Escola Tècnica Superior
d´Enginyeria Química

MASTER THESIS

MASTER'S IN ENVIRONMENTAL ENGINEERING AND SUSTAINBLE ENERGY

Process study and research to ensure compliance with current and future legislation on wastewater discharges and waste gas emissions

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Tarragona, Spain.

February 2022

Contents

List of tables

List of figures

Acronym table

ABS	Acrylonitrile-butadiene-styrene
ACA	Agencia Catalana del Agua
AITASA	Aguas Industriales de Tarragona S.A.
BAT	Best Available Technique
BREF	BAT Reference documents
CAPCA	Catálogo de Actividades Potencialmente Contaminadoras de la Atmósfera
CO	Carbon monoxide
CO_2	Carbon dioxide
CWW	Common Wastewater Treatment and Management in the Chemical Sector
GHS	Globally Harmonised System of Classification and Labelling of Chemicals
HAZOP	Hazard and Operability Study
IM	Inhibiting Matter
LSV	Limit Set Value
LVOC	Large Volume Organic Chemical
MCB	Monochlorobenzene
MDA	Metilendifenilamina
MDI	Difenilmetandiisocianato
MeOH	Methanol
MTD	Mejores Técnicas Disponibles
NaOH	Caustic soda
NH_4	Ammonium
NO_2	Nitrite
NO_3	Nitrate
PAH	Polycyclic Aromatic Hydrocarbons
PCDD/F	Polychlorinated dibenzo-dioxins and furans
PFD	Process Flow Diagram
PUR	Polyurethanes
SAN	Acrylonitrile-styrene
SSM	Solid Suspended Matter
TAR	Waste gas Thermal Oxidation
TOC	Total Organic Carbon
TSM	Total Suspended Matter
TSS	Total Suspended Solids
TVOC	Total Volatile Organic Carbon
WGC	Common Waste Gas and Treatment Systems in the Chemical Sector
WWTP	Wastewater Treatment Plant

Abstract

This Master Thesis develops the research process carried out during six months for the proposal of corrective actions to improve the environmental performance of a polymer producer, while complying with the legal requirements established by the European Union. The methods used to obtain results are described, discussed and lead to the conclusion of proposals; these include the organisation of analytical campaigns, collection of existing information and literature research. The study focuses on the Wastewater discharges regarding one specific parameter: the Inhibiting Matter; and on Waste gases relating to the emissions of nitrogen oxides. For the discussion of the results, graphs and tables are presented to have a simpler and more visual understanding of the data. Finally, the work carried out led to the following proposals: to continue the study of the Inhibiting Matter parameter (periodical monitoring of the different partial effluents) to maintain constant control of the same and, to identify the methanol generated in the production processes as a waste to be managed by a third party. With these corrective actions, it is expected to comply with the current applicable regulations and their future modifications.

Key words: wastewater, waste gas, legislation, Inhibiting Matter, nitrogen oxides.

Resumen

El presente Trabajo de Fin de Máster desarrolla el proceso de investigación realizado durante seis meses para la propuesta de acciones correctivas con el fin de mejorar el desempeño ambiental de una empresa productora de polímeros, al mismo tiempo que se cumplen los requisitos legales establecidos por la Unión Europea. Se describen los métodos utilizados para obtener resultados, los cuales se discuten y conducen a la conclusión de propuestas; estos incluyen la organización de campañas analíticas, recopilación de información existente e investigación bibliográfica. El estudio se enfoca en el vertido de aguas residuales orientado a un parámetro en específico: la Materia Inhibidora; y la emisión de gases residuales, con respecto a las emisiones de óxidos de nitrógeno. Para la discusión de resultados, se presentan gráficos y tablas que ayudan a tener una comprensión de los datos más sencilla y visual. Finalmente, el trabajo realizado condujo a presentar como propuestas: continuar el estudio del parámetro de Materia Inhibidora (control periódico de los diferentes efluentes parciales) para mantener un constante monitoreo de este y el identificar el metanol generado en los procesos de producción como un residuo que sea gestionado por un tercero. Con estas acciones correctivas, se espera cumplir con la normativa aplicable y sus futuras modificaciones.

Palabras clave: aguas residuales, gases residuales, legislación, Materia Inhibidora, óxidos de nitrógeno.

1. Introduction

This Master Thesis is done to present the research completed to propose alternatives to the company to comply with the current and future modifications on the applicable legislation established by the European Union thus, applicable in Spain. Emphasis is placed in wastewater discharges and gas emissions of nitrogen oxides (NOx), presenting the up-to-date legislation and the possible modifications, while complying with the regulation, it is expected to improve the company´s environmental performance when applying the proposed changes on the processes.

First of all, the goal and scope for the project are identified to expose the reasons for its development and the way to accomplish it. Then, the state of the art is presented; in this section all the relevant information of the existing processes is explained, as well as the wastewater and waste gas treatments and their current applicable legal frameworks, including laws not yet published. All the sections are catalogued by the two topics: wastewater and waste gas.

Afterwards, the methods are described for both matters, including the analysis campaigns and referring to previous campaigns and experiments done in the past years. Subsequently, the results are discussed to interpretate the data and to propose corrective actions as a tool to obtain conclusions, which are presented in last section, where all the work done, the results obtained and the proposals for the company are described.

Finally, in the conclusion the results are summarised, and the goal scope are discussed for determining if they were correctly achieved. Also, there is an extra section of appendices which includes the updates on two different subjects and extended tables are presented, in order to improving the readability of the project and having them present as a reference.

1.1. Problem statement:

The main problems to be solved are, as mentioned previously, focused on the future modifications on the European Union Legislation, specifically on the Best Available Techniques Reference Document, or well known as BREF, on Common Waste Gas and Treatment Systems in the Chemical Sector. The new version of the applicable BREF (BREF WGC) has not been published yet, but it expected to be published during the second semester of year 2022, and since that moment, the company has four years to comply with the requirements. This is one of the key reasons why the preventive actions are being studied and will be presented in this Master Thesis.

One of the requirements that are established on the BAT 2 from BREF CWW published in 2016 is to have an inventory with specific information from the processes. Although the company has the information, the objective was to compile it into a useful and effective file, including the most relevant information about the wastewater discharges and waste gas emissions. This will work as a tool to identify if any of the substances involved in the processes is relevant for monitoring purposes. Likewise, the BREF modifications will provide new limits for the nitrogen oxides emissions so, with the compiled information this is another matter to be discussed: to analyse and propose preventive or corrective actions to solve this issue and to improve the sustainable development of the current processes.

On the other hand, there is a parameter that has drawn attention to the monitoring of wastewater discharges since October 2020 when it was found higher anomalous values in internal controls; this is the Inhibiting Matter (IM). Therefore, the behaviour of the wastewater discharges must be analysed to discover the reason of the anomalous high values on the IM and at the same time, to figure out an alternative to manage it and prevent this episode from happening again.

The methods used to develop the project involved bibliographic research, compilation of existing information from the company, gathering information from personnel with specific subject matter expertise and organization of analysis campaigns to obtain new and reliable data from the current processes. Moreover, all the data analysis was done with the cooperation of the company´s supervisor with the aim of obtaining conclusions to propose efficient alternatives for the stated problem.

This project was done as a conclusion of the work experience developed from July 2021 to December 2021 in the company; it gathers all the research and job done during these months as a representation of the effort made and the conclusions obtained. Simultaneously, the motivation for solving the issue focuses on wanting to help improve the sustainable development of an international company, at the same time of demonstrating the capacity of applying the acquired knowledge through the bachelor´s and master´s degree.

2. Goal and scope

The goal of this project is to do research which results may help propose alternatives to reduce the environmental impact by Covestro processes regarding the wastewater discharges and waste gas emissions. The improvements are mainly addressed to comply with the future modification on the European Union normative, aiming to be in accordance with the legislation before it is applied.

The project was developed during six months, from July 2021 to December 2021. The planning involved research, experiments, and analysis of results to get a conclusion and proposal for assuring the continuous improvement of Covestro´s processes while reducing their environmental impact.

3. State of the art

3.1. Covestro

Covestro is a manufacturer that aims for the development of high-tech polymer materials focusing on innovation and sustainability. It became independent in the year

2015, coming from the German chemical company Bayer. Currently, Covestro maintains around 50 production sites around the world including small – scale and large – scale plants, all of them setting the standards for quality, efficiency, and safety.

The site of Covestro Tarragona is located in the municipality of La Canonja, in a Chemical Park, managed by Covestro which includes four external companies, which will be referred as Company A, Company B, Company C, Company D and the newest plant: ELO (CATAR project) by Covestro. The production processes of each of the companies are the following:

- **Company A**: logistics and transport for the chemical industry.
- **Covestro – ELO (CATAR project)**: production of chlorine and caustic soda (NaOH); an intermediate product used to produce Covestro´s main product: MDI. This plant is being constructed and will be put in service during 2022.
- **Covestro – Utilities**: energies department; production of steam and electricity by a cogeneration plant run by natural gas and a back-up boiler that can work by natural gas or gasoil when needed (tests and emergency situations). This plant provides steam and electricity to Covestro plant and supplements resources to other plants in the industrial park, such as cooling water, industrial water, air, among others.
- **Covestro – MDI Train**: production of MDI isocyanate, which is integrated by the following sub-plants: carbon monoxide, MDA and MDI.
  - **Production of carbon monoxide:**
    Made by an uncomplete combustion of coke with oxygen and carbon dioxide. This is carried out by washing with water, filtration, desulfurization and drying.
  - **Production of Diamino diphenyl methane MDA:**
    This production process is an intermediate step for the MDI manufacturing. Aniline and formaldehyde are used to produce MDA. The process consists of stages of neutralization, decantation and drying.
  - **Production of Diphenyl methane diisocyanate MDI:**
    The MDI is Covestro´s main product, which is produced from chlorine, carbon monoxide and MDA, using monochlorobenze as solvent media for the synthesis.
- **Company B**: manufacture of plastics Acrylonitrile-Butadiene-Styrene (ABS) and Acrylonitrile-Styrene (SAN).
- **Company C**: production of compounds for wastewater treatment and for the paper industry. Its main production processes are mentioned below.
  - Manufacture of aluminium polychloride (PAX unit).
  - Manufacture of aluminium sulphate (ALS unit).
  - Manufacture of ferric chloride (PIX unit).
  - Manufacture of hydrores (AKD unit).

- **Company D**: production of polyurethane and polyester systems from isocyanates and other raw materials.

3.2. Wastewater discharges

3.2.1. Flowrates

The flowrates of each of the companies must be taken into account for the analysis and study of the wastewater behaviour; this because the flowrate is a variable that can affect either in a positive or a negative way to the final discharges. Figure 3.1 presents the percentage of the partial flows into the total discharge. This tool helps visualize which flowrate has the most influence on the final discharge; therefore, which one of them could be the responsible of unusual values on the monthly analysed parameters.

The ELO´s discharges are not counted into the total final discharge yet, since the plant is still under construction, so the flowrate value cannot be taken as representative as the rest of them.

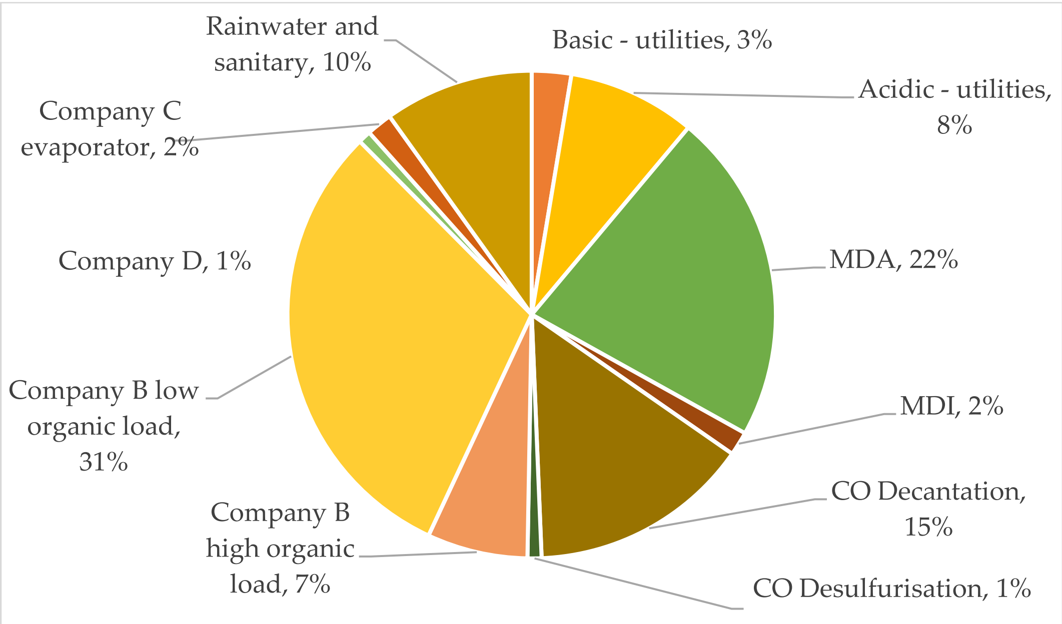

FIGURE 3.1 PARTIAL FLOWRATES

Source: own elaboration.

3.2.2. Temperature

Furthermore, it is important to maintain a temperature control in order not to affect the wastewater treatment facilities. Table 3.1 presents the average and maximum temperatures of the partial flows with available measurement; this information was obtained from documents and personal answers from the head personnel of the processes. These data are taken as indicative and as a tool to monitor the performance of the discharges and prevent possible damage to the pipelines and equipment.

TABLE 3.1 ENDPOINT AND PARTIAL FLOWS TEMPERATURES

	Usual temperature, °C	Maximum theoretical temperature, °C
Endpoint	≈30	50
Tank 15B100 Company B	≈30	60
Underground pit	<50	<50
MDI´s pit	40	100
Desulphurisation Company B	RT[1]	RT[1]
Decantation CO	60	100
Utilities – Acidic	35	45
Company D pit	RT[1]	RT[1]
Company D distillation pots	80	NA[2]
Company D cleaning water	60	NA[2]
Company D condensate drain	90	NA[2]
Company C evaporator	NA[2]	NA[2]
ELO (CATAR project)	<40	NA[2]
Utilities – Basic	25	45
MDA AW2	40	100
Desulfurization CO	45	100

Source: own elaboration.

Even though the maximum temperature is established to be 100°C, the data collected from previous years demonstrates that 80ºC happens to be a more realistic approximation of this scenario. Also, about the Company D wastewater which normal temperature is of 90°C, it only occurs when there are maintenance periods.

Regarding the two homogenisation tanks, the temperature from the previous two years has been maintained lower than 40°C. According to the HAZOP made in 2019, it is recommended the temperatures not to get higher than 50°C since this could cause corrosion into the discharging pipelines; hence, for all the pipelines there are control probes installed in order to avoid an anomalous temperature elevation.

3.2.3. Composition

As said before, the wastewater discharges of the companies are treated by the Industrial Park Covestro, which has the responsibility for the management and final treatment (homogenisation and neutralisation) of the wastewater before discharging it into AITASA (by its acronym in Spanish: *Aguas Industriales de Tarragona*) wastewater system. The composition of the discharges depends on the processes of each one of the industries productions, however, the final discharge shall comply with the established limits by the environmental authorization following the Law 20/2009.

Every month, an external laboratory oversees doing the monitoring analysis of the endpoint water discharges, and the results must be sent to the Administration

[1] RT: Room Temperature

[2] NA: Not Available; Information could not be obtained.

quarterly. On the other hand, approximately every three months in addition to these monthly monitoring, the site undergoes an inspection by the Administration (Water Agency of Catalonia, ACA) and simultaneously a counter sample is taken and analysed to demonstrate that the monitoring presents veridical results. Also, once a year, the external laboratory checks up the collected rainwater to maintain a control of the main parameters regarding this flow.

These monthly monitoring help the company keep control of their discharges, the wastewater composition, and the performance of the wastewater treatments. The main parameters that are checked every month are presented on Table 3.2; once a year it is done a total check-up including more parameters such as heavy metals and compounds that are used in any of the industry´s processes.

TABLE 3.2 MONTHLY MONITORED PARAMETERS

Parameter	Units
pH	ud pH
Total Organic Carbon (TOC)	mg/l
Total Suspended Matter (TSM)	mg/l
Chemical Oxygen Demand (COD) [3]	mg O_2/l
Biological Oxygen Demand (BOD5)	mg O_2/l
Chlorides	mg Cl/l
Total Hydrocarbons	mg/l
Anionic surfactants	mg LSF/l
Organic and ammoniacal nitrogen	mg N/l
Total phosphorus	mg P/l
Phosphates	mg P/l
Inhibiting Matter (IM)	Equitox/m^3

Source: own elaboration.

For simplicity, hereafter the unit for IM: equitox/m^3, will be referred as "ut" meaning units of toxicity.

Main parameters

All the parameters are monitored by an external laboratory that collects the samples and analyses them once a month. Regarding the aniline it is monitored as an intern requisite following what is established in the BREF for the production of Large Volume Organic Chemical (LVOC) (for further information see section BREF Large Volume Organic Chemical), even though there is no specific limit. Correspondingly, the styrene is checked monthly as a matter of intern requisite to maintain record of the values in case there are unusual, punctual, episodes. On the following pages, are

[3] When the effluent contains a high concentration of chlorides, the control parameter of the organic content in the discharged water will be the TOC.

briefly described the most relevant parameters for this study, which are: the pH, Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and Inhibiting Matter (IM); nevertheless, it is important to mention that the parameter used to monitor the organic matter in the endpoint discharge is the TOC, because when the rest of the mentioned parameters had been checked, usually there are some analytical interferences (i.e. the high chlorides concentration) that affect the results; however, the monitoring of these parameters let have a record of the data.

PH

This is one of the most usual measured parameters for the water´s characterisation; this, due to the importance of an optimal pH value for having an efficient biological performance of the wastewater treatment (Martínez Soza, n.d). the pH refers to the negative logarithm of the Hydrogen ion concentration and it is recommended to be neutral, having values around 6 – 9 units to protect the organisms (Goksel, Oznur, Gulyas, & Bust). It is important to measure the pH because have excessive low or high pH can have negative effects on human and aquatic life; also, when disinfecting the water, the chlorine is inhibited and it is needed to use more of it in order to disinfect the effluent and hence, raise the pH to a higher value. When talking about an acidic flow, it can dissolve and corrode metals polluting the discharge (AnalyticalTechnology, 2019); also important, an acidic water is capable of degrading the pipes thus driving up maintenance costs (Nyle & Weil, 2002).

TOTAL ORGANIC CARBON

This parameter measures the organic matter present in water, the TOC it only comprises the carbon compounds identified as organic; when talking about inorganic carbon such as carbon dioxide, hydrogen carbonate, cyanides, etc., is identified as Total Inorganic Carbon (Goksel, Oznur, Gulyas, & Bust). The TOC helps assess the organic load of an effluent, which is important to recognize the presence or absence of organic compounds, such as alcohols or proteins that could affect the wastewater treatment (HACH, 2016).

Figure 3.2 specifies the chemistry of the Total Organic Carbon, the Dissolved Organic Carbon, the Biological Oxygen Demand and the Chemical Oxygen Demand; this, in order to differentiate the two kinds of parameters since they differ on the measurement principle: the first two of them are used to measure the emission of carbon dioxide (CO_2) once the oxygen has been converted, while the BOD and COD measure the demand of oxygen, as their name indicates.

Same figure (Figure 3.2), exposes the reaction between Tyrosine ($C_9H_{11}NO_3$) and oxygen, when converting into carbon dioxide, water, and ammonia (NH_3). This is just an example of the reaction of one of the main 20 standard amino acids that are used to synthesize proteins (Mantech, 2018).

The measurement of the TOC is done following the guidelines of the UNE-EN 1484:1998 for the determination of total organic carbon (TOC); the methodology consists of a catalytic combustion of the organic carbon to obtain carbon dioxide, which is then detected by infrared spectrometry (UNE, UNE-EN 1484:1998 (NPOC), 2013).

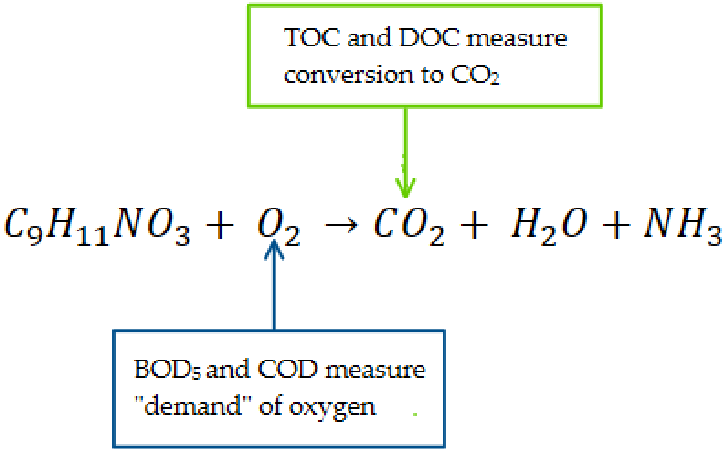

FIGURE 3.2 CHEMISTRY OF BOD, COD, TOC, AND DOC

Source: own elaboration

CHEMICAL OXYGEN DEMAND

The Chemical Oxygen Demand (COD) refers to the measurement of the Oxygen consumed by organic matter present in the effluent; it is expressed as how much oxygen is consumed by an oxidant when doing the test (Programs, COD, 2019). This parameter is used to tune the short – term impact of the effluents on the discharging water (Hach, 2021); this helps to have an accurate modeling of the biotransformation for designing the corresponding wastewater treatment for the effluent concerned (Hu & Grasso, 2005).

Normally, the COD value is higher than the BOD because it is easier the organic compounds to be oxidised chemically than biologically (Butlerms, 2013); nevertheless, the ratio between both of them in implicated in the Biodegradability parameter, which is described below.

BIOLOGICAL OXYGEN DEMAND

Then, another parameter relevant in the characterisation of the effluent is the Biological Oxygen Demand (BOD), which is used to determine the pollution load of the waste water, measuring the oxygen consumed by the micro-organisms contained in the water, usually analysed over five days (Programs, BOD5, 2019); the parameter is expressed as the milligrams of Oxygen used to break down the organic matter contained in one litre of water [mgO_2/L] (Leverage, n.d). The value of the BOD also indicates how clean the water is, if the BOD has a high value, it means that the water is highly polluted, while when the value is low the water is less polluted (AOS, 2018).

The method to estimate the BOD_5 requires five days to evaluate it, which sometimes means a drawback for the analysis of the characterisation of the effluent, since it is not suitable for real-time evaluation (Kumar & Kumar, 2005).

BIODEGRADABILITY

Water biodegradability can be evaluated by the biodegradability index which is given by the ratio of the Chemical Oxygen Demand and the Biochemical Oxygen Demand (COD/BOD_5), even though it can also be established inversely (BOD_5/COD). Table 3.3 presents the used values to determine the water´s biodegradability (Martínez Soza, n.d). Even though this parameter is not directly evaluated, it is relevant for the characterization of a flow, therefore it is useful for this study.

TABLE 3.3 BIODEGRADABILITY INDEX

	Biodegradable	Moderately biodegradable	Non biodegradable
COD/BOD_5	< 2,5	2,5 – 4	> 4

Source: own elaboration.

INHIBITING MATTER

The characterization of the wastewater in Spain and the European Union is focused not only on complying environmental standards but on objectives related to the water quality; that is why the biotoxicity is one of the parameters that must be analysed when discharging water back to the environment. The test consists of verifying the natural conditions to be optimal for the reproduction of the living organisms (Marín Galvín R. , 1995).

The *Vibrio fischeri* test is used due to its simplicity and accuracy regarding the biotoxicity of the wastewater. This work out by the bioluminescence of the bacteria, meaning that the more toxic the water is, the less luminescence the bacteria present (Marín Galvín, Pérez de Siles, & Chamber Pérez). The *Vibrio fischeri* bacteria is used as it is a photobacteria that presents bioluminescence when there is enzyme catalysis, being suitable for the IM test (Abbas, et al., 2018). It is worth mentioning that the bioluminescence test cannot qualify a flow as toxic; instead, it is needed to develop different tests in order them to be complementary and determine the biotoxicity of the effluent. However, there is no evidence of a direct relation between the biotoxicity and the biodegradability (important parameter described further on section Biodegradability), so the determination of this relation is not relevant for this study.

The method used by the external laboratory complies with the specifications established by the ISO UNE-EN 11348-1; the pH is adjusted to be neutral either with chloride acid or with sodium hydroxide, since it has been demonstrated that it can affect the testing; however, this variable is studied and discussed on this project. In addition, partial flows samples are taken before collecting the sample of the final discharge in order to have coherent results, the most similar to a real situation.

VARIABLES AFFECTING THE INHIBITING MATTER

It has been demonstrated that the pH is one of the variables that may affect the inhibiting matter parameter on the water discharges. Following the experiments made in 2017[4] and the bibliography studied, it has been proven that it exists an interference when analysing the samples; that is why it is required the test to be done with an adjustment of pH to be neutral (around 7).

In 2017, a series of experiments were organised, and these helped demonstrate the influence of the pH on the samples; specifically, with one partial flow which results varied significantly when adjusting the pH. During the period of June 2017 and January 2018, the IM parameter was analysed as usual, for the monthly monitoring and the Administration´s inspections.

For a specific partial flow, the first result obtained (without pH neutralisation) was around 6.000 ut, this was unexpected although, the endpoint IM result resulted to be lower than 2. Then, again a sample of the same partial effluent without pH adjustment gave results >100 ut, while the endpoint flow had IM values lower than 2 ut.

Following the analytical interferences that can exist when analysing the Inhibiting Matter indicated in the UNE-EN 11348-1, the pH directly affects the bacteria´s luminescence, recommending an optimal range between 6 upH and 8,5 upH (UNE, UNE-EN 11348-1, 2009). Therefore, as the endpoint discharges have neutral pH, it was demonstrated the influence of the pH and it was decided to require the neutralisation of the pH before testing the samples; later, the results started to have more realistic values lower than 25 ut.

When it was proven that the pH has an influence on the IM, it was established to study the chemical substances that could cause toxicity in the wastewater to identify them and thus, have a control on the IM. Detecting the compounds causing toxicity, could be of help to know their behaviour when being in contact with any other compound and to know if they can be degraded before being discharged into the endpoint effluent.

Similarly, as mentioned in the section Flowrates it has been proved that it is an important variable regarding the IM, due to the fact that they can act either as dilution factor or as a large input that can affect the flow composition. It is important to have knowledge of the wastewater discharges behaviour and their regime, in order to know their real influence on the endpoint discharge.

The influence of the flowrate on the IM parameter can also be proven with was previously mentioned, whenever a partial flowrate had a high value, the endpoint

[4] Company´s internal file.

discharge resulted to have an IM value lower than 2 ut; this demonstrate the capacity of a flow for being influential or non-representative.

As well, heavy metals can represent affectation on the water toxicity; according to the retrieved bibliography there is a study made in 2004, in which it was found that the four main heavy metals that can affect it are: mercury, lead, arsenic and cadmium (Hsieh, Tsai, Ryan, & Pancorbo). Then, in other retrieved experiment made in 2006 (Ishaque, et al.) the effect of these metals was studied, and it was determined that the degree of toxicity from highest to lowest is the following:

Mercury > Lead > Cadmium > Arsenic

(Ishaque, et al., 2006).

Heavy metals are analysed three times per year on the endpoint flow, in order to maintain control and tracking of their concentrations. However, analysing the data compiled from the past years 2016 – 2021[5], the values for the heavy metals were not found to be representative in the IM study samples.

On the other hand, the partial flows contain certain compounds that may be the cause of the high values on the Inhibiting Matter parameter. According to the compounds used in the different production processes involved on the wastewater discharges, a risk assessment is presented below, to help identify the compounds that have the highest toxicity rating, meaning that they must be kept under continuous tracking and monitoring.

The extended version for the risk assessment done for the mentioned compounds is included in the Appendices section (Table 8.3), all the hazard categories for the compounds are presented.

Table 3.4 presents the main compounds that were identified as relevant for the study on the influence of their concentration for the IM parameter. The toxicity category is established on the regulation 1272/2008 (MinisteriodeSanidad, 2008) following the classification established by the European Commission.

H stands for Hazard identification and classification established by the United Nation´s Globally Harmonised System of Classification and Labelling of Chemicals (GHS); which is responsible for providing "uniform physical, environmental, and health and safety information on hazardous chemical substances" (EuropeanComission, 2008). This system was created in 2002 and regularly it is updated; the current version that is implemented is from year 2008.

[5] Company´s internal file.

The categories are described below:

- **Category 1: H400** – Very toxic to the aquatic environment with long lasting effects - Acute hazard.
- **Category 2: H401** – Toxic to aquatic organisms with lasting effects – Acute danger.
- **Category 3: H411** – Toxic to aquatic life with long lasting effects.
- **Category 4: H412** - Harmful to the aquatic environment with long lasting effects.

TABLE 3.4 RELEVANT COMPONENTS AND THEIR ESTABLISHED LIMIT

Component	Maximum established limit, mg/L	Toxicity category
Aniline	No limit	H400
Acrylonitrile	No limit	H411
Phenol	2	H411
Monochlorobenzene	0,5	H411
Styrene	0,5	H412
Ethylbenzene	0,5	H412

Source: own elaboration.

3.2.4. Wastewater treatments

There are wastewater treatments for every partial effluent from the plants before entering into the final wastewater tank, which leads to the endpoint flow. These treatments are unique for each of the processes since they are adapted to their flow characteristics and necessities. As it is known, a wastewater treatment can be of different kinds and for different objectives, depending on what use the water will have; this has to be with the current legislation, which is explained in section Legal framework, Wastewater discharges.

The assurance and control wastewater system of the Industrial Park can be easily explained by the distribution of pipelines, which is according to the type of flow: acidic and neutral flows, basic flows, sewage water, high organic load water and rainwater. Figure 3.3 presents a simplified version of the flow diagram of the wastewater discharges before getting to the final discharge point, which is sent to AITASA pipeline system.

AITASA refers to "*Aguas Industriales de Tarragona*", which is a public limited company founded in 1965 to supply water to industries in Tarragona, in this case to the chemical industries. Covestro is currently one of the shareholders of AITASA and the wastewater from the Covestro Industrial Park is sent to the joined wastewater pipeline managed by AITASA. Furthermore, AITASA is leading a project to have a Common Wastewater Treatment Plant for the companies of the Chemical Cluster. Covestro is participating in this AITASA project (AITASA, 2021). The Common

Wastewater Treatment Plant is under construction and will be put in service during the 1st semester of 2022.

In Figure 3.3 it is seen that depending on the type of flow, the water first goes to a specific tank in order to be treated or for storage, before entering into the main homogenisation tank which is the last step before discharging the wastewater into AITASA´s installations. As it is shown, there are two big tanks before AITASA, both are for homogenising the wastewater, but one of them is used as a back-up tank in case of emergency or in case of maintenance of the other tank.

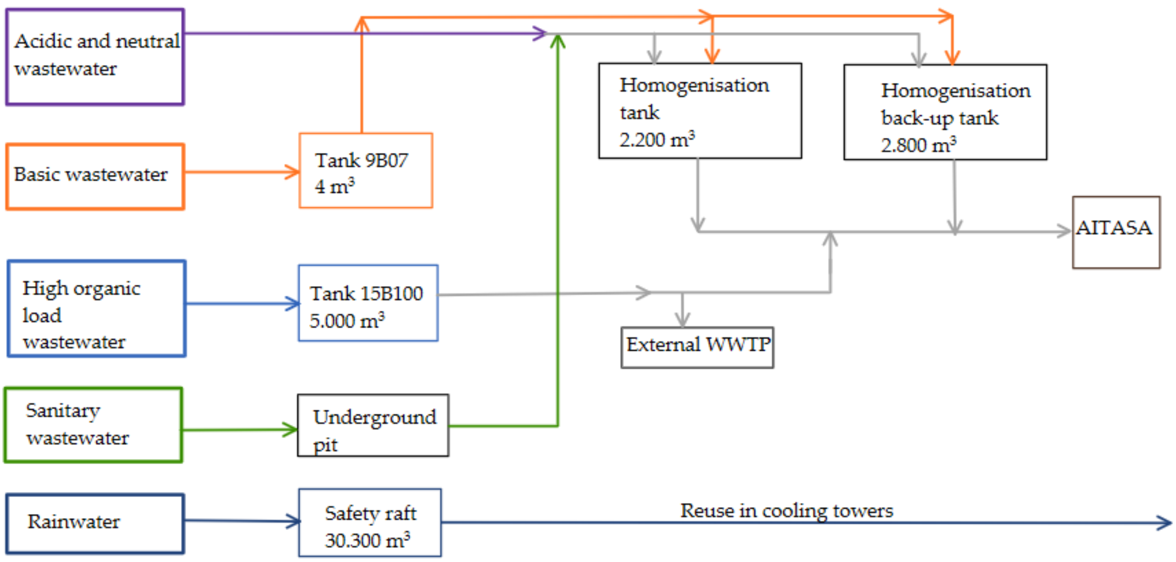

FIGURE 3.3 SIMPLIFIED FLOW DIAGRAM OF WASTEWATER DISCHARGES

Source: own elaboration.

Wastewater treatment differs on every process because of the characteristics of the discharges, but it can include physical-chemical treatment, external biological treatment, or adsorption with activated carbon. Rainwater flow doesn't have a specific treatment, it is monitored once a year by the external laboratory, to have control of their characteristics, to treat it in case of unusual composition and to comply with the regulation; nevertheless, fortnightly conductivity is registered internally and quarterly other parameters such as pH, TOC. It is worth to mention that since 2014, the rainwater collected in the rainwater pond is reused in the cooling towers (instead of being discharged into the Sea), taking advantage of a natural resource, and decreasing the use of new water.

As seen in Figure 3.3, the wastewater discharges are mainly classified by its pH, separating them using different pipelines and, in for the basic wastewater, a previous tank before mixing them in the homogenisation tank, which is the previous step before discharging them into AITASA´s system. Similarly, for an effluent from company B with a high organic load, wastewater is previously collected into another tank before including them into the last pipeline with the mixed effluents from other discharges, also, a fraction of their discharges is diverted into an external Wastewater Treatment Plant (WWTP).

For the acidic and neutral discharges, both are treated as a whole and managed directly with the homogenisation tank. However, the sanitary wastewater is previously collected in an underground pit before joining them with the acidic and neutral wastewater.

Regarding the wastewater treatment, there is not a central treatment plant, but each process has its own specific integrated treatment to manage their wastewater before discharging them. Covestro´s treatment processes are briefly described next:

- Cleaning water from CO production
  1. Coagulation – flocculation
  2. Decantation and filtration
  3. Adsorption by activated carbon

- Desulphurisation water from CO production
  1. Chemical oxidation with hydrogen peroxide (H_2O_2)
  2. Adsorption by activated carbon

- Water from MDA production
  1. Counter current liquid – liquid extraction
  2. Stripping with vapour or distillation
  3. Neutralisation
  4. Adsorption by activated carbon

- Water from MDI production
  1. Adsorption by activated carbon

- Water from the new chloride plant
  1. Neutralisation and reaction with disulphide

3.3. Waste gas emissions

Currently, in Covestro the monitoring only must be made for 6 combustion emission sources and 6 process emission sources. Following the current Tarragona Covestro´s Environmental Authorization, the Waste gas emission sources that are monitored are the boilers 5 and 6 of the thermal power plant and the backup boiler 4, also the TAR-MDI is a gas emission source, as so as is the hydrochloric acid scrubber and the emergency stack; Table 3.5 presents these mentioned emission sources and their classification regarding the type of source which are: combustion source or process source, both identified as systematic emissions.

The emission sources are characterized by their type of emission, they can be of combustion or process, these differ in the parameters that must be analysed. Sources 2 and 3 constitute the cogeneration thermal plant. The TAR/MDI refers to the installation of Waste gas Thermal Oxidation (TAR for its acronym in German), where the volatile organic compounds are eliminated by thermal oxidation using natural gas as fuel to maintain the high temperature in the burner. Additionally, as complementary fuel is used methanol coming from MDA production process

TABLE 3.5 EMISSION SOURCES

Nº source	Type of source	Description
1.	Combustion	Boiler 4
2.		Gas turbine 1 + Natural gas boiler 5
3.		Gas turbine 2 + boiler 6
4.	Process	TAR/MDI
5.		MDI emergency stack
6.		HCl scrubber

Source: own elaboration.

On Table 3.6 it can be seen the difference between the analytics and how they depend on the type of emission source and the fuel used.

TABLE 3.6 WASTE GAS EMISSION ANALYTIC PARAMETERS

Analytic parameter	TAR–MDI[6]	Boiler 5 (TG1-C5)	Boiler 6 (TG2-C6)	Back-up boiler 4
NOx (NO_2)	X	X	X	X
Carbon monoxide (CO)	X	X	X	X
Hydrochloric acid (HCl)	X			
Chlorine (Cl_2)	X			
Volatile Organic Compounds (VOC)	X			
Phosgene	X			
Aniline	X			
MDI	X			
MDA	X			
Formaldehyde	X			
Chlorobenzene	X			
Dichlorobenzene	X			
Dioxins and Furans (PCDD/PCDF)	X			
Total Suspended Particles (TSP)				X[7]
Sulphur dioxide (SO_2)				X[7]

Source: own elaboration.

[6] Maximum downtime: 200 h/year, waste gases must be sent to an emergency stack.
[7] In case the boiler is run with gasoil.

The depuration systems of the TAR consist of thermal oxidation and a wet scrubber. While the TAR operates either with natural gas or the mix of natural gas plus methanol which comes as a waste flow from the MDA production process. With this method the natural gas consumption in the TAR is reduced and the emissions, related to the methanol transport to an external treatment, are avoided.

3.3.1. Nitrogen oxides emissions

The emissions of nitrogen oxides come from the oxidation of air in the thermal waste gas treatment in the TAR, as well as from the oxidation of methanol condensates, which has the following composition: 75% methanol, water 15%, 10% ammonia (NH_3) and <1% of aniline. Methanol (MeOH) is used as a stabilizer in the formalin, a raw material for the production of MDA, which is an intermediate product for the MDI´s production.

Also, methanol is used as fuel substitute in the TAR at the same site where methanol is generated, thus there is no need to further manage it. Regarding an environmental impact assessment made by Covestro Deutschland in 2021 for the methanol removal, this is the process that represents the lowest environmental impact comparing to other four alternatives (Covestro, 2021). In this study, the alternatives studied included incinerating the methanol as waste or high caloric fuel or using it as auxiliary material for anaerobic or aerobic wastewater treatment plant processes.

In 2017, a study of the NOx emissions was made; the relation between the NOx emissions versus the methanol burned were studied. At the same time variables as: the boiler temperature and the air flowrate were considered for the study. It is important to mention that the NOx emissions are originated from the ammonia (NH_3) contained in methanol condensates, not directly from burning the methanol.

In conclusion, the values obtained for having optimal conditions were: 900ºC for the thermal oxidation in the TAR, 2.000 Nm^3/h of air flowrate and 45 kg/h for the methanol mass flow. Applying these conditions, the NOx emissions proved to be sufficiently complying with the current BREF WGC´s limit of 350 mg/Nm^3.

3.4. Legal framework

As said in the previous pages, the applicable legislation depends on the type of production the industries have and the kind of compounds they use. In order to summarize this information, this section presents the enforceable legislation for Covestro, beginning with the applicable legislation for both matters: wastewater and waste gas, then Covestro´s activity classification is described, next the current regulations for wastewater and for waste gas involved in the processes is stated.

3.4.1. BREF Large Volume Organic Chemical

The Best Available Technique Reference Document (BREF) for the Large Volume Organic Chemical (LVOC) applies to the company since their production complies with the characteristics of a manufacturer of LVOC, such as continuously operating plants of capacity higher than 20 Kton/year, and production of "chemicals used in large quantities as raw materials in the synthesis of other chemicals" (European Commission, 2017). This BREF follows the Directive 2010/75/EU of the European Parliament and of the Council, for the production of Large Volume Organic Chemicals.

Wastewater discharges

For the wastewater discharges que BAT to be followed are the following:

- BAT 72
  This has to be applied for the wastewater discharges to recover solvents and thus, to reuse the water in order to optimise the design and the performance and to reduce the organic load that could be discharged from the processes.

- BAT 68
  As mentioned before (see section Main parameters), the aniline must be monitored once a month because that component is used for the MDI production established by the BREF LVOC and concluded in this BAT. The aniline is used in the MDA´s installations nevertheless, this parameter is only measured at the endpoint, monthly for legal matters, but internally it is analysed weekly and with the external laboratory periodically.
  Also, this BAT establishes the need of monitor the Total Organic Carbon (TOC) which is mainly found in the MDI´s installations as so as the chlorinated solvents; both of them are monitored once per month at the MDI´s endpoint. In case of discontinuous discharges, the minimum frequency required for doing the monitoring is every time the discharge is made.

Waste gas emissions

For the waste gas emissions matter, the BREF LVOC applies to the MDI/MDA production plant, and the Best Available Techniques applicable to the MDI/MDA production plant are the following:

- BAT 2
  This requires monitoring not continuously but every month. Except for the Polychlorinated dibenzo-dioxins and furans (PCDD/F) which must be monitored every 6 months or annually if the emission levels demonstrate to be stable. The parameters monitored and their limits are:

  - TVOC: 1 – 5 mg/Nm^3.
  - Tetrachloromethane: <0,5 g/tMDI
  - Cl_2: <1 mg/Nm^3

- HCl: 2 – 10 mg/Nm^3
- PCDD/F: 0,025 – 0,08 ng I-TEQ/Nm^3

- BAT 66
  Then, the BAT 66 refers to the treatment of the mixed flows of the waste gas using a thermal oxidiser followed by caustic scrubbing. This has the objective of reducing the emissions to atmosphere of organic compounds, HCl and chlorine. The parameters monitored and their limits are same as in the BAT 2 (previously mentioned).

The emission limits for the NOx are not established in this BREF LVOC, but in the BREF Common Waste Gas Treatment in the Chemical Sector (not published yet, and mentioned below).

3.4.2. Covestro´s activity classification

Law 20/2009 establishes three classifications for the Covestro´s production processes, which are the following:

- Chemical installations manufacturing product basic organic chemicals (nitrogenous hydrocarbons, isocyanates) [Annex I.1 Section 5.1d].
- Installations for combustion with a power thermal energy of more than 50 MW [Annex I.1 Section 1.1].
- Activities and facilities affected by accident legislation serious [Annex I.2 Section 12.1].

This classification requires Covestro to have an integrated environmental authorization to operate its activity.

3.4.3. Wastewater discharges

There are different normative regarding the wastewater discharges that shall be followed, they are commented on the following pages and listed as follows:

- Environmental authorization.
- Environmental evaluation.
- BREF Common Wastewater (CWW).
- BREF Large Volume Organic Chemical (LVOC).

Environmental authorization and evaluation

The Environmental Authorisation was requested following the procedures established on Law 20/2009 on prevention and environmental control of activities. All the documentation and the content of it, complies with the mentioned law and with Law

16/2002 on integration pollution prevention and control, which has been modified by Law 5/2013.

The compliance of the established conditions is done by monitoring and inspections, following what is established on the mentioned laws and the article 12 from the Real Decreto 815/2013.

The limits for the wastewater discharges are established on the Environmental authorization, specifically for 36 parameters. These are controlled by intern analysis, using online analysers (either made internally or externally), made by external laboratories and inspections made by the authority. The parameters with their respective limits and monitoring frequency are presented in Table 8.1 Parameters, limits and monitoring frequency in section of ivAppendices.

The environmental evaluation follows what is established in Law 21/2013, aiming to protect the environment, incorporating sustainability criteria through the evaluation of the programs and projects to prevent environmental impact, and helping to have efficient correction and compensation methods (BOE, 2013).

Within the environmental authorization it is stipulated that the administration must do monitoring regularly as is presented in Table 8.1 Even though the monitoring is done with more frequently than what is established, this is made for intern control matters and to have a record of the effluents´ behaviour.

BREF Common Wastewater Treatment and Management in the Chemical Sector

The CWW covers the issues for the water discharges in the chemical sector, as their treatment, and management systems. The parameters that are monitored and that have to comply with the established limits are included in Appendices section on Table 8.1; these limits are reviewed in the Environmental authorization according to Industrial Emissions Directive.

Covestro Industrial Park must maintain these limits as currently, the water discharges go straight to the emission point. Nevertheless, there is a project leaded by AITASA to construct and operate a Common Wastewater Treatment Plant for the Chemical Cluster. Covestro is participating in this project. It is estimated that the Common WWTP will be put in service during the first semester of 2022; that will imply that in the near future the wastewater from the Covestro Industrial Plant will be sent to an external WWT before being discharge to the Mediterranean Sea.

3.4.4. Waste gas emissions:

There are normative that must be followed, nevertheless, the limit that must be applied is always the one indicated on the current Environmental Authorization, which is reviewed to comply with the applicable BREF, that in the case of the gas's emissions are the following.

- Current limit by the Environmental Authorization T1RA140033
    - BREF LVOC / Directive (UE) 2015/2193
    - BREF Common Waste Gas Treatment in the Chemical Sector WGC (still not published).

There is other normative that must be followed (explained further below), which consists of having an emissions inventory; this is the:

- Real Decreto 100/2011.

Environmental Authorization

This has as objective to comply with the current legislation for the activity of production of MDI. The requirements of the documents and content of the authorization is established on the laws:

- Law 20/2009: environmental prevention and controls.
    - Requirements for the documents to present.
    - Procedure and procedures.
    - Content.
    - Art 71.2: Compliment follow-up.
- Law 16/2002: integrated pollution prevention and control | Modified by the Law 5/2013.
    - Requirements for the documents to present.
    - Content.
    - Art 12 from Real Decreto 815/2013: integrated inspections.
    - Art 8.3: emissions´ annually notifications.

BREF Common Waste Gas Treatment in the Chemical Sector

The WGC Treatment in the Chemical Sector exposes the BAT for the proper management and treatment of the gas emissions in the chemical sector. This BREF applies for the production processes that emit to atmosphere nitrogen oxides and carbon monoxide from any thermal treatment; in this case the TAR (which is explained previously in section Waste gas emissions) emits these compounds. This matter is important, because of the modifications of the BREF which are expected to be published in this year, 2022. Currently, the limit for the NOx emissions is of 350 mg/Nm^3, nevertheless, according to the final draft of BREF WGC this limit will decreased to 200 mg/Nm^3 when having nitrogen process gases that are precursors of NOx. This BREF could apply also for emissions coming from storage tanks such as the HCl scrubber.

On Table 8.2 (included in the Appendices section) are presented the emission points, the parameters analysed for each of them and their frequency, either if the analysis is made officially or internally.

NOx emissions

Out of the emission points presented on Table 8.2, the most relevant source for the study is the Thermal Oxidiser, though it is the main emitter of nitrogen oxides. As it is explained in section Waste gas emissions/Nitrogen oxides emissions, methanol condensates are used as complementary fuel in the TAR, and this contributes to the emission of NOx. This stage is the one that was analysed during the months of research; Also, this means that the modifications on the legislation will mainly apply to the TAR NOx emissions, therefore to the TAR.

Real Decreto 100/2011

Following the RD 100/2011 it is required to have an inventory of the emissions involved in the company´s processes. This is known as CAPCA, for its acronym in Spanish for *"Catálogo de Actividades Potencialmente Contaminadoras de la Atmósfera"*. It has as objective to present a list of the potentially anthropogenic air pollution activities; this leads to creating an inventory of the atmosphere emissions. The catalogue includes the activity identification regarding their power range (Eurofins, 2021). Covestro´s processes have different category, thus there is specific classification for each of their emission sources.

There are criteria established by the Real Decreto 100/2011 regarding the control measurements of these emission; in unison, following what stipulated in Law 34/2007 (2017) the emissions´ catalogue shall include the activity identification and capacity or power range if applies, the group classification (Art. 13, Law 34/2007), the activity code and the specific considerations. For the monitoring and measurements, they must be done based on normativity UNE-EN 15259:2008, or updates of the same (BOE M. d., 2011).

4. Methods

For the development of the study, it was necessary plan activities in order to cover all the requirements of the project. They were divided into two main topics: wastewater discharges and gas emissions. Figure 4.1Figure 4. presents the dates from July until December in which 6 activities were distributed to be accomplished. Nevertheless, this Gant diagram was used as a guiding tool, but it was not strictly followed as the dates had to be adapted to the drawbacks presented through these months. The tasks are described below.

1. Bibliographic research about the wastewater composition, particularly regarding the influence on the parameter Inhibiting Matter, analysis results study and Covestro´s processes (regarding wastewater).
2. Coordination of the wastewater analysis campaign and analysis of the results.

3. Hydraulic wastewater discharges inventory (wastewater pipeline configuration with diameters and flowrates).
4. Inventory of the composition of the wastewater discharges (according to BAT 2 of BREF CWW) and identification of potential corrective actions to reduce the content of Inhibiting Matter.
5. Gas emissions inventory (according to BAT 2 of BREF CWW) and study of the requirements established in the future BREF WGC.
6. NOx emissions analysis from historical emissions results and new online measurements at the thermal oxidizer of the MDI plant and proposal of corrective actions to meet future requirements of BREF WGC.

- TFM Integrated Final Master Project.

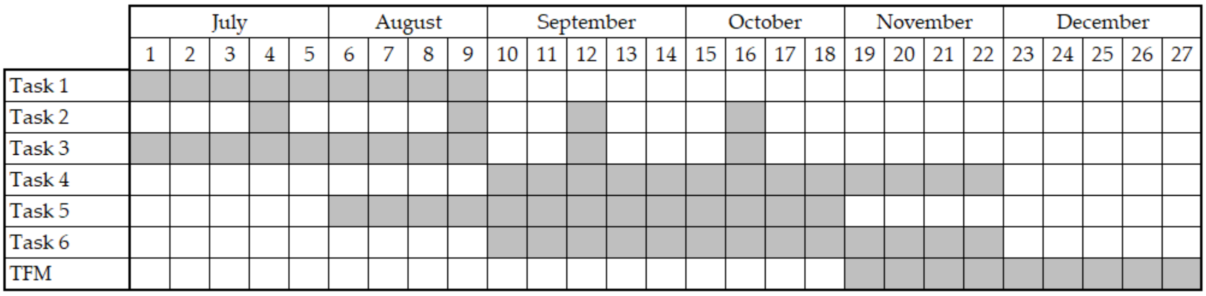

FIGURE 4.1 PROJECT´S GANT DIAGRAM

Source: own elaboration.

All the studies done were planned to find the way to improve or correct the actual processes and operations mode. Basically, the three campaigns done were: tracking of the Inhibiting Matter parameter on the partial flows and endpoint discharges, have a more complete knowledge of the biodegradability of the partial effluents (DBO/DQO ratio) as required in the inventory according to BAT 2 of BREF CWW and the characterization of the Covestro – utilities pits. All of these campaigns were planned hand in hand by the company´s tutor and the student.

4.1. Wastewater discharges and gas emissions inventories

One of the first activities done for the development of the project was to create the compilation of the available data from the past years regarding the discharges and emissions. These inventories were done following the standards presented in the BAT 2 (Best Available Technique) of BREF CWW, including the pipeline´s diameters, the average flowrate, and the maximum flowrate. The objective of including these data in addition to complying with the regulations but for the company to ensure having the information altogether; this is to be used as a tool to help have control of it with the modifications made lately on the processes and installations.

For the wastewater discharges the inventories done were classified into three different categories, which are: hydraulic inventory, composition inventory and BAT inventory. They differ between them on the information included and the used software or sources for obtaining the data. The partial flows are organised by the discharge´s pH, either basic or acidic.

4.1.1. Hydraulic inventory

First, the hydraulic inventory compiles the information obtained from the PI Builder software. This tool is an Excel complement which is linked to the online analysers in the pipelines and their outflows. It works with unique IDs or tags that each of the online analyser have and that throw different values depending on it; for example, it can give information regarding the temperature, the flowrate, the totalised flowrate, among others.

With PI Builder data can be collected from any wanted date, as long as there has been online analyser already installed. Also, the values can be obtained with specific interval of time, such as minutes, hours, days, etc. The hydraulic inventories have Excel tabs for hourly data, daily data, and annual data (if available information).

Both hydraulic inventories include information for the partial flows and the endpoint. The main characteristics are listed below, not all of them are included in all the inventories

- Pipeline diameter.
- Average flowrate.
- Maximum flowrate.
- Limiting diameter.
- Average temperature.
- Maximum temperature.
- Discharge regime: continuous or discontinuous.
- Functional hours.

Regarding the data known from the past years, May 2017 is the month in which were registered the highest values of flowrates. So, another file of hydraulic inventory was made only compiling the information from the dates between May the 1st and June 1st of that year. This, with the objective of having an example of the maximum scenario. This data can help to have record of the maximum capacity of the pipelines, equipment, and processes operation.

With the information obtained from these inventories, it was able to calculate the expectations or summarise the values for the current partial flows and in that way, compilate the information of all the discharges on the graph (Figure 3.1 Partial flowrates) show in the Wastewater discharges section, subsection: Flowrates. As it is a relevant variable for the Inhibiting Matter parameter, it was important to have it available.

4.1.2. Composition inventory

This inventory is the assembling of the values collected by the external monitoring of several years, from 2016 until 2021 (for further information go to section Composition). This information includes the parameters required by the current normative for each of the flows, every tab has the compilation for each of the partial flows and there is one tab which includes the average values for each of the flows.

With this inventory, the composition for each flow is available altogether; this helps analyse easier the parameters, thus identify if there are unusual values that may affect the partial or endpoint discharges. The composition inventory has the information required by the current legislation and its modifications throughout time.

4.1.3. BAT inventory

Finally, the BAT inventory includes the theoretical information required by the BAT2_CWW. The main tab has a simplified process flow diagram, to show the distribution of the pipelines and tanks regarding the processes involved in the wastewater treatment plant. This distribution is mainly done by the discharge´s pH, either it the effluent is acidic or basic. Also, they are classified by the tank where the process´ water is discharged, having three options: the buried pit, a tank of 5.000 m3meters for the specific flow of high TOC, or to the main tanks of 2.200 m^3 or 2.800 m^3; for these last it depends on which one of them is available or currently working.

Even if the process flow diagram is a simplified version, the pipelines include their basic information such as the limiting diameter and their installation mode: aerial or underground. Likewise, there is another tab for a process flow diagram with the modifications that expected to be done for year 2022.

Then, the following tabs contain the main information for the processes, regarding the requisites on the regulation, such as the discharge regime, the average and maximum flowrate, the discharge tank, and the functional hours. Some of the tabs also include the main processes or the main components used.

4.2. Wastewater discharges

As it is said in the previous section Wastewater , the monthly monitoring campaigns give the necessary data to analyse if the wastewater treatments are working properly or need to be corrected. These campaigns were used as one of the main methods to obtain information to study and propose corrective actions.

4.2.1. Inhibiting matter analysis campaigns

Following the results given by the monthly monitoring, on October 2020 presented high values on the Inhibiting Matter (IM) parameter; also, oxidation on the samples was observed and the laboratorians identified an acidic smell coming from the samples. Then it was when it was decided to start organizing analytical campaigns to find out the reason of the unusual behaviour of the incoming wastewater discharges.

Nine rounds were organised in total. The first was planned right after the first punctual scenario in October, therefore in November of 2020, and then gradually from January 2021 until December 2021. Simultaneously, the study regarding the composition of the partial flowrates was made, to analyse the influence of the products and the components on the wastewater regarding the ecotoxicity of the final discharge.

Every time the results from the campaigns were obtained, the following round of analysis was organised. This way the experiments were more focused on the representative data from the wastewater discharges. The IM for the endpoint is evaluated more often thus, there are more data regarding this emission point.

These analysis campaigns are presented next. It is important to have as reference the Limit Value Set (LVS) for the Inhibiting Matter which is of 25 ut. Then, in the next section of Results and discussion on Wastewater discharges, the results are interpretated regarding this LVS.

Round 0 – November 2020

This first round was done for all the partial flows and the endpoint; this was organised because of the episode on October 13th, 2020, which had a value of 47 ut, clearly higher than the LVS of 25 ut. The samples for the round 0 were taken during the week from 02 to 06, the value for the endpoint was of 22 ut.

In total, there were 11 partial flows from the wastewater discharges, these are listed below:

1. 15B100
2. Underground pit
3. Desulfurization of CO (DES CO)
4. Decantation of CO (DEC CO)
5. Utilities – acidic
6. Utilities – basic
7. MDA
8. MDI
9. Company C Evaporator
10. Company B low organic load
11. Company D pit

Out of the 11 samples, 6 of them resulted with an IM value less than 2 ut, meaning that they were not representative to the study. Then the remaining 5 had values under 25 ut.

Endpoint: 22 ut
6 samples: <2 ut
5 samples: >2 ut, <25 ut
Total: 12 samples.

Round 1 – January 2021

Then, the next round was done between the 20th and 21st of January 2021, having as propose taking the samples the same day or with the less difference of time for them to be more realistic and representative of the real scenario.

As in the previous round 5 samples got exceedingly small values, only the remaining 5 were analysed, as so as the endpoint. This time, the endpoint got a value under 2 ut and the average value of the partial flows was less than 7 ut, having only one high value of 20.

Endpoint: <2 ut
5 samples: >2 ut, <25 ut
Total: 6 samples.

Round 2 – April 2021

For the following round, the same 6 samples analysed before were studied. Nevertheless, this time the average value was of 18 ut, having two samples with values higher than 25 ut: of 25 ut and 32 ut; the rest of them had lower values. Despite this, the endpoint got a value of 16 ut.

Endpoint: 16 ut
5 samples: average 18 ut
High values: 32 ut and 18 ut
Total: 6 samples.

Round 3 – June 2021

For the third round the sample taking was achieved on the same day, this helped the results to be more precise than before. Once again, the same 5 samples were studied as so as the endpoint, which had a value lower than 2 ut, while the average value for the 5 samples was of 19 ut: with maximum values of 30 and 29 ut.

Endpoint: <2 ut.
5 samples: average 19 ut.
High values: 29 – 30 ut.
Total: 6 samples.

Round 4 – August 2021

Then, the following campaign was made when the processes were re calibrated after the May´s shutdown, and it was decided to analyse all the samples once again (except from one) and now including the two pits from Covestro – utilities: energies and infrastructure. These 2 pits samples, in addition to being used for this study, were also used for their characterization regarding different parameters; this is explained in the section below: Pit study.

The value for the endpoint got <2 ut, 7 of the 13 samples taken had values lower than 2 ut, too. Other 2 samples got not representative values. Though, one sample got a value higher than 100 ut, another one 63 ut and the another of 28 ut; the sample that had the highest value usually is a basic flow, which could be de reason of the high IM result.

For the partial flows that resulted to have higher IM values, the hypothesis stands for the influence of the pH. Meaning, that for the next analysis campaigns it was emphasized to the external laboratory the necessity of having a pH adjustment for the samples before analysing the Inhibiting Matter.

Endpoint: <2 ut.
12 samples:
- 7 samples: <2 ut.
- 3 samples: high values of >100, 63 and 28 ut.
- 2 samples: <25 ut.

Total: 13 samples.

Round 5 – September 2021

For this round, it was decided to choose 5 of the samples that got the highest values on the previous round, nevertheless, it was not possible taking one of the samples of Covestro (septic pit from utilities) due to the difficulty in retrieving the sample so, only 4 samples were analysed this time.

Unfortunately, 3 out of these 4 samples got values higher than 100 ut, and the remaining a value of 22 ut. Once again, the three samples that had the highest IM results are basic effluents. It was required to the external laboratory to adjust the pH to a neutral value before analysing the IM; however, the hypothesis of the pH influence on the parameter, remains.

Still, the endpoint´s value was lower than 2 ut.
Endpoint: <2 ut.
4 samples:
- 3 samples: >100 ut
- 1 sample: 22 ut

Total: 5 samples.

Round 5.1 – September 2021

On this round, another experiment was planned. This consisted of preparing samples of distillated water mixed with the components that could be affecting the IM parameter, previously studied, and exposed in section Variables affecting the inhibiting matter. These components were selected because they can be found in the endpoint effluent, coming from the processes involved in the wastewater discharges.

Table 3.4 Relevant components and their established limit, previously exposed, presents the maximum established limit for the studied components that can be a cause of the high value on the inhibiting matter parameter. For this experiment, it was decided to use higher concentrations that the permitted, to overestimate the probability of having high values of inhibiting matter caused by any of these components.

One of the samples was prepared with two of the most common compounds and the rest of them only with one compound. The concentration used for each of them is presented below.

- 20 ppm Styrene + 20 ppm Ethylbenzene
- 2 ppm Monochlorobenzene
- 2 ppm Aniline
- 2 ppm Phenol
- 2 ppm Acrylonitrile
- 2 ppm Styrene
- 2 ppm Ethylbenzene

The results obtained from this experiment is presented below in Table 4.1. It is noticed that none of the samples got relevant IM values; This is later discussed in Section: Results and discussion/Wastewater discharges.

TABLE 4.1 RESULTS OF DIFFERENT COMPOUNDS AND THE INHIBITING MATTER

	Inhibiting Matter (Ut)
20 ppm styrene + 20 ppm ethylbenzene	2,9
2 ppm Monochlorobenzene	<2,0
2 ppm Aniline	<2,0
2 ppm Phenol	<2,0
2 ppm Acrylonitrile	<2,0
2 ppm Styrene	<2,0
2 ppm Ethylbenzene	<2,0

Source: own elaboration.

Round 6 – October 2021

On round 6, same as on round 5, it was planned to take samples from 5 partial flows, but it was not able to take from one of the Covestro – utilities pit. The endpoint discharge had a value lower than 2 ut; The remaining samples´ results were either lower than 2 ut or lower than 8 ut.

It should be noted that, in the previous campaign one of the partial flows' samples got a value higher than 100 ut, while this time got a value lower than 2 ut.

Also, it is important to take into consideration that for this campaign, the pH of the samples was adjusted by the internal laboratory before handing them over to the external laboratory.

Endpoint: <2 ut.
4 samples: average <4 ut.
Total: 5 samples

Round 7 – November 2021

The last round was planned for the same 5 samples from the previous planning, but in this case adding the one that got the highest value in round 2, to verify its current performance in relation to the inhibiting matter, although previously it got values lower or close to 2 ut. Fortunately, this time, it resulted to be lower than 4 ut, proving its correct behaviour.

Out of the 5 samples, 2 of them got values higher than 100 ut and another one of 36 ut.
The endpoint result was lower than 2 ut.

Endpoint: <2 ut.
5 samples:
- 2 samples: >100 ut.
- 1 sample: 36 ut.
- 1 sample: <25 ut.
- 1 sample: <4 ut.

Total: 6 samples

Round 7.1 – November 2021

On this occasion, for one of the samples that has been presenting values higher than 100 ut on the previous campaigns, another sample taken the next day was analysed too, the value was of 2,7 ut; Figure 4.2 presents the overview of the historical results obtained for this partial flow.

Regarding the monitoring made internally, the pH for this sample was of 7,48 upH, while generally, this flow has pH values around 13 upH. Also, the conductivity had a value of 1.332 μS, when normally it is in the order of hundred thousand as the last measurement on October was 163.200 μS.

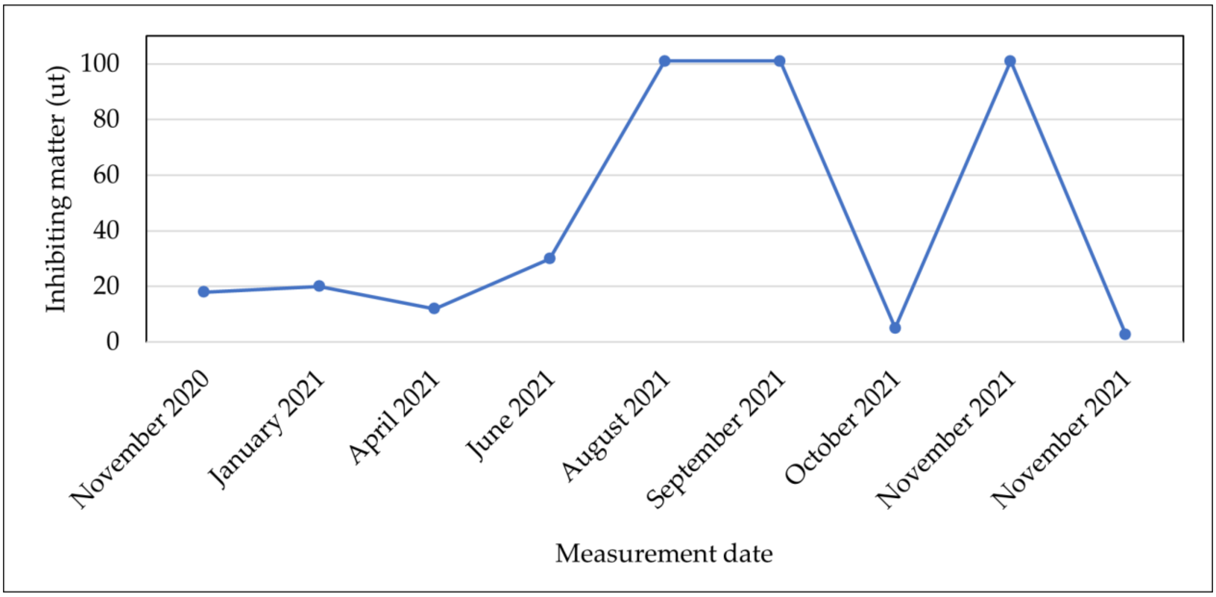

FIGURE 4.2 SPECIFIC PARTIAL FLOW RESULTS ON INHIBITING MATTER

Source: own elaboration.

Round 8 – December 2021

With the previous campaign results, it was decided to plan one last round. This one focused in the unusual flow that presented very different results on the samples taken consecutive days; one having a value higher than 100 ut and the other sample a value rounding the 2 ut.

This time, it was requested the samples to be taken under as similar conditions as possible and the pH to be neutralised in the internal laboratory before handing the samples to the external laboratory. Also, it was taken a sample including the pots from the process, so the possible influence of this variable could be studied. For both samples, there were taken duplicates to obtain more reliable results.

Regarding the endpoint discharge, it was done the monthly monitoring as usual, even though, the sample was not taken in the same date.

Endpoint: <2 ut.
Sample 1: 4,4 ut.
Sample 2: <4 ut.
Sample 1 – pots: <4 ut.
Sample 2 – pots: <4 ut.

4.2.2. COD/BOD$_5$ ratio

Taking advantage of the IM analysis campaign, the biodegradability of the wastewater discharges was also studied evaluating the COD/BOD$_5$ ratio; this was studied as it is a requirement established on the inventory from BAT 2 (BREF CWW). The biodegradability is determined by the biodegradability index explained in the State of the art, in section Biodegradability.

For this study, four rounds were organised from July 2021 until November 2021. Same as for the Inhibiting matter analysis campaigns, the flows were selected following the results from the previous campaigns, beginning by analysing all the flows and then choosing the most relevant for the study.

Round 0 – August 2021

As mentioned previously, for this first round all the 12 partial flows were tested as so as the endpoint discharge. In this way it was possible to get a general idea of the behaviour of the water´s discharges in relation to biodegradability.

From the 13 taken samples, the results obtained were the following:

Biodegradable: 3 samples.
Moderately biodegradable: 3 samples.
Non-biodegradable: 7 samples
<u>Endpoint: biodegradable</u>

Round 1 – September 2021

For this round, the samples taken were chosen because of the results obtained in the IM campaign. Five samples were analysed, including the endpoint discharge. The results were:

Biodegradable: 1 sample.
Moderately biodegradable: 2 samples.
Non-biodegradable: 2 samples
<u>Endpoint: biodegradable</u>

Round 2 – October 2021

In this round, again five samples were studied: chosen on account of the results of the IM parameter. This time any of the samples resulted to be non-biodegradable.

Biodegradable: 1 sample.
Moderately biodegradable: 4 samples.
<u>Endpoint: biodegradable</u>

Round 3 – November 2021

The campaign organised in November included the same samples previously analysed and selected again, by the IM results.

Biodegradable: 2 samples.
Moderately biodegradable: 2 samples.
Non-biodegradable: 1 sample.

Endpoint: moderately biodegradable.

Round 3.1 – November 2021

As in the IM study, in November a sample was taken in duplicate and its result was negative, being non-biodegradable. Nevertheless, the IM result for this sample was positive, having a value of 2,7 ut.

4.2.3. Pit study

Taking advantage of the IM analysis campaigns, a study for the pits of the Covestro – utilities department was planned. This, aiming to have a better characterisation of the sanitary wastewater collected in the septic pits, specifically information about the biodegradability of their discharges and to reject the possibility of them being the reason of the high values of the IM on the final discharges.

The analysis campaign started on August and ended in November. The parameters studied were the following:

- Nitrate (NO_3)
- Nitrite (NO_2)
- Total nitrogen
- Nitrogen Kjeldahl (TNK)
- Ammonium (NH_4)
- Chemical Oxygen Demand (COD)
- Biological Oxygen Demand (BOD_5)
- Inhibiting Matter (IM)
- Sulphides

The objective was to analyse both pits from infrastructures and energies departments, nevertheless, only for the first campaign it was able to take samples of both due to the difficulty for obtaining them, since they are underground, and it was needed extra equipment to reach the wastewater and take a sample with a significant volume (at least 1 L). For the remaining campaign rounds, they were analysed intermittently, i.e., one month one pit and for the next month, the other pit. Even though, it was not as planned, this analysis gave the results that were needed to characterise them.

Both pits resulted to be moderately biodegradable or biodegradable, except for the first-time sampling, which both presented non-biodegradability; also, one of them had an IM higher than 60 ut and a high value on Kjeldahl nitrogen.

Either way, both pits are showing favorable results and their influence on the endpoint flow is not as relevant as it could be to alter the Inhibiting Matter on the wastewater.

4.3.Waste gas emissions

For the gas emissions of the processes, there are analysers that help monitor the flowrate and concentration of the waste gas to have a record of them. This helps to prevent dangerous emissions to the atmosphere but also to know how the emissions perform throughout time.

4.3.1. NOx emissions

As mentioned previously, the online analyser is used to have a record of the emitted gasses. Regarding the NOx emissions, the analyser is a new acquisition of the company, therefore it still is on the installation and calibration process, and it is expected to start working on December 2021. This will be a useful tool to maintain a monitoring on the concentration of the NOx emissions, which might be helpful for complying with the established goals and mentioned future legislation (BREF WGC). The online analyser was installed in December 2021, it is in calibration and installation process. Even though the results were not available to be included in this report, it will be helpful for the further research and control of this parameter[8].

For the analysis of the NOx emissions behaviour, ramp-up campaigns must be done. A ramp-up consists of doing simulations of different scenarios and recording the results. In other words, the TAR is configurated with various conditions to identify the optimal and to study the alternatives. Generally, the ramp-up is done with variations on the methanol flowrate, air flowrate, burner temperature, among other parameters; this is done by a certain period for having more precise values.

Regarding the previous ramp-up campaigns, the data from the last four done before the last one on October this year, is presented below. These campaigns helped record information of the conditions in which the TAR was operating, such as the gas flowrate, the temperature of the burner, the flowrate of the methanol (MeOH) the natural gas and finally, the NOx emission both in ppm and in mg/Nm^3 obtained in measurements done by an accredited company. The results are presented in this same section and discussed in the following (Results and discussion/Waste gas emissions), the data in marked with red colour, represent the results that are approaching to the established limit; then, the data in green are the minimum value obtained in the ramp-up campaign. In the last campaign (Table 4.Table 4.5) there are seen some results in red, meaning that they exceeded the set value.

The first campaign was made in April 2017, 7 measurements were made with an average burner temperature of 935ºC, two different gases flowrate and with four methanol flowrates. This was done to simulate when burning different MeOH to see the behaviour of the NOx emissions. Results are presented on Table 4.2.

[8] NOx online analyser installation update mentioned in Section: Appendices.

TABLE 4.2 APRIL 2017 RAMP-UP RESULTS

	Burner temperature	Gases flowrate	MeOH flowrate	Natural gas flowrate	NOx	
	ºC	Nm³/h	Kg/h	Nm³/h	ppm	mg/Nm³
07/04/2017	930	1.400	60	77	360	739,08
	936		30	83	220	451,66
	931		0	100	23	47,22
	934		25	94	188	385,96
	924	1.500		92	187	383,91
	940			100	189	388,02
	950			100	190	390,07

Source: own elaboration.

The next campaign was made in June of the same year, adjusting the gas flowrate to a unique value, adjusting it to be 1.400 Nm³/h, since the best results were given with this flowrate on the previous ramp-up campaign. Once again, the MeOH flowrate was adjusted to five different values to study the emissions behaviour; the results are shown on Table 4.3.

TABLE 4.3 JUNE 2017 RAMP-UP RESULTS

	Burner temperature	Gases flowrate	MeOH flowrate	Natural gas flowrate	NOx	
	ºC	Nm³/h	Kg/h	Nm³/h	ppm	mg/Nm³
20/06/2017	930	1.400	45	84	200	410,60
			60	78	260	533,78
			0	99	25	51,33
	940		30	89	205	420,87
	930		30	ND[9]	170	349,01
	940		35	ND[9]	170	349,01
	950			ND[9]	180	369,54
	960			ND[9]	200	410,60

Source: own elaboration.

Then, Table 4.4 shows the ramp-up results made in July 2017, in which the gases and MeOH flowrates were adjusted to a value, according to the values obtained in the previous campaign. The gas flowrate was established to 1.400 Nm³/h and the MeOH flowrate to 45 kg/h. This time, the air flowrate was set up to two values to determine which one of them could be the optimal for the burning of MeOH.

[9] ND: No data

TABLE 4.4 JULY 2017 RAMP-UP RESULTS

	Burner temperature	Gases flowrate	MeOH flowrate	Air flowrate	Natural gas flowrate	NOx	
	ºC	Nm³/h	Kg/h	Nm³/h	Nm³/h	ppm	mg/Nm³
12/07/2017	870	1.400	45	2.000	71,4	110	225,83
	890				81,1	125	256,63
	910				79	121	248,41
	930				88,9	140	287,42
	950				97	215	441,40
	870			2.200	76,3	125	256,63
	890				83,6	150	307,95
	910				87,2	190	390,07
	930				94,5	218	447,55
	950				105	280	574,84

Source: own elaboration.

The next campaign (results on Table 4.5) was made with a specific gas flowrate, air flowrate, natural gas flowrate and four different flowrates for MeOH in order to choose which one could be the optimal for emitting the less NOx as possible; The oven temperature was set to a value of 900ºC or close to it.

TABLE 4.5 JULY 2020 RAMP-UP RESULTS

	Burner temperature	Gases flowrate	MeOH flowrate	Air flowrate	Natural gas flowrate	NOx	
	ºC	Nm³/h	Kg/h	Nm³/h	Nm³/h	ppm	mg/Nm³
07/07/2020	898	1.361	0	2.000	89	17,12	35,15
	900		30			110,79	227,45
			45			139,17	285,72
			60			179,14	367,77

Source: own elaboration.

With these campaigns, the optimal conditions were established to be the following:

- Burner temperature: 900ºC
- MeOH flowrate: 45 kg/h
- Air flowrate: 2.000 Nm³/h
- Natural gas flowrate: approximately 90 Nm³/h

To verify that these are still adequate, in October 2021 two analysis ramp-up campaigns were conducted with different methanol flowrate and keeping the burning temperature and air mass flow constant. Table 4. presents the results obtained during the ramp-up campaigns. These are expressed under normal conditions: 0ºC, 1.013 hPa and gas sec.

TABLE 4.6 RESULTS OF LAST RAMP-UP CAMPAIGNS FOR NOX EMISSIONS

	Burner temperature	Gases flowrate	MeOH flowrate	Air flowrate	Natural gas flowrate	NOx	
	ºC	Nm^3/h	Kg/h	Nm^3/h	Nm^3/h	ppm	mg/Nm^3
15/10/2021	900	1.353	45	2.000	71	**458,92**	942,16
	899		30			332,17	681,95
	898		0			25,76	52,89
	897		60			527,04	1082,01
18/10/2021	900	1.377	45		67	**405,44**	832,37

Source: own elaboration.

As mentioned in the section Legal framework, the current limit for the NOx emissions is of 350 mg/Nm^3, but in 2026 (4 years after the publication of BREF WGC, expected during 2nd semester of 2022) it is expected to be lower to a value of 200 mg/Nm^3.

Nevertheless, even burning different methanol mass flowrate the values for the NOx concentration were higher than 200 mg/Nm^3; only when there was no methanol burning the value was lower than the current and future limit. These results lead to the hypothesis that this last ramp-up campaign does not let confirm the results obtained in 2017 and 2020; nevertheless, the new online analyser will be helpful to identify the real reason of this behaviour. However, this is discussed in section Results and discussion/Waste gas emissions.

5. Results and discussion

An analysis of the results obtained for the wastewater and waste gas studies is presented in the following pages. A series of graphs and tables are presented as well as their interpretation, with the aim of proposing corrective actions for the existing problem presented at the beginning of the project.

5.1. Wastewater discharges

As mentioned in section Inhibiting matter analysis campaigns the partial flows and the endpoint discharges had monitoring campaigns to characterise the wastewater regarding the composition, to comply with the current legislation and to have a record of the performance of the wastewater discharges.

These analytical campaigns aimed to study the Inhibiting Matter parameter, to identify which could be the flow or compound that was affecting the endpoint discharge by causing a high value of IM. Figure 5.1 presents the behaviour of each of the partial flows over the months of analysis; it is also indicated the Limit Set Value (LSV) of 25 ut, as so as the intern objective set for 2021 by Covestro of 17,5 ut.

In the same graph, it is seen how some of the partial flows always presented low values, lower than the intern objective and hence, lower than the LSV. Despite this, the remaining partial flows had relevant performance and some of them presented values higher than 100[10] ut. To confirm or reject hypotheses on the possible variables affecting the IM, it is important to determine if the anomalous values are caused by the pH influence and not due to the presence of certain substances causing toxicity.

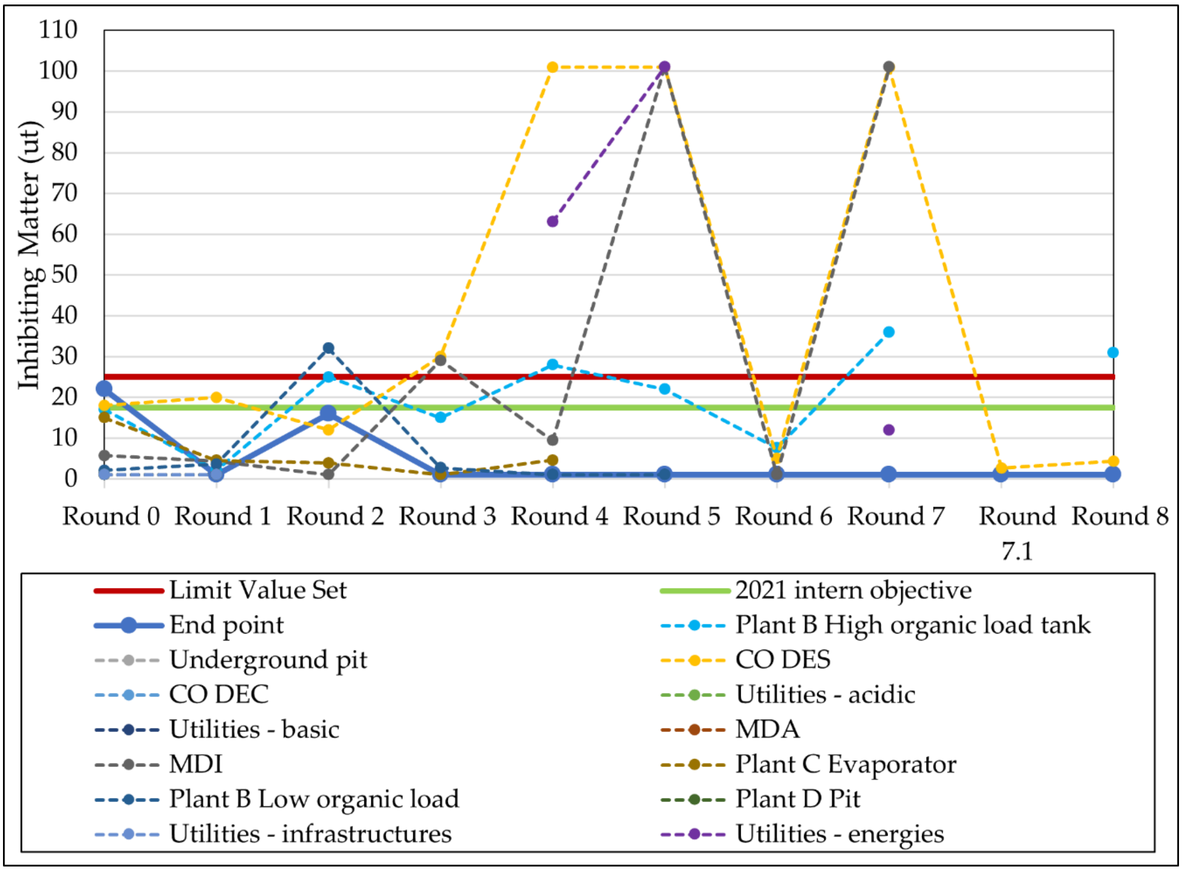

FIGURE 5.1 INHIBITING MATTER IN PARTIAL FLOWS

Source: own elaboration.

Regarding the influence of the pH in the IM analysis, previously it was mentioned (see section Variables affecting the inhibiting matter) that the samples shall be neutralised before making the analysis, this because it was demonstrated that whenever the pH of the sample is too basic or too acidic the Inhibiting Matter parameter had higher results and that couldn´t be taken as veridic data.

With the experiments made during the campaign of July 2021 – December 2021, again this performance was proven; specifically on Round 7 (November) and 7.1, the flow that was analysed both days presented values significantly different. On round 7, this flow had an IM value higher than 100 ut, there is no record of the pH of that sample, but it is known that usually this flow has basic pH values around 13 upH, while for the round 7.1 the pH was measured, and it was 7,48 upH and it presented and IM value of 2,7.

[10] For results higher than 100 ut, 101 ut was established for plotting the graphic.

Another important factor regarding the pH adjustment is that the flow that was studied on 2017 (see section Variables affecting the inhibiting matter), is the same that is just mentioned above. This can be considered as a demonstration of the importance of the adjustment of the pH before doing the analytic for the IM.

In Figure 5.2. the graph presents the partial flows that could have more influence on the endpoint discharge because the values obtained from the analysis campaigns were higher than the LSV. It is seen that three out of the four flows presented similar behaviour demonstrating results higher than 100 ut, but also in the following campaign, two of them decreased their values to be lower than 2 ut. There is no clear explanation as to why this has happened, it is unknown what could have caused the sudden drop in values.

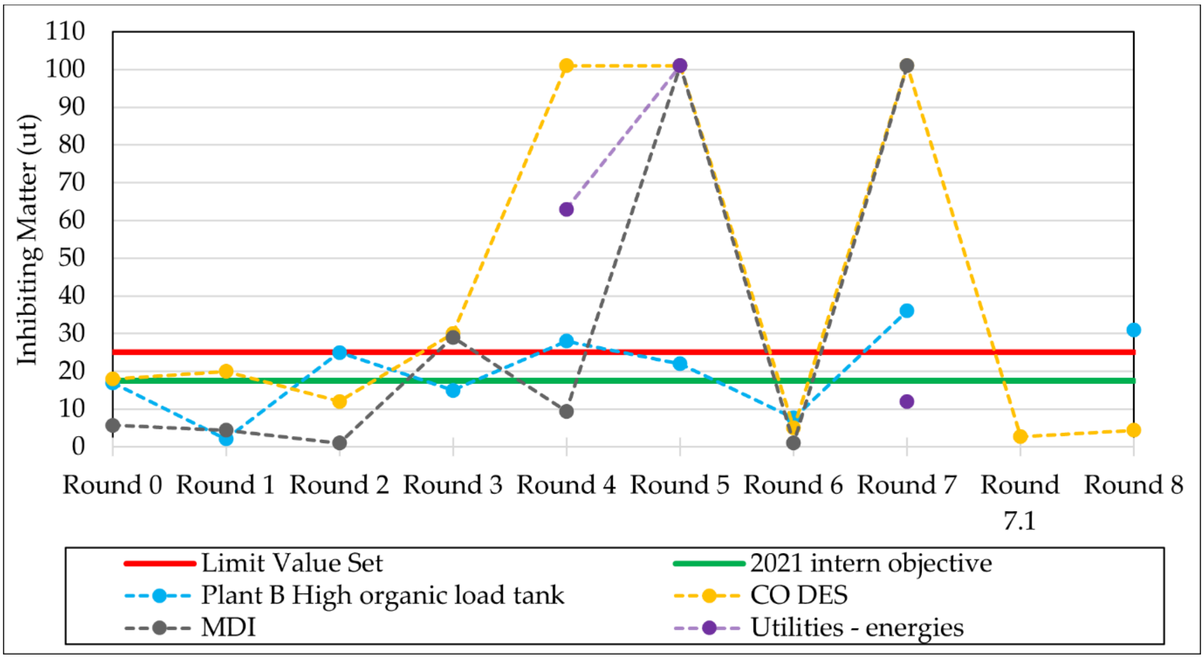

FIGURE 5.2 MOST RELEVANT PARTIAL FLOWS FOR IM STUDY

Source: own elaboration.

Furthermore, Figure 5.3 summarises the results obtained on the analytical campaigns during the 2021 for the endpoint discharge. With a red line presents the current discharge limit of 25 ut, and with the green the internal objective for the current year is indicated, which is to have values lower than 17,5 ut, then, the dotted green line shows the cumulative average of the external controls, the orange squares the values obtained when the inspections by the ACA were made and finally, the blue string shows the results obtained from the analysis made by the external laboratory.

In the previous graph (Figure 5.2) some of the partial flows present values higher than 100 ut with fluctuations of values lower than 2 ut. This behaviour cannot be explained but the hypothesis relies on the pH influence and on the chemical compounds involved in the processes. These compounds were particularly studied (see Inhibiting matter analysis campaigns/ Round 5.1) but the results were not conclusive, and it was not possible to demonstrate that their reactions or degradation processes can affect the IM analysis.

Therefore, Figure 5.3 exposes the performance of the IM parameter throughout the monthly inspections; the conclusion is favourable, since the behaviour of the flow never exceeded either the internal objective nor the discharge limit which means that the parameter has being controlled and that, indeed, the scenario presented in October – November of 2020 was a punctual situation.

Also, the Inhibiting Matter has been complying with the discharge limit of 25 ut, as it has been having values lower than 15 ut from January 2021 to December 2021. As the endpoint discharge is the most relevant, the partial flows do not seem to be affecting it significantly, which, increases the concerning on the punctual scenarios.

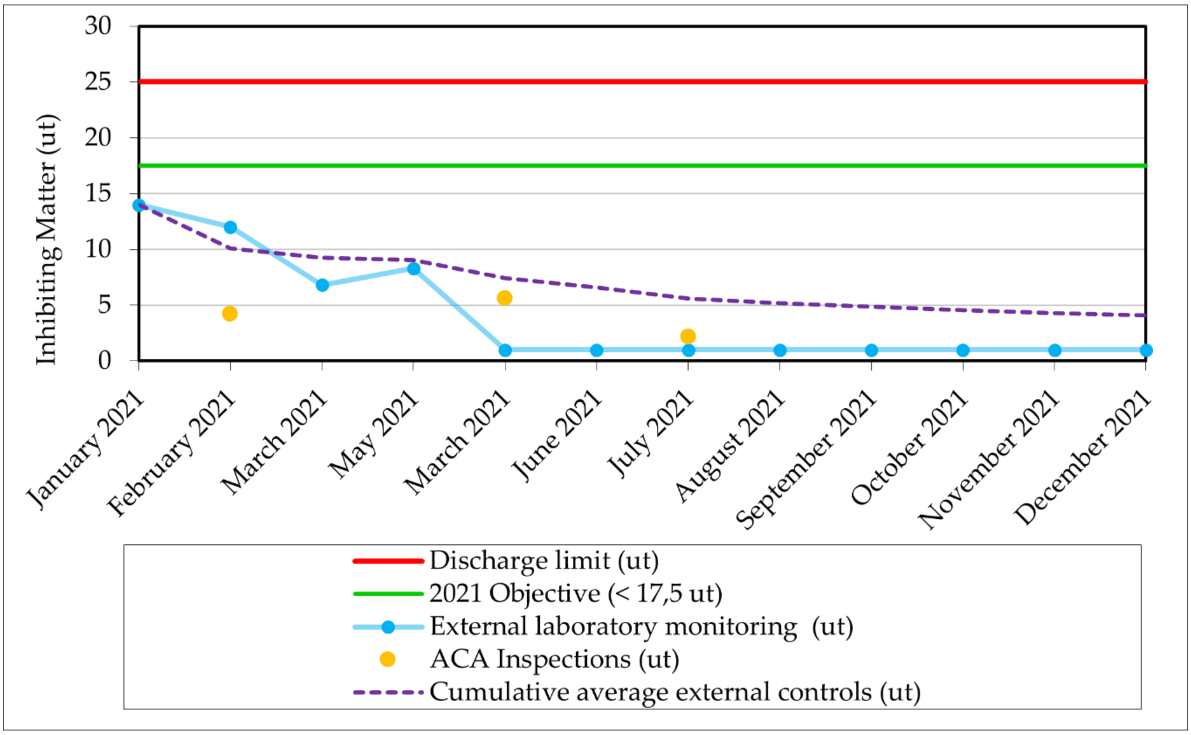

FIGURE 5.3 INHIBITING MATTER IN THE DISCHARGE OF WASTEWATER

Source: own elaboration.

As mentioned in section Methods (Wastewater discharges/Inhibiting matter analysis campaigns), in the experiment Round 5.1 made on September 2021, the intern laboratory prepared seven samples mixing water with high concentrations of the compounds that could be affecting the wastewater, these were studied before and presented in section Variables affecting the inhibiting matter.

Table 4.1. includes the results obtained (presented in Section Methods/Wastewater discharges / Inhibiting matter analysis campaigns /Round 5.1); these lead to the conclusion that even with high concentrations of the toxic compounds in the water,

the inhibiting matter parameter presented values lower than 2 ut. Therefore, none of the compounds used in the processes and that could be present in the wastewater discharges can be identified as the main reason of the Inhibiting Matter´s high value obtained in October 2020.

It is interesting to emphasise the result given by the sample that included 20 ppm of styrene + 20 ppm of ethylbenzene, as even if the concentration of these two compounds was extremely out of their concentration limits, the Inhibiting Matter resulted to have a value close to 3 ut when this was expected to be much higher.

Then, according to the COD/BOD_5 study, there is no direct relation between the biodegradability and the Inhibiting Matter parameter since none of them depend on the other. With this study it was proven that even if the water resulted to be moderately biodegradable or non-biodegradable, it is possible to present low values of IM, due to the fact that the IM refers to the ability to inhibit the degradation of compounds in the water not directly affecting the biodegradability or vice versa.

After having interpreted the results of the analytical campaigns for the Inhibiting Matter, the conclusions reached can be summarised as the scenario that occurred in October-November 2020 was a one-off situation, which has not been repeated in the following months. The specific campaign on the compounds that could be affecting the parameter, demonstrated that even with high concentrations of them, the IM still presents a value lower than 2 ut. With this, the corrective actions for the IM parameter are mentioned on the following section.

5.1.1. Corrective actions regarding wastewater inhibiting matter parameter

As mentioned before, the IM parameter has been controlled since the scenario presented on October 2020, the monthly monitoring has helped to have a record of the IM values and to have control on the behaviour of the effluents. When it was demonstrated that even with high concentrations of the toxic compounds used in the production processes the IM resulted to have a low value, it was concluded that the emissions of the partial flows were not significantly affecting the endpoint discharge.

Said this, the main recommendation on the Inhibiting Matter is to maintain constant monitoring on the parameter on the partial effluents as well as on the endpoint to prevent having another episode of high results of the IM. Currently, the monthly monitoring has been done correctly, but it is vitally important to be sure the pH is adjusted before doing the *Vibrio fischeri* test, as it has been done for the last few rounds of analysis.

Additionally, for the partial flow that has received most attention in the last rounds, it is also recommended to monitor its behaviour to study their variables and their influence on the IM. Even though it was demonstrated that the flowrate is not representative in the final discharge, it is important to have record of its performance to prevent future problems.

5.2. Waste gas emissions

As mentioned before, the ramp-up campaigns helped determine the optimal conditions to operate the TAR burning the methanol to have the lowest NOx emissions possible to comply with the current and future legislation; In total, five analysis campaigns were organised from April 2017 to October 2021. These were made with different conditions, and they were adjusted as the results from the previous campaign were available.

With the results from the first ramp-up, it was seen that the lowest value for the NOx emissions was obtained when the flowrate of the treated gases was of 1.400 Nm^3/h and the flowrate of the burned MeOH was 0 kg/h, nevertheless, the next value with the same gas flowrate was when the MeOH flowrate was 30 kg/h, with a value of 220 ppm of NOx.

That first campaign was used to establish a gas flowrate of 1.400 Nm^3/h and the burner temperature to be close to 900ºC. This way, the next campaign was adjusted to have a gas flowrate of 1.400 Nm^3/h and the MeOH flowrate was alternating between 0, 30, 45 and 60 kg/h. With these experiments, the results lead into conclusion that the best result, apart from no burning MeOH (when burning 0 kg/h the NOx concentration was of 25 ppm) was to burn a MeOH flowrate of 45 kg/h. This demonstrated that burning 45 kg/h gave better results than burning 30 kg/h.

The ramp-up made in July 2017, was adjusted with a gas flowrate of 1.400 Nm^3/h and MeOH flowrate of 45 kg/h. This campaign was organised to establish the air flowrate, which finally was decided to set it up to 2.000 Nm^3/h since the lowest NOx concentrations were obtained when burning that air flowrate.

Finally, the last round made before the one organised this year was done to prove that which MeOH flowrate was the optimal option to obtain the less NOx emission concentration. This ramp-up demonstrated that the methanol flowrate of 45 kg/h was the best option when having an air flowrate of 2.000 $Nm^3/h$and an oven temperature of 900ºC or close to it. The results of the NOx emissions complied with the current legislation and with the future applicable legislation.

With these experiments, the optimal conditions were established, as mentioned previously and these were adjusted in the last campaign done in October 2021. Nevertheless, the results obtained were anomalous, since even if the optimal conditions were followed, the NOx concentration resulted to be high values. The MeOH flowrates applied where 0, 35, 45 and 60 kg/h, and even if the optimal was supposed to be 45 kg/h the NOx concentrations in ppm resulted to be higher than 400 ppm, which did not happen in the previous campaigns. Then, when burning 30 kg/h the NOx concentration did not comply with the current established limit.

It was concluded that this was an unusual behaviour of the NOx concentration when burning the MeOH, thus, the conditions are being investigated in order to identify if there was a problem with the air flowrate or the oven temperature. It could

be a problem of the online indicator of any of these parameters that is not calibrated or any other minimum issue that may be disturbing the burning of MeOH.
Yet, it is being studied that it could be an alternative of stop burning the MeOH and instead, manage it as a waste; this corrective action is described in the next section.

5.2.1. Corrective actions regarding NOx emissions

With the results obtained and interpretated in the previous section (NOx emissions), it was discussed that the variations on the NOx flowrate concentration could be caused by the temperature of the combustion boiler or by the vapour flowrate generated during the burning process. Said this, one of the corrective actions proposed for this issue is to monitor both parameters in order to discard the option of these two variables being responsible of the high values on this parameter; currently checks are being carried out to have record of them. Similarly, the new on-line analyser is being installed and calibrated, which will be of help to have real-time data on the NOx emissions.

Results obtained in the last ramp-up campaign made in October 2021 were astonishing and unexpected; making it impossible to confirm the results obtained in 2017 and 2020 campaigns. Since that happened, the company is analysing the behaviour of the different conditions as the burner temperature, the air flowrate and methanol flowrate, looking to find out if there are any problems in the online indicators or in any other part of the processes.

However, after a couple of discussion meetings on the issue, it was concluded that the main corrective action is to stop burning the methanol in the TAR. This means that it will be needed to classify the methanol as a waste, having its corresponding management with a tertiary company in charge of it.

Though, currently there is no option to load methanol condensates in a tank truck for the external shipment, therefore Covestro has a project for having the appropriate methanol loading area. To have a correct management, it would be needed to have an external company commissioned to collect the methanol wastes to treat them.

6. Conclusions

In conclusion, the results obtained from the analysis campaigns for wastewater and gas emissions led to recommendations for corrective actions to improve the company´s environmental performance. These actions are presented in this Master Thesis to both supervisors in the company as a proposal of possible modifications on the company´s processes.

Nevertheless, the results obtained were not as conclusive as expected, and the corrective actions are intended as a generic solution to the problems. That is why, at the same time, it is recommended to continue with the analysis campaigns in order to maintain control of the parameters and, to gather more information to be able to draw more specific conclusions.

In the case of the NOx emissions, it is expected that with the installation of the new on-line analyser, real-time information will be obtained, and it will be possible to verify that methanol should be managed as a waste instead of being burned on site. It is important to note that the alternative of using the methanol as a complementary fuel for the TAR was demonstrated to be the option with the lowest environmental impact, following the results of the "Environmental Impact Assessment of different methanol removal options" made by Covestro Germany in February 2021. However, the behaviour of the burner and its temperature, as well as the air flow when burning methanol, shall be monitored to have a regular control and record of data in case of unusual scenarios to happen.

On the Inhibiting Matter, it is concluded that no clear explanation on the behaviour of this parameter was obtained. However, it was found that the scenario presented in 2020 was punctual and that, after that, it has been well controlled. At the same time, it was demonstrated the influence of pH on the measurement of the parameter and the importance of adjusting the pH when evaluating it. Finally, by having a low value at the factory end discharge, the problem has been kept under control, but still the monitoring of this parameter will continue as a relevant matter to avoid having high values of IM.

At the other hand, the chemical compounds that were studied in this project, were not demonstrated to be causing of the IM high values, nevertheless, it would be important to identify their reactions between them or any other substance in the processes or their degradation processes to prove that they are not responsible of the IM parameter to be high.

Finally, the work conducted during the months of research and work in the company were effective in finding alternative to improve the company´s environmental performance and to help comply with the current and future applicable legislation. Also, the organization of campaigns, data analysis and information gathering were successfully achieved to meet the objectives set at the beginning of the project; it is important to emphasize that the teamwork with the environmental and other departments was of great help in meeting these objectives.

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8. Appendices

Updates after the internship period:

NOx online analyser

Between the months of December and January, the NOx online analyser has been installed, and it has demonstrated that it is working properly. The installation and calibration are done, and currently it has been set in motion. This will be a useful tool to follow in real time the behaviour of the NOx emissions to identify easier anomalous scenarios and to have more exact and precise ramp-up analysis. Also, it will help to analyse the reasons of the behavioural change on the NOx emissions of the last ramp-up campaign done in October 2021. Even though the plan to externally manage the methanol as a waste is already under discussion for implementation.

Inhibiting Matter

Regarding the IM parameter, the results obtained in the campaigns were not as conclusive as they were expected to be, the influence by the pH on the test was proven, nevertheless, the research on the possible toxic compounds will continue to identify if their reactions or degradation could be the cause of the high values of IM.

TABLE 8.1 PARAMETERS, LIMITS AND MONITORING FREQUENCY

<table>
<tr><th>Parameter</th><th>Limit</th><th>Units</th><th>Legal control frequency</th><th>External laboratory control frequency</th><th>Internal laboratory control frequency</th></tr>
<tr><td>pH</td><td>5 - 9</td><td>upH</td><td rowspan="11">Monthly</td><td rowspan="11">Once per month</td><td>Daily</td></tr>
<tr><td>Total Suspended Matter</td><td>250</td><td>mg/l</td><td>Twice a week</td></tr>
<tr><td>COD</td><td>700</td><td>mg/l</td><td></td></tr>
<tr><td>TOC</td><td>300</td><td>mg/l</td><td>Daily</td></tr>
<tr><td>BOD$_5$</td><td>300</td><td>mg/l</td><td></td></tr>
<tr><td>Total Hydrocarbons</td><td>15</td><td>mg/l</td><td></td></tr>
<tr><td>Anionic surfactants</td><td>6</td><td>mg/l</td><td></td></tr>
<tr><td>Organic and ammoniacal nitrogen</td><td>80</td><td>mg/l</td><td>Daily</td></tr>
<tr><td>Total phosphorus</td><td>30</td><td>mg/l</td><td></td></tr>
<tr><td>Phosphates</td><td>90</td><td>mg/l</td><td></td></tr>
<tr><td>Inhibiting matter</td><td>25</td><td>Ut</td><td></td></tr>
<tr><td>Nickel</td><td>1,7</td><td>mg/l</td><td rowspan="26">Annual</td><td rowspan="25">3 times per year</td><td></td></tr>
<tr><td>Aniline</td><td>none</td><td></td><td>Weekly</td></tr>
<tr><td>Arsenic</td><td>1</td><td>mg/l</td><td></td></tr>
<tr><td>Cyanides</td><td>1</td><td>mg/l</td><td></td></tr>
<tr><td>Copper</td><td>1,25</td><td>mg/l</td><td></td></tr>
<tr><td>Total chrome</td><td>2,5</td><td>mg/l</td><td></td></tr>
<tr><td>Chrome VI</td><td>0,25</td><td>mg/l</td><td></td></tr>
<tr><td>Mercury</td><td>0,00175</td><td>mg/l</td><td></td></tr>
<tr><td>Aluminium</td><td>20</td><td>mg/l</td><td></td></tr>
<tr><td>Cadmium</td><td>0,011</td><td>mg/l</td><td></td></tr>
<tr><td>Lead</td><td>0,7</td><td>mg/l</td><td></td></tr>
<tr><td>Zinc</td><td>3</td><td>mg/l</td><td></td></tr>
<tr><td>Phenols</td><td>2</td><td>mg/l</td><td>Weekly</td></tr>
<tr><td>Oil and fat</td><td>50</td><td>mg/l</td><td></td></tr>
<tr><td>Polycyclic Aromatic Hydrocarbons (PAH)</td><td>0,01</td><td>mg/l</td><td>Weekly</td></tr>
<tr><td>Δ temp</td><td>5</td><td>ºC</td><td></td></tr>
<tr><td>Colour</td><td>Inappreciable</td><td>dil.1/30</td><td></td></tr>
<tr><td>Nonylphenol</td><td>0,05</td><td>mg/l</td><td></td></tr>
<tr><td>Ammonia</td><td>50</td><td>mg/l</td><td></td></tr>
<tr><td>Nitrates</td><td>100</td><td>mg/l</td><td></td></tr>
<tr><td>Monochlorobenzene</td><td>0,5</td><td>mg/l</td><td>Weekly</td></tr>
<tr><td>Benzene</td><td>0,5</td><td>mg/l</td><td></td></tr>
<tr><td>Toluene</td><td>0,5</td><td>mg/l</td><td></td></tr>
<tr><td>Ethylbenzene</td><td>0,5</td><td>mg/l</td><td></td></tr>
<tr><td>Xylene</td><td>0,5</td><td>mg/l</td><td></td></tr>
<tr><td>Styrene</td><td>0,5</td><td>mg/l</td><td>12 times per year</td><td>Weekly</td></tr>
</table>

Source: own elaboration.

TABLE 8.2 GAS EMISSION POINTS, ANALYSIS PARAMETERS AND FREQUENCY OF MEASUREMENTS

Emission point	Parameter	Frequency of measurements
TAR (Thermal Oxidiser)	Chlorine Carbon monoxide Hydrochloric acid Nitrous oxide Total Volatile Organic Compounds (TVOCs)	**Official**: every 2 years **Internal**: every month
	Benzene Tetrachloromethane Total Suspended Solids (TSS)	**Official**: not required **Internal**: yearly
	Aniline Chlorobenzene Dichlorobenzene Formaldehyde MDA MDI Phosgene	**Official**: every 2 years **Internal**: yearly
	Sulphur dioxide	**Official**: not required **Internal**: quarterly
	Dioxins	**Official**: every year
Gas Turbine 1 + Boiler 5 **Gas Turbine 2 + Boiler 6** **Boiler 4**	Carbon monoxide	For the TG1-C5 there are made by an online analyser. **Official**: every 3 years. **Internal**: quarterly.
	Nitrous oxide	**Official**: every 3 years. **Internal**: quarterly.
Hydrochloric acid Scrubber	Hydrochloric acid	Not official measurements because the emission point is not included in the permit yet.

Source: own elaboration.

Table 8.3 EXTENDED TABLE OF COMPOUND´S TOXICITY

Compound	Hazard class and category code	Hazard indicator code
	Carcinogenicity 2	H351: Suspected of causing cancer <state route of exposure if it is conclusively proven that no other routs of exposure cause the hazard>.
	Germ cell mutagenicity 2	H341: Suspected of causing genetic defects <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>.
	Acute toxicity inhalation 3	H331: Toxic if inhaled.
	Acute toxicity dermal 3	H311: Toxic in contact with skin.
Aniline	Acute toxicity oral 3	H301: Toxic if swallowed.
	Specific target organ toxicity - repeated exposure, 1	H372 (*) (*): Causes damage to organs <or state all organs affected, if known> through prolonged or repeated exposure <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>
	Serious eye damage/eye irritation 1	H318: Causes serious eye damage.
	Skin sensitisation 1	H317: May cause an allergic skin reaction.
	Hazardous to the aquatic environment - Acute hazard, 1	H400: Very toxic to aquatic life.
	Flammable liquid 2	H225: Highly flammable liquid and vapour.
Acrylonitrile	Carcinogenicity 1B	H350: May cause cancer <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>
	Acute toxicity inhalation 3	H331: Toxic if inhaled.

TABLE 8.3 CONT. EXTENDED TABLE OF COMPOUND´S TOXICITY

Compound	Hazard class and category code	Hazard indicator code
Acrylonitrile	Acute toxicity dermal 3	H311: Toxic in contact with skin.
	Acute toxicity oral 3	H301: Toxic if swallowed.
	Specific target organ toxicity - single exposure, 3 respiratory tract irritation	H335: May cause respiratory irritation.
	Skin Irritation 2	H315: Causes skin irritation.
	Eye Damage 1	H318: Causes serious eye damage.
	Skin Irritation 1	H317: May cause an allergic skin reaction.
	Aquatic Chronic 2	H411: Toxic to aquatic life with long lasting effects
Phenol	Germ cell mutagenicity 2	H341: Suspected of causing genetic defects <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard.
	Acute toxicity inhalation 3	H331: Toxic if inhaled.
	Acute toxicity dermal 3	H311: Toxic in contact with skin.
	Acute toxicity oral 3	H301: Toxic if swallowed.
	Specific target organ toxicity - repeated exposure 2	H373 (**): May cause damage to organs <or state all organs affected, if known> through prolonged or repeated exposure <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>.
	Skin Corrossion 1B	H314: Causes severe skin burns and eye damage.
	Aquatic Chronic 2	H411: Toxic to aquatic life with long lasting effects

TABLE 8.3 CONT. EXTENDED TABLE OF COMPOUND´S TOXICITY

Compound	Hazard class and category code	Hazard indicator code
Monochlorobenzene	Flammable liquid 3	H226: Flammable liquid and vapour.
	Acute toxicity inhalation 4	H332: Harmful if inhaled.
	Hazardous to the aquatic environment - Chronic hazard 2	H411: Toxic to aquatic life with long lasting effects.
Styrene	Acute toxicity (inhalation) 4	H332: Harmful if inhaled.
	Eye Irritation 2	H319: Causes eye irritation.
	Skin Irritation 2	H315: Causes skin irritation.
	Flammable liquid 3	H226: Flammable liquid and vapour.
Ethylbenzene	Flammable liquid 2	H225: Highly flammable liquid and vapour.
	Acute toxicity inhalation 4	H332: Harmful if inhaled.
	Hazardous to the aquatic environment - Chronic hazard 3	H412: Harmful to aquatic organisms with long lasting harmful effects.

Source: own elaboration.