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

## **Revision history**

Version NumberChangesTime of publicationVersion 1.0Initial publication of the ZDHC Man-Made Cellulosic Fibres Production Wastewater Guidelines2020

### **Related Work**

This document is one part of a series of solutions provided by ZDHC. Manufacturing facilities are expected to comply with the solutions applicable to them, considering the type of processes conducted in their facility. For that the following documents must be taken into account:

ZDHC MMCF Guidelines - The three guidelines are related among each other.

#### **ZDHC MMCF Interim Air Emissions Guidelines**

ZDHC Air Emission Guidelines - under development

<u>Chemical Inventory List (CIL)</u>

## **Definitions**

To help understanding the implementation of our documents the following definitions will be used to indicate requirements, recommendations, permissions and/or possibilities:

- Shall: Used to indicate a requirement.

Should: Used to indicate a recommendation.

May: Used to indicate permission.

Can: Used to indicate possibility or capability.

For more definitions please <u>click here</u>.

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## **Abbreviations**

ETP	Centralised	EffluentTreatm	ent Plant

**CIL** Chemical Inventory List

**CMS** Chemical Management System

**Cupro** Cuprammonium rayon

**EN** European Norm

**ETP** Effluent Treatment Plant

**EU BAT BREF POL** EU-BAT BREF Reference Document on Best Available Techniques in the

Production of Polymers (August 2007)

**GB** Guojia Biaozhun (Chinese required national standard)

GB/T Guojia Biaozhun/Tuījiàn, (Chinese recommended national stadard)

HJ/T Chinese recommended environmental protection standard (Chinese

industry standard)

IPE Institute of Public & Environmental Affairs - Chinese Non-

Governmental Organization

**ISO** International Organization for Standardization

**LC** Liquid Chromatography

**MMCF** Man-Made Cellulosic Fibres

MRSL Manufacturing Restricted Substances List

**N/A** Not Available or Not Applicable

PTE Potential to Emit

RL Reporting Limit

**USEPA** United States Environmental Protection Agency

WHO World Health OrganizationWWTP Wastewater Treatment Plant

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## Summary

In the last years MMCF has become an increasingly important fibre category, stimulated by the growing number of brands that have committed to use of preferred fibres<sup>a</sup>. With its production volume doubled in past decades it is expected to continue its market growth due to MMCF's sustainable potential. The ZDHC Roadmap to Zero Programme (ZDHC) recognises the value of addressing hazardous substances that may be discharged into the environment, generated across the value chain of the textile and footwear industry, and decided to address MMCF production process by collaboratively creating an aligned approach for manufacturing

facilities by working towards a circular approach for the substances present in the process and to generate cleaner outputs from production.

As a multi-stakeholder initiative working towards a common goal, ZDHC understands that achieving it requires collaborative efforts in the industry. The ZDHC MMCF Guidelines is a set of guidelines that addresses integrated expectations for discharge wastewater quality, emissions to air, and chemical recovery for manufacturing facilities producing Man-Made Cellulosic Fibres.

## ZDHC MMCF Responsible Fibre Production Guidelines

ZDHC MMCF Interim Wastewater Guidelines

**ZDHC MMCF Interim Air Emissions Guidelines** 



Responsible practices to be verified

- % of Sulphur recovered and feeded again into the process.
- Sulphate recovery %
  - Sodium Sulphate Kg. of salt
     per tonne of fibre
     produced.
- Wastewater parameters in Load per tonne of fibre.
- To help give context to these values facillities can also share the raw material consumption.

By third parties, to be

defined by ZDHC

Wastewater parameters shall be tested

#### **Parameters**

#### Conventional

PH, Temp, Colour, COD, BOD, Oil & Grease, Total-N, NH4-N, TSS, Total-P, AOX, and Phenols.

#### Additional

Total Cr, Cd, Cu, Ni, Cr (VI), Pb, Hg,  $\Sigma$ -Hydrocarbons, and APEOs.

#### Specific

Zn, Sulphide, and CS2.



By ZDHC Accepted wastewater testing Laboratories

Ambient air parameters shall be tested

 $CS_2$  and  $H_2S$ 

Sulphur emissions to air shall be calculated

Mass balance calculations shall be used to estimate the Sulphur emissions to air

By third parties, to be defined by ZDHC

ZDHC MMCF Guidelines Version 1.0 | April 2020

<sup>&</sup>lt;sup>a</sup> Textile Exchange – Preferred Fibre & Materials.

### Introduction

The ZDHC Roadmap to Zero Programme (ZDHC) is a collaboration of brands, value chain affiliates and associates committed to eliminating hazardous substances from the textile, apparel and footwear value chain. ZDHC recognises that achieving this goal requires collaborative efforts in the industry, especially in regard to capacity building, time, technology, and innovation.

The ZDHC Programme recognises the value of addressing hazardous substances that may be discharged into the environment during the manufacture of materials used in the textile and footwear industry. That is hazardous substances, which could be used deep within the value chain and not just those substances that could be present in finished goods. Discharge of wastewater or air emissions containing hazardous substances could have a significant impact on the environment.

## **Background**

In January 2018 ZDHC commissioned an expert report on the production of Man-Made Cellulosic Fibres (MMCF). The report concluded that due to technical limitations, the inclusion to the ZDHC MRSL of the chemical substance Carbon disulphide (CS<sub>2</sub>) (used as a solvent for the production of Viscose and Modal) was not feasible - because a restriction of this chemical would halt the Viscose and Modal production processes. The conclusion was that the ZDHC Roadmap to Zero Programme could have substantial impact by collaboratively setting guidance around good chemical management. Alongside setting guidance limits for wastewater, sludge, air emissions and chemical recovery during fibre production while calling for continued further research into processes for the production of MMCF, using alternative and less hazardous substances.

## Objective

#### **ZDHC MMCF Guidelines**

During the last years MMCF has become an increasingly important fibre category, incentivised by the growing number of brands committed to the use of preferred fibres<sup>a</sup>. With its production volume doubled in past decades it is expected to continue its market growth due to MMCF's sustainable potential. For this reason, ZDHC decided to address its production process by collaboratively creating an aligned approach for manufacturing facilities to generate cleaner outputs from production while including a circular approach to its process.

The ZDHC MMCF Guidelines is a set of guidelines that addresses integrated expectations for discharge wastewater quality, emissions to air, and chemical recovery for manufacturing facilities producing Man-Made Cellulosic Fibres.

The complete set includes:

- ZDHC MMCF Responsible Fibre Production Guidelines
- ZDHC MMCF Interim Wastewater Guidelines
- ZDHC MMCF Interim Air Emissions Guidelines

The ZDHC MMCF Guidelines should be implemented as one, as the outputs from the production process of fibres cannot be seen as separate. These three documents provide guidance for an aligned industry approach. With this set of documents, ZDHC appeals to its members and the entire industry to improve the quality of discharged industrial wastewater and production-related emissions to air. With this, ZDHC expects also to support the transition of the production of MMCF towards a circular approach, by proposing recovery rates for substances such as Sulphur compounds.

ZDHC aims to catalyse a roadmap to define milestones for fibre manufacturing facilities to advance towards the production described in <u>EU BAT BREF Reference Document on Best Available Techniques for the Production of Polymers</u> (EU BAT BREF POL). Aiming to achieve integrated prevention and control of pollution arising from the production, leading to a high level of environmental protection (EUROPEAN COMMISSION - IPPC Bureau 2007).

<sup>&</sup>lt;sup>a</sup> Textile exchange – Preferred Fibre & Materials.

The scope expansion plan of this document includes the outputs proceeding from the dissolving pulp<sup>a</sup> for MMCF fibres, and other fibres including but not limited to:

- Viscose Filament Yarn<sup>a</sup>
- Modal Filament Yarn<sup>a</sup>
- Lyocell<sup>a</sup>
- Cupro
- Acetate
- Triacetate
- Fibres based on next generation feedstock

In this document a three-level approach is proposed:

- As manufacturing facilities are not identical in terms of capabilities, knowledge, strategic priorities or resources, this document provides a three-level (foundational, progressive, aspirational) approach for the limit values and/or recovery rates of the proposed parameters.
- Manufacturing facilities shall proactively develop and manage a datadriven, continuous improvement plan to reach the next level. To create this continuous improvement plan, ZDHC MMCF Implementation Guidelines should be observed.

#### Levels defined:

- Foundational: First level to be achieved by manufacturing facilities at minimum.
- Progressive<sup>b</sup>: AAn intermediate level to be achieved by manufacturing facilities through the application of technologies such as, but not limited to, those mentioned in the Reference Document: <u>EU-BAT BREF Reference Document on Best Available Techniques in the Production of Polymers</u>, (EU BAT BREF POL) corresponding to the viscose production processes.
- Aspirational: To become best in class, manufacturing facilities shall achieve the third level, through the application of technologies such as, but not limited to, those mentioned in the Reference Document: <u>EU-BAT BREF Reference</u>

Document on Best Available Techniques in the Production of Polymers (EU BAT BREF POL) applicable to viscose and beyond. This achievement sits alongside the supplier further enhancing their chemical management.

To learn more about the continuous improvement roadmap, see ZDHC MMCF Guidelines Implementation Plan.

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<sup>&</sup>lt;sup>a</sup> The work in order to add these fibres/process to the scope of this document will start in June 2020, and the publication date is yet to be defined,

<sup>&</sup>lt;sup>b</sup> Approximately 43% of the global production market have active commitments of reaching this level by 2023-2025.



## **ZDHC MMCF Air Emissions Guidelines**



This document will address the integrated expectations of the emissions to air, related to the priority hazardous chemicals used during production processes of MMCF.

This document specifies a unified set of parameters and limit values related to the production of Man-Made Cellulosic fibres. 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 emissions to air from the fibre production of MMCF and to minimise adverse impact in the environment and surrounding communities.
- Provide a unified approach for monitoring and testing for manufacturing facilities, for them to systematically and efficiently share emission data with brands(s) they work with, and/or other interested parties.
- Increase operational efficiencies by defining a standard cadence for air emission monitoring and reporting requirements, applicable to all brands and manufacturing facilities adopting this document.

## 1. Scope

This document applies to process-related air emissions 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

## 2. Requirements

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

Manufacturing facilities are expected to:

- Have a valid license to operate.
- Understand any air emissions dilution of exhausted systems to purposefully minimise concentration of pollutants is prohibited.

### 2.1. Minimum Requirements

- Quantify and track emissions of all parameters, consistent with standards and best practices of measurement and transparency.
- Follow generally accepted process engineering best practices for air emissions,
   to minimise environmental impact.

## 2.2. Inventory Management

To implement this guideline, all facilities shall have a live and functioning inventory management programme.

- Chemical Classification is required for input related chemical products which may have an impact on air emissions.
- Potential to Emit (PTE) can be calculated for key pollutants, as listed throughout this guideline.

## 2.3. Parameters and Limits for Viscose and Modal - Staple Fibre

Within the fibre production of viscose and modal there are two major Sulphur emissions,  $CS_2$  and  $H_2S$ , originating from  $CS_2$ . These should be condensed and recovered using different state of the art technologies such as condensation, Wet Sulphuric Acid (WSA) and Carbon Adsorption Process (CAP), mentioned in the EU BAT reference BAT technologies.

This document will focus on the following:

- A. Sulphur emission to air
- B. Ambient air outside the facility

Parameters and limit values can be found in Appendix A.

## General Principles for Monitoring, Testing and Reporting

The approach taken to monitor the selected parameters, include direct and indirect measurement methods. Complementing the mass balance (indirect method) the testing of ambient air (direct method) shall be conducted, to corroborate that those concern substances are not present above the given concentration.

#### To streamline efforts:

- Manufacturing facilities are encouraged to align the testing of this document with the testing required in their legal permit.
- Manufacturing facilities are expected to allow brands to conduct unannounced visits by ZDHC Accepted Laboratories or third-party verification bodies. Terms in which unannounced visits shall conducted are to be discussed with soliciting brand.

### 3.1. Monitoring

It is imperative that a measurement system or a continuous sampling/testing procedure shall be established in order to measure all necessary parameters. Any fugitive emissions shall be controlled and avoided using state-of-the-art technologies. It is therefore important, that MMCF manufacturers shall implement plans to reduce or avoid fugitive emissions.

## 3.2. Mass balance for the establishment of Sulphur Emission to air

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 a holistic balancing of all incoming and outgoing material flows, and it recommended to follow in principle the Directive 2010/75/EU of the European Parliament on industrial emissions - integrated pollution prevention and control. (European Union, 2010)

#### 3.2.1 Sulphur emission to air calculation

By applying a mass balance, the effectiveness of the emission control of Sulphur release to air can be calculated. 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 form or liquid form. Those recovered chemicals can be either re-used as part of the process or sold as a product. Some remaining Sulphur can be trapped in the sludge or liquid streams.

The formula for the mass balance can be found in Appendix A, Table 1.B.

## 3.3. Control Technologies for Sulphur release to Air

The viscose industry uses several technologies to control the emission of Sulphur to air during the manufacturing process. The major technologies in use in the industry are listed Appendix A, Table 1.B along with the product recovered.

## 3.4. Ambient Air Testing

Manufacturing facilities shall test the ambient air concentration outside the facility, of the key substances involved in the viscose and modal production process (CS<sub>2</sub> and H<sub>2</sub>S) to prove that the emissions-to-air do not exceed reporting limits set in this document.

The intention of air sampling and corresponding analytical testing, is to identify whether harmful substances related to the manufacturing process are present in the ambient air and if the concentration of these substances is within or above given limits.

In order to follow one standardised approach for the measurement of ambient air in the surrounding of the production facility, the ZDHC proposal therefore is attached in Appendix B.

#### 3.5. Test Methods

Where specific testing is required, standardised test methods shall be utilised, such as:

- Standard test methods shall be chosen for the region where the manufacturing occurs.
- 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 Reporting Frequency

- Sampling, testing, and reporting of ambient air parameters shall be completed at least twice a year. The reporting shall be at latest, following the 30 April and 31 October reporting deadlines.
- Sampling, testing and reporting can occur anytime during each of the reporting cycles, so long as there are at least three months between sampling for the two reporting deadlines. To illustrate:

April 30 reporting deadline	October 31 reporting deadline
<ul> <li>Sampling: 30 March</li> <li>Testing: 1 April</li> <li>Reporting: 18 April</li> </ul>	<ul> <li>Sampling: 2 July (this is at least three months after the above example sampling date for the 30 April reporting deadline)</li> <li>Testing: 3 July</li> <li>Reporting: 30 July</li> </ul>

- The reporting frequency for the mass balance calculation will be based on an annual verification. The reporting cycle shall start 1 May and will have a reporting deadline of 30 April. The reporting deadline shall be completed of 30 April of each year.
- 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 re-test ambient air as often as necessary to demonstrate the issue has been resolved.

## **Appendix A**

Table 1.A Parameters and Limit Values for production emissions and concentration of CS<sub>2</sub> and H<sub>2</sub>S in ambient air related to fibre production of Viscose and Modal

ZDHC limits	Sulphur emissions to air calculated through Mass balance	CS <sub>2</sub> (ambient air concentration outside the facility) - Reporting limit	H <sub>2</sub> S (ambient air concentration outside the facility) - Reporting limit
Unit	kg/ton dry MMCF (annual basis)	mg/Nm³	Reporting limit
Foundational	35 (a)		
Progressive	20 ( <sup>d</sup> )	0.10 ( <sup>b</sup> )	0.10 ( <sup>b, c</sup> )
Aspirational	12 ( <sup>d</sup> )		

<u>Disclaimer</u>: Due to an active review process of the TA Luft for Rayon and the EU BAT BREF WGS, CS<sub>2</sub> and H<sub>2</sub>S in total air(a) will not be included in this document, which were the basis of the literature review used in the creation of this document.

<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>&</sup>lt;sup>b</sup> Ministry of environment, forest and climate change of India from January 17, 2018.

<sup>&</sup>lt;sup>c</sup> In the next review process of this document the understanding of the possibilities of reaching a lower detection limit will be discussed.

d EU BAT BREF POL recommendation

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## Table 1.B Mass balance of special Sulphur flows

#### Formula for Mass Balance:

Sulphur emission to air = 11 - (O1 + O2 + O3 + O4 + O5 + O6 + O7)

Inpu	uts	Notes	L/S/G	Test method
11	$\mathrm{CS_2}$ addition to reactor including fresh input and $\mathrm{CS_2}$ recovered from the pro-cess (Churn/Xanthator).		Liquid	As per Flowmeter/ Tank Level Difference.
Rec	overy/Recycle/Outputs			
01	CS <sub>2</sub> recycled by condensation re-covery.		Liquid	As per Flowmeter/ Tank Level Difference.
O2	CS <sub>2</sub> recycled by activated carbon adsorption.		Liquid	As per Flowmeter/ Tank Level Difference.
О3	Removal of H <sub>2</sub> S as NaHS or Na <sub>2</sub> S by alkaline wash and spray.	Effluent/By-Product.	Liquid /Solid	Method 1: Product of inlet Gas flow by flowmeter and differ-ence in concentration of CS <sub>2</sub> /H <sub>2</sub> S at inlet & 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.
O4	Converted $H_2S$ and $CS_2$ into $H_2SO_4$ by conversion into Sulphuric Acid with oxidation.	Wet Sulphuric acid (WSA) Technology.	Liquid	Product of Quantity (as per Flowmeter or Tank Level Difference) and concentration as per Lab or Density meter. Estimate equiva-lent Sulphur by calculation. Deduct the supplementary Sulphur if fed (any).
O5	Converted H <sub>2</sub> S and CS <sub>2</sub> into SOx by exhaust gas incineration/ boil-er followed by scrubbing of flue gases by lime to produce Gyp-sum.	Flue gas de-sulphurisation.	Solid	Calculation given below.
06	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 con-centration of CS <sub>2</sub> /H <sub>2</sub> S at inlet & 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.

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#### **Calculation Method for O5 (Gypsum):**

#### Incineration in coal fired boiler

Sulphur is fed to the boiler from the viscose process and also there is Sulphur in coal, both get converted to SOx in boiler/incinerator. The SOx are scrubbed by lime to make Gypsum. The flue gas from boiler have some remaining unscrubbed Sulphur as SOx. The purity of Gypsum varies depending on the flue gas desulphurization process applied. Calculation method to estimate the Sulphur scrubbed by Gypsum: mass balance of Sulphur across the boiler/incinerator.

#### Sulphur In

A= Calculation of Sulphur with Exhaust gases of Viscose: Product of Exhaust gas flowrate and concentration of  $CS_2$  &  $H_2S$  (calculated as equivalent Sulphur) / day B= Sulphur content in Coal (total of the day) - Product Coal fed to boiler /day and Sulphur content in coal (as measured in Lab)

#### Sulphur Out

C= Sulphur out with Flue gases: product of flowrate of flue gases and SOx (as equivalent Sulphur) / day

Sulphur Released to air from Viscose Staple Fibre Process

 $D = (A \times C)/(A+B)$ 

O5 = A-D

# Appendix B Measurement of ambient air in the surroundings of the production facility

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#### Proposal

The definition of the assessment area must enable the proper assessment of the problem in question; the concentration of H<sub>2</sub>S and CS<sub>2</sub> 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 center of the emission within radius of maximum 1 kilometer from the source.

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

That production is running;

#### AND

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 the air sampling procedure.

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#### Relevant Organisations and Contributions

- Canopy <u>click here</u>
- Bluesign System <u>click here</u>
- The European IPPC Bureau (EU-BAT BREF Reference Document on Best Available Techniques in the Production of Polymers August 2007) <u>click here</u>
- The Collaboration for Sustainable Development of Viscose (CV) <u>click here</u>
- EU Eco Label <u>click here</u>
- World Health Organization Making Water a Part of Economic Development <u>click here</u>
- ZDHC Roadmap to Zero Programme click here

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#### **End Notes**

<u>i EUROPEAN COMMISSION - Reference Document on Best Available Techniques in the Production of Polymers August 2007</u>