactu
			ammonium-nitrogen, TSS,			the sludge dispo
			total-phosphorus, AOX, phenol			Wastewater Guid
						Document V1.0,
2	Indirect discharge	APEOs (MRSL wastewater	N/A	Cd, Cr <sup>+6</sup> , Pb, Hg	N/A	Same as direct d
	with pretreatment	parameter)				
3	Indirect discharge	APEOs (MRSL wastewater	N/A	N/A	N/A	N/A
	without pretreatment	parameter), Cd, Cr <sup>+6</sup> , Pb,				
		Hg				
4	Zero Liquid Discharge	APEOs (MRSL wastewater	N/A	N/A	N/A	Same as direct d
	(ZLD)	parameter)				

#### 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 means effluent goes directly to the CETP without any influence by the facility.

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gal requirement or if no such regulation cturing facilities can refer to and implement posal pathways, described in the ZDHC uidelines V2.1 and ZDHC Sludge Reference ), best suited to their facility's operations. discharge

discharge

## 2.3 Testing requirements

#### 1. Conventional parameters

These parameters, their limit values (Foundational, Progressive and Aspirational), and recommended standard test methods for analysis are defined in Appendix A - Table 1.A (Conventional parameters)

#### 2. Additional parameters

These parameters, their limit values (Foundational, Progressive and Aspirational), and recommended standard test methods for analysis are defined in Appendix A - Table 1.B (Additional parameters). The applicable parameter and reporting limit values of the ZDHC MRSL can be found there.

#### 3. Parameters specific to man-made cellulosic fibre or filament production process

These parameters, their limits (Foundational, Progressive and Aspirational), and recommended standard test methods for analysis are defined in Appendix A -Table 1.C (Parameters specific to MMCF production).

Where local legislation or permits cover conventional parameters that are additional to those listed in this document, manufacturing facilities are expected to test for those additional parameters. These should be conducted according to the requirements applicable to local law (legal discharge permit) and the timeline identified by local authorities.

#### 4. Sludge parameters

At a minimum, existing local legal regulations for the treatment and handling of industrial wastewater sludge shall be observed. Under such a situation, additional testing of sludge is considered optional.

If no such regulation exists, manufacturing facilities can refer to and implement the sludge disposal pathways, described in the ZDHC Sludge Reference Document V1.0, best suited to their facility's operations.

Further discussions will be held with MMCF stakeholders to align sludge testing and disposal requirements for MMCF manufacturers with those outlined in the ZDHC Wastewater Guidelines V2.1 – Tables 4.A-4.D for the next update to the MMCF Guidelines.

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## 2.4 Methods for analysis and testing

The methods for analysis and testing recommended in this document are based on internationally recognised standard water and wastewater testing methodologies, as well as government recognised testing requirements in the EU, USA, China and India.

Other requirements for the methods of analysis and testing of conventional, additional and specific parameters for wastewater, as mentioned in this document, are directly linked to the methods for analysis and testing the conventional parameters for wastewater in the ZDHC Wastewater Guidelines V2.1 and ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan V2.1.

#### A. Conventional parameters for wastewater

Standard methods for analysing these parameters are specified in Appendix A - Table 1.A.

#### B. Additional parameters for wastewater

Standard methods for analysing these parameters are specified in Appendix A – Table 1.B.

#### C. Parameters specific to the man-made cellulosic fibre or filament production process

Standard methods for analysing these parameters are specified in Appendix A – Table 1.C.

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# Chapter 2: Appendix A – MMCF wastewater Parameters, limit values and test methods

## Table 1.A Conventional parameters

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									(	Conver	ntional W	astewate	er Para	neters								
									Limit V	alues										Test Methods		
	Unit	VSF	VSF/ Lycocell	Found		Cupro	Acetate	VSF/ Lycocell	Progre Lyocell		Cupro	Acetate	VSF	VSF/ Lycocell		ational VFY	Cupro	Acetate	International / Europe	US	China	India
рН	pH units	<u>δ.0 - 9.0</u> Δ+15 Δ+10 Δ+5												ISO 10523	USEPA 150.1 SM 4500H+-B	GB/T 6920 HJ 1147	IS 3025 (Part 11)					
Temperature difference*	°C															DIN 38 404-4 or equivalent	USEPA 170.1 SM 2550-B	GB/T 13195	IS 3025 (Part 9)			
Colour (436nm; 525nm; 620nm)	m-1		7;5;3 5;3;2												4;	2;1			IS	О 7887-В		IS 3025 (Part 4)
COD discharge to sea			150	300	200	15	0	100	200	150	1	00		60	120	100		60	ISO 15705	USEPA 410.4.	HJ 828	IS 3025
COD discharge to other bodies of water	mg/L		120	240		120		100	200		100			60	120	80		60	ISO 6060**	SM 5220-D**	GB/T 11914**	(Part 58)**
BOD 5-day concentration			30		60	30	)	15		40	1	5		5		30		5	EN 1899-1 ISO 5815-1	USEPA 405.1 SM 5210-B	HJ 505	IS 3035 (Part 44) seeded dilution water (BOD5)

\*\*Validated cuvette methods can be used alternatively.

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<sup>\*</sup> Field measured. Take the temperature of the discharged wastewater and the receiving body of water upstream. Subtract the temperature of the receiving body from the temperature of the discharge to give the delta temperature difference, which can be a positive or a negative value. The discharge limit values only refer to a positive value, which produces an overall increase in the temperature of the receiving body of water. This test is to be done on-site by the sampler and is applicable only for direct discharge where it is discharged into a water body.

Where the receiving body is inaccessible, the sampler's own safety is at risk in accessing it or the upstream receiving body is located far away from the facility (e.g. a pipeline from the facility that goes several kilometres into the sea), then the sampler should not carry out this on-site test and the temperature parameter will be not applicable.

											Conver	ntional V	Vastewate	er Para	ameters								
								1		Limit V	/alues			1							Test Metho	ds	
	Unit	VSF	VSF/ Lycocell	Found			Acetate	VSF	VSF/ Lycocell	Progre Lyocell		Cupro	Acetate	VSF	VSF/ Lycocell		ational VFY		Acetate	International / Europe	US	China	India
Oil and Grease			8		10		8		5		8		5		2		4		2	ISO 9377-2	USEPA 1664 revision B, SM 5520-B/ C	HJ 637 (Total oil and grease)	IS 3025 (Part 39) partition gravimetric or partition infra-red
Total Nitrogen			30 80 30				30		2!	5		70	25			2	20			ISO 29441, 11905- Part 1	USEPA 351.2, SM 4500P-J, SM 4500N-B 4500N-C	HJ 636	IS 3025 (Part 34) measure and total all forms of nitro- gen (ammonia, nitrate, nitrite, organic)
Ammonium- Nitrogen			5 75 5				5		3	ł		65	3		1			15	1	ISO 6778 ISO 11732 ISO 5664 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 elec- trode only
TSS	mg/L			7	70					5	0					3	30			ISO 11923	USEPA 160.2, SM 2540D	GB/T 11901	IS 3025 (Part 17) 103 to 105 deg C
Total- Phosphorus		70 3.0								1.	0					C	).5			ISO 6878, ISO 11885 (ICP-OES), ISO 17294-2 (ICP- MS)	USEPA 365.4 SM 4500P-J USEPA 200.7 USEPA 200.8 USEPA 6010C USEPA 6020A	GB/T 11893 HJ 700 (ICP-MS) HJ 670	IS 3025 (Part 31), IS 3025 part 65 (ICP- MS)
AOX			5.0							2.	0					C	).2			ISO 9562	USEPA 1650, HACH LCK 390 Merck 1.00675.0001	HJ/T 83-2001	CPPRI Saharanpur, AOX analyser, ISO, 9562
Phenol				1	.0					0.	.5					C	).1			ISO 14402, ISO 6439 (chloroform extraction)	SM 5530 B/C	HJ 503	IS 3025 (Part 43)

## Table 1.A Conventional parameters (continued)

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											A	dditio	onal Wa	stewater	Param	eters								
										Liı	mit Valu	Jes			1							Test Methods		
	Unit	VSF	VSF/ Lycocell	Found		nal Y Cupro	Acetate	VSF	VSF/ Lycocell		ocell V		Cupro	Acetate	VSF	VSF/ Lycoc	/		VFY	Acetate	International / Europe	US	China	India
Chromium (Cr), total				(	).2						0.1							0.	0.05				GB 7466, HJ700	IS 3025 (Part 52)
Cadmium (Cd)				0.1			N/A			0.0	)5			N/A			(	0.01		 N/A		USEPA 200.7	GB7475,	IS 3025 (Part 41), AAS, instrumental method
Copper (Cu)			1.0								0.5							0.	).25		ISO 11885, ICP-OES, ISO 17294-2 ICP-MS	USEPA 200.8 USEPA 6010C USEPA 6020A	HJ700	IS 3025 (Part 42), AAS, instrumental method
Nickel (Ni)	mg/L			(	).5						0.2							0.	0.10				HJ700 GB 11912	IS 3025 (Part 54), AAS, instrumental method
Chromium (VI) (Cr <sup>+6</sup> )				0	.05						0.005							0.0	.001		ISO 18412	USEPA 218.6	GB 7467	IS 3025 (Part 52)
Lead (Pb)				(	D.1						0.05							0.	0.01		ISO 11885 ICP-OES, ISO 17294-2 ICP-MS	USEPA 200.7 USEPA 200.8 USEPA 6010C USEPA 6020A	GB7475. HJ700	IS 3025 (Part 47) AAS, instrumental method
Mercury (Hg)			0.01								0.005							0.0	.001		ISO 12846 or ISO 17852, ISO 17294-2 (ICP-MS)	USEPA 245.1 USEPA 245.7 USEPA 200.8 -(SIM), USEPA 6020A-SIM	НЈ 597, НЈ 700	IS 3025 (Part 48) cold vapor AAS only, IS 3025 part 65 (SIM mode)
	Unit									Rep	porting	limit										Test methods		
APEOs	ug/L										5.0										ASTM D7065 (GC/M 18254-1 OPEO/NPEC methan		857-2(modif	

## Table 1.B Additional parameters

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										Paramet	ers spe	ecific to	to the pro	oductio	on of MM	CF							
							-	,		Limit V	alues			,							Test N	lethods	
				Found	ationa	1				Progre	essive					Aspira	ational			Internation-			
	Unit	VSF	VSF/ Lycocell	Lyocell	VFY	Cupro	Acetate	VSF	VSF/ Lycocell	Lyocell	VFY	Cupro	Acetate	VSF	VSF/ Lycocell	Lyocell	VFY	Cupro	Acetate	al / Europe	US	China	India
Zn			2.5	N/A	5	N/A	2.5		1	N/A	3	N/A	1		0.5	N/A	2	N/A	0.5	ISO 11885 ICP-OES ISO 17294-2 ICP-MS	USEPA 200.7 USEPA 200.8	GB 7475 HJ 700	IS 3025 (part 49) AAS, instrumental method
Sulphide	mg/litre		2	N/A	5	1	N/A		1	N/A	3	1	N/A		0.5	N/A	2	٦	N/A	ISO 10530	SM 4500S2 -C&D 4500S2 -G	GB/T 16489 HJ 824 (flow injection methylene blue)	IS 3025 (part 29)
CS <sub>2</sub>			0.5	N/A	0.5	1	N/A		0.2	N/A	0.2	1	N/A		0.1	N/A	0.1	1	N/A	ISO 15680 ISO 11423-2 (headspace method)	USEPA 8260B	HJ 810, GB/T 15504 (head- space method)	N/A

## Table 1.C Specific parameters related to MMCF production

#### Note:

Wastewater testing and conformance requirement for MMCF suppliers does not depend on the volume of wastewater generated as outlined in the ZDHC Wastewater Guidelines V2.1. Even if generated wastewater is less than 15m<sup>3</sup> per day, all parameters mentioned under Table 1.A-1.C are applicable for a MMCF facility.

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## 3.0 Testing and reporting by ZDHC Approved **Laboratories**

The sampling, testing and reporting of MMCF Wastewater by ZDHC Approved Solution Providers of this document is directly linked to the testing requirements of the ZDHC Wastewater Guidelines V2.1 and ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan V2.1.

## 3.1 Minimum frequency for sampling, testing and reporting

The minimum frequency for sampling, testing and reporting of this document is directly linked to the minimum frequency for sampling, testing and reporting of the ZDHC Wastewater Guidelines V2.1. The list of ZDHC Approved Solution Providers for ZDHC MMCF Wastewater V2.2 parameters is available on our website.

## 4.0 Data reporting in the ZDHC Gateway -Wastewater Module

The data reporting in the ZDHC Gateway - Wastewater Module should follow the ZDHC Wastewater Guidelines V2.1. To learn more click here.

## 5.0 Determining conformance to this document

Sampling, testing and reporting requirements are the same for manufacturing facilities whether they discharge wastewater directly, indirectly, or have zero liquid discharge (ZLD). The only difference is what the resulting concentration data is compared to in order to determine conformance with this document.

Manufacturing facilities with *direct discharge* are expected to have:

- parameters for the MMCF production process in Appendix A Table 1.A-1.C. AND
- Appendix A Table 1.B for wastewater.

Manufacturing facilities with indirect discharge (with) pretreatment are expected to have: All conventional parameters in compliance with their agreements with the receiving centralised effluent treatment plant (CETP).

- Table 1.B for wastewater.

AND

A Table 1.B for wastewater.

Manufacturing facilities with indirect discharge (without) pretreatment are expected to have:

- ing centralised effluent treatment plant (CETP).
- for wastewater.

AND

. wastewater.

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Ø

ZDHC MMCF Guidelines Version 2.2 | August 2023 • Achieved the Foundational limit values for conventional, additional, and specific

• The applicable ZDHC MRSL wastewater parameter (APEOs) in untreated raw wastewater<sup>a</sup> at concentrations which are at, or below, the reporting limit values in

Achieved the foundational limit values for additional parameters (cadmium, chromium [VI], lead, mercury) in pretreated wastewater as mentioned in Appendix A

Applicable ZDHC MRSL wastewater parameter (APEOs) in untreated raw wastewatera at concentrations that are at, or below, the reporting limit values in Appendix

All conventional parameters in compliance with their agreements with the receiv-

 Achieved the Foundational limit values for additional parameters (cadmium, chromium [VI], lead, mercury) in raw wastewater as mentioned in Appendix A Table 1.B

Applicable ZDHC MRSL wastewater parameter (APEOs) in the raw wastewatera at concentrations at, or below, the reporting limit values in Appendix A Table 1.B for

<sup>&</sup>lt;sup>a</sup> Wastewater discharge types and sample locations can be found under Table No.12: Wastewater discharge types, sample locations and test parameters for MMCF facilities.

Manufacturing facilities with *ZLD* are expected to have:

· Applicable ZDHC MRSL wastewater parameter (APEOs) in the untreated raw wastewater<sup>a</sup> at concentrations at, or below, the reporting limit values in Appendix A Table 1.B for wastewater.

Manufacturing facilities should proactively develop and manage a data driven plan to continuously meet Foundational limit values and achieve Progressive and Aspirational limit values in the conventional parameters.

## 6.0 Resolution of non-conformances

#### A. Definition of non-conformance

Non-conformance for wastewater is defined through conventional, additional, and specific parameters for the MMCF production process. This is when test results either:

- For direct discharge facilities: Exceed the Foundational limit values in this document (Appendix A Tables 1.A-1.C) and MRSL (APEO) parameter reporting limit value for untreated raw wastewater in this document (Appendix A Table 1.B).
- · For indirect discharge with pretreatment facilities: Exceed the limit values of the receiving CETPs' requirements, the Foundational limit values for additional parameters (cadmium, chromium [VI], lead, mercury) for pretreated effluent, and the MRSL (APEO) parameter reporting limit value for untreated raw wastewater in this document (Appendix A Table 1.B).
- For indirect discharge without pretreatment facilities: Exceed the limit values of the receiving CETPs' requirements, the Foundational limit values for additional parameters (cadmium, chromium [VI], lead, mercury) and the MRSL (APEO) parameter reporting limit value for raw wastewater in this document (Appendix A Table 1.B).
- For ZLD facilities: Exceed the MRSL (APEO) parameter reporting limit value for untreated raw wastewater in this document (Appendix A Table 1.B).

<sup>a</sup> Wastewater discharge types and sample locations can be found under Table No.12: Wastewater discharge types, sample locations and test parameters for MMCF facilities.

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#### B. Actions by manufacturing facilities with non-conformance(s)

If a test report indicates non-conformance as defined above, the supplier is expected to: • Develop a root-cause analysis and Corrective Action Plan with a defined completion date. An input stream management review can be part of the initial root cause

- analysis, with actions such as:
  - the ZDHC MRSL.

  - . APEOs used in cleaning products).
  - Gateway Wastewater Module.
- . experts to help determine the root cause and identify suitable solutions.

· Checking if chemical formulations used in production processes conform to

Sending out specifications to textile raw material manufacturing facilities.

Checking chemicals used in non-production related areas (for example,

Upload a Corrective Action Plan with defined completion date on the ZDHC

Manufacturing facilities may resolve non-conformities through a root cause analysis to prepare and implement a Corrective Action Plan. For example, they could contact clients (brands) to see if they can offer any advice, or reach out to technical

# Chapter 3: ZDHC MMCF Air Emissions Guidelines V2.2

The MMCF Air Emissions Guidelines addresses the integrated expectations of the air emissions related to the priority hazardous chemicals used during production processes of manmade cellulosic fibre (MMCF).

This document specifies a unified set of parameters and limit values related to the production of man-made cellulosic fibres and filaments. It also includes the analytical test methods and sampling procedures, with the ultimate objective of allowing brands and manufacturing facilities to share their testing results in a systematic and efficient manner.

The expected outcomes of using this document are to:

- Address air emissions from MMCF fibre or filament production and to minimise any adverse impact to the environment and surrounding communities.
- Provide a unified approach to monitoring and testing for manufacturing facilities, so that they can systematically and efficiently share emission data with brands they work with and other interested parties.
- Increase operational efficiencies by defining a standard cadence for air emissions monitoring and reporting requirements that is applicable to all brands and manufacturing facilities adopting this document.

## 1.0 Scope

This document applies to process-related air emissions associated with the production of man-made cellulosic fibres and filaments from different feedstock sources such as, but not limited to, wood and bamboo.

The fibres within the scope are:

- Viscose staple fibres
- Modal staple fibres
- Viscose filament yarn

- Lyocell
- Cupro
- Acetate

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2.0 Requirements

The basic expectations listed below are considered to be out of the scope of this document, and although these are considered to be basic requirements, ZDHC will not be held liable for their verification.

Manufacturing facilities are expected to:

- Have a valid license to operate.
- minimise the concentration of pollutants is prohibited.

## 2.1 Minimum requirements

- practices of measurement and transparency.
- Follow generally accepted process engineering best practices for air emissions to minimise environmental impact.

2.2 Parameters and limit values for viscose and modal – staple fibre, viscose filament yarn, cupro and acetate

This document will focus on the following:

- Sulphur air emissions for viscose and modal staple fibres.
- Acetone air emissions for acetate fibre.
- yarn and cupro.

Parameters and limit values can be found in Appendix B.

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• Understand that any dilution of air emissions from exhaust systems to purposefully

· Quantify and track emissions of all parameters, consistent with standards and best

Ambient air outside the facility for viscose and modal staple fibres, viscose filament

# 3.0 General principles for monitoring, testing and reporting

The approach taken to monitor the selected parameters include indirect and direct measurement methods.

The indirect method of mass balance calculation is to be used for sulphur air emissions (viscose and modal fibre) and acetone air emissions (acetate fibre).

The direct testing method of ambient air emissions of  $CS_2 \& H_2S$  (viscose and modal staple fibre, viscose filament yarn) and ammonia (cupro) should be conducted to corroborate that those substances of concern are not present above the given concentration.

To streamline efforts, manufacturing facilities are encouraged to align testing of the parameters listed in this document with testing required for their legal permit.

## 3.1 Monitoring

To ensure accurate reporting, it is important that either a measurement system, or a continuous sampling or testing procedure, is established to measure all necessary parameters.

MMCF manufacturers must implement plans to reduce or avoid fugitive emissions. Any fugitive emissions must be controlled and avoided using state-of-the-art technologies.

# 3.2 Mass balance for the establishment of sulphur or acetone air emissions

When establishing a methodology with corresponding limit values for substances of concern, it is important that the selected methodology is internationally accepted and implemented. The methodology requires an integrated balance of all incoming and outgoing material flows. In principle, it is recommended to follow the Directive 2010/75/EU of the

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European Parliament on industrial emissions – integrated pollution prevention and control (EU, 2010).

## 3.2.1 Sulphur or acetone emission to air calculation

The effectiveness of the emission control of sulphur release to the air can be calculated by applying a mass balance. Any methods used should include the total mass of sulphur removed from the exhaust gases. Depending on the outputs, it can be either in solid or liquid form. Those recovered chemicals can be either reused as part of the process or sold as a product. Some remaining sulphur can be trapped in the sludge or liquid streams.

Acetone is easily regenerated by the distillation process of acetone-water mixture and the regenerated solvent is reused for the process. Any possible escaped solvent vapours are captured through charcoal filters and are recycled and regenerated back to the system. This reduces the loss of acetone solvent to the environment during the whole production process, even though acetone is a highly volatile solvent and may easily escape to the environment. The formula for the mass balance of sulphur or acetone can be found in Appendix B, Table 2.C.

# 3.3 Control technologies for sulphur or acetone release into the air

The viscose/acetate industry uses several technologies to control the emission of sulphur/ acetone to the air during the manufacturing process. The major technologies used in the industry are listed in Appendix B, Table 2.C, with the mass balance calculations.

## 3.4 Ambient air testing

Manufacturing facilities shall test the ambient air concentration outside the facility for the key substances involved in viscose, modal and VFY production ( $CS_2$  and  $H_2S$ ) as well as key substances involved in the cupro production ( $NH_3$ ) to prove that the ambient air emissions do not exceed reporting limit values set out in this document.

ZDHC MMCF Guidelines Version 2.2 | August 2023 The intention of air sampling and corresponding analytical testing is to identify if there are harmful substances related to the manufacturing process in the ambient air, and if the concentration of these substances is within or above given limit values.

ZDHC proposes one standardised approach for the measurement of the ambient air in the surrounding area of the production facility see Appendix C.

## 3.5 Test methods

Standardised test methods shall be used where specific testing is required:

- 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, shall be used, such as the ISO, EPA or GB.

## 3.6 Minimum testing frequency

- The testing frequency for the mass balance calculation is based on an annual verification. The testing cycles run from 1st January to 31st December within the same calendar year. The data is reported in the MMCF Module (on the ZDHC Supplier Platform).
- The testing cycle for direct monitoring of ambient air emissions (annual average sampling and testing) or air dispersion modelling data run from 1st January to 31st December within the same calendar year. The data is reported in the MMCF Module (on the ZDHC Supplier Platform).
- Where a test shows that a supplier does not meet the requirements of this document, manufacturing facilities shall identify the root cause, resolve the issue and retest the ambient air as often as necessary to ensure the issue has been resolved.

# Chapter 3: Appendix B – Air emission parameters & limit values

## Table 2.A Air emissions (Calculated using mass balance)

Air emission parameters and their limit values are defined under Table 2.A Air emissions (calculated using mass balance) and Table 2.B Ambient aird emissions in the surrounding environment (outside the facility). Table 2.B indicates limits values for CS<sub>2</sub> and H<sub>2</sub>S in ambient air related to viscose and modal fibre and filament production & NH<sub>2</sub> in ambient air is related to cupro fibre production.

Air emissions	Units	Foundational	Progressive	Aspirational
Sulphur air emissions for VSF	kg/ton of fibre (annual basis)	35ª	20 <sup>ь</sup>	12 <sup>ь</sup>
Acetone air emissions for acetate fibre	% (annual basis)	7°	5°	2°

#### Note:

The air emission using mass balance is calculated based on the yearly average of the calendar year.

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<sup>&</sup>lt;sup>a</sup> Based on average between norms assigned to new plants in India and EU Ecolabel criteria for textile products. <sup>b</sup> EU BREF POL recommendation.

<sup>&</sup>lt;sup>c</sup> % of acetone not recovered as per mass balance calculation is considered as air emission for acetone (acetate fibre).

## Table 2.B : Ambient air<sup>d</sup> emissions in the surrounding environment (outside the facility)

Ambient air emissions parameters	CS <sub>2</sub> (ambient air concen- tration outside the facility) reporting limit value for VSF/ modal and VFY	H <sub>2</sub> S (ambient air con- centration outside the facility) reporting limit value for VSF/modal and VFY	NH <sub>3</sub> (ambient air outside the facility) reporting limit value for cupro
Unit	mg/m³	mg/m³	ppm
Limits	0.10 <sup>e,f</sup>	0.10 <sup>e,f</sup>	2 <sup>g</sup>

WHO recommended ambient air quality norms

CS,: The lowest concentration of carbon disulphide for which an adverse effect was observed in occupational exposure was about 10 mg/m<sup>3</sup>, which may be equivalent to a concentration in the general environment of 1 mg/m<sup>3</sup>. In selecting the size of the protection (safety) factor, the expected variability in the susceptibility of the general population was taken into account, and a protection factor of 10 was considered appropriate. This leads to the recommendation of a guideline value of 100 ug/m<sup>3</sup>, with an averaging time of 24 hours. It is believed that below this value adverse health effects of environmental exposure to carbon disulphide (outdoor or indoor) are not likely to occur. (Ref: WHO Air Quality Guidelines, Year 2000, Pg No. 73)

H,S: The lowest-adverse-effect level of hydrogen sulphide is 15 mg/m<sup>3</sup>, when eye irritation is caused. In view of the steep rise in the dose-effect curve implied by reports of serious eye damage at 70 mg/m<sup>3</sup>, a relatively high protection (safety) factor of 100 is recommend-

ZDHC MMCF Guidelines Version 2.2 | August 2023 ed, leading to a guideline value of 0.15 mg/m<sup>3</sup> with an averaging time of 24 hours. A single report of changes in haem synthesis at a hydrogen sulphide concentration of 1.5 mg/m<sup>3</sup> should be borne in mind. (Ref: WHO Air Quality Guidelines, Year 2000, Pg No. 147).

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<sup>&</sup>lt;sup>d</sup> Ambient air limits values refer to the levels of air quality with an adequate margin of safety, to protect public health

<sup>&</sup>lt;sup>e</sup> Based on WHO recommended ambient air quality norms for (Ref: World Health Organization, Air quality guidelines for Europe. 2nd Edition, 2000)

<sup>&</sup>lt;sup>f</sup> Ministry of Environment, Forest and Climate Change of India from 17th January 2018. Notification 17th Jan 2018 - G.S.R. 35(E)

<sup>&</sup>lt;sup>g</sup>Under Japanese offensive odour control law (<u>https://www.env.go.jp/en/air/odor/regulation.html</u>).

## Table 2.C Mass balance of sulphur or acetone flows

Formula for mass balance

Sulphur air emissions = I1 - (O1 + O2 + O3 + O4 + O5 + O6)

Acetone air emissions = 11 - (O1 + O2)

Inputs		Notes	L/S/G	Test
11	$CS_2$ addition to reactor including fresh input and $CS_2$ recovered from the process (condensation and CAP).		Liquid	As per flowmeter / tank lev
	Acetone addition to reactor including fresh input and acetone recovered from the process			
Recovery / re	cycle / outputs			
O1	CS <sub>2</sub> recycled by condensation		Liquid	As per flowmeter / tank lev
	Acetone recycled by distillation			
O2	$CS_2$ recycled by activated carbon adsorption		Liquid	As per flowmeter / tank lev
	Acetone recycled through charcoal filters			
O3	Removal of $H_2S$ as NaHS or Na <sub>2</sub> S by alkaline wash and spray	Effluent / by-product	Liquid / Solid	Method 1: Product of inle difference in concentration outlet of the reactor or wet Method 2: Product of difference and concentration Estimate equivalent sulphu
04	Converted $H_2S$ and $CS_2$ into $H_2SO_4$ by oxidation using wet sulphuric acid process (WSA)	Wet sulphuric acid (WSA) technology	Liquid	Product of quantity (as p difference) and concentration Estimate equivalent sulphu supplementary sulphur (if a

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#### Method

evel difference

evel fifference

evel difference

let gas flow by flowmeter and ion of  $CS_2$  /  $H_2S$  at inlet and et scrubber.

quantity as per tank level tion as per lab or density meter. nur by calculation.

per flowmeter or tank level ition as per lab or density meter. hur by calculation. Deduct the f any).

## Table 2.C Mass balance of sulphur or acetone flows (continued)

Inputs		Notes	L/S/G	Test Method
Recovery / recycle / outputs (continued)				
O5*	Converted $H_2S$ and $CS_2$ into SOx by exhaust gas incineration / boiler followed by scrubbing of flue gases by lime to produce gypsum		Solid	Calculation given below
O6	Converted H <sub>2</sub> S, CS <sub>2</sub> or both to sulphur by biological or catalytic processes or redox process		Solid / Liquid	Method 1: Inlet gas flow by flowmeter and difference in concentration of $CS_2 / H_2S$ at inlet and outlet of the reactor or wet scrubber. Method 2: Product of quantity as per tank level difference and concentration as per lab or density meter. Estimate equivalent sulphur by calculation.

#### Incineration in coal fired boiler

Sulphur is fed into the boiler from the viscose process and is present in the coal itself. Both get converted to SOx in the boiler or incinerator. The SOx is scrubbed by lime to make gypsum. The flue gas from the boiler contains some remaining unscrubbed sulphur as SOx. The purity of gypsum varies depending on the flue gas desulphurisation process applied.

\*Calculation method for O5 (gypsum)

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Method				
, by flowmeter and differenc $H_2S$ at inlet and outlet of th				
ntity as per tank level differenc				

## Explanation about gypsum on scrubbing of flue gases from CPP Boilers (O5)

#### O5: (A+B) - (C+D)

Sulphur in: (A + B) where A: exhaust flow rate from VSF in m<sup>3</sup>/hr x equivalent sulphur mg/m<sup>3</sup> (from CS<sub>2</sub> and H<sub>2</sub>S) B: % sulphur in coal + quantity of coal (burnt in boilers in MT)

#### Sulphur out: (C+D)

C: (SO<sub>2</sub> in CPP boiler stack flue gas flow rate Nm<sup>3</sup>/hr x SO<sub>2</sub> mg/Nm<sup>3</sup>) x 32/64 D: (gypsum produced MT) x (32/120)

#### **Reactions:**

Dry scrubbing  $CaCO_{3(s)} + SO_{2(g)} \xrightarrow{\longrightarrow} CaSO_{3(s)} + CO_{2(q)}$ 

Wet Scrubbing  $Ca(OH)_{2(s)} + SO_{2(g)} \rightarrow CaSO_{3(s)} + H_2O_{(l)}$ 

# Chapter 3: Appendix C – Measurement of ambient air in the surroundings of the production facility

### Proposal

The ambient air emission measurement in the surrounding area of the production facility could be from direct monitoring (sampling and testing by an ISO 17025 accredited laboratory) or from air dispersion modelling. In both cases, the reported value is the estimated yearly average of the calendar year.

concentration of H<sub>2</sub>S and CS<sub>2</sub> for VSF/modal, VFY and NH<sub>3</sub> for cupro and the possible impact on the surrounding environment.

It is proposed that the assessment area begins at the fence and is completely within a circumference around the centre of the emission within a radius of one kilometre or less from the source.

#### Ambient air emission data from direct monitoring

Sampling and testing by an ISO 17025 accredited laboratory shall be done at least once a year considering:

- 1. That production is running AND
- the air sampling procedure.

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The definition of the assessment area must enable the proper assessment of the

2. The direction of the wind and potential areas are covered. It is imperative that an air sampling protocol contains all relevant and important information applicable to

#### Ambient air emission data from air dispersion modelling

Air dispersion modeling uses mathematical formulations to characterise the atmospheric processes that disperse a pollutant emitted by a source. Based on emissions and meteorological inputs, a dispersion model can be used to predict concentrations at selected downwind receptor locations.\*

Assessment of the ambient air emission of H<sub>2</sub>S, CS<sub>2</sub>, NH<sub>3</sub> and the possible impact on the surrounding environment can also be reported by air dispersion modelling which is estimated yearly average of the calendar year.

## Relevant organisations and contributions

- Canopy <u>click here</u>
- Techniques in the Production of Polymers August 2007) click here
- The Collaboration for Sustainable Development of Viscose (CV) click here
- <u>here</u>
- ZDHC Roadmap to Zero Programme click here
- Textile Exchange Recycled Claim Standard click here

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• The European IPPC Bureau (EU-BAT BREF Reference Document on Best Available • World Health Organization – Making Water a Part of Economic Development - click

<sup>\*</sup>Air Quality Dispersion Modeling, United State Environmental protection Agency, https://www.epa.gov/scram/air-quality-dispersion-modeling

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#### ZDHC MMCF Guidelines

