CHEMICAL EXPLOSION AT IQOXE IN TARRAGONA

Incident Investigation Report

GENERALITAT DE CATALUNYA, DEPARTAMENTO DE EMPRESA Y CONOCIMIENTO, DIRECCIÓN GENERAL DE ENERGÍA, SEGURIDAD INDUSTRIAL Y SEGURIDAD MINERA

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Applicable contract(s) governing the provision of this Report:

Objective:

This report outlines the incident investigation, and its findings, undertaken for the chemical explosion at IQOXE in Tarragona happened on 14th of January 2020.

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1 EXECUTIVE SUMMARY

The IQOXE plant in Tarragona, suffered a large explosion on 14th of January 2020. Two people were killed, one by a missile fragment from the explosion inside his flat in Torreforta about 2.5km away, one IQOXE employee working on site. A second IQOXE employee died as a result of his injuries one day later in hospital. Missile fragments also damaged neighbouring plants in the industrial area of Tarragona. The explosion happened at the end of the production of a batch of MPEG 500, an ethoxylation derivative used as an additive for cement. MPEG 500 was being produced in the reactor R3131 of the derivates plant U3100.

The responsible department for Industrial Safety and Mining Safety of the Catalonian Government (GenCat) commissioned DNV GL to investigate the explosion. The purpose of DNV GL's investigation was to find out:

- What has happened?
- Why could it happen?
- What changes are required, to avoid such an incident from happening again?

Verification of regulatory compliance is not the purpose of this investigation.

The investigation took place from 9th of April until 13th of July. On 13th May GenCat made the decision to adapt the purpose of the investigation to focus on the information available which was limited by several factors including:

- Secrecy of the judicial police investigation;
- Absence of process record data due to destruction by the explosion;
- Prevention by the court of access to the site of the damaged unit (until the end of May);
- Restrictions on travel and physical meetings due to COVID-19

Based on the limitations the team proceeded with event and hypothesis identification and evaluation, barrier identification and assessment, and causal analysis for the high and medium likelihood hypotheses.

As a result, DNV GL identified the following chain of events starting with a hypothesis for the initiation of the thermal decomposition of ethylene oxide by a formation of ethylene oxide (EO) decomposable mixture and the creation of a hot spot in the reactor system.

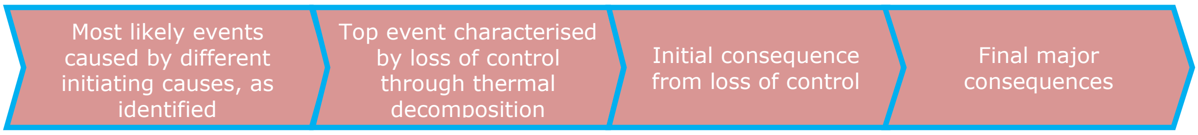
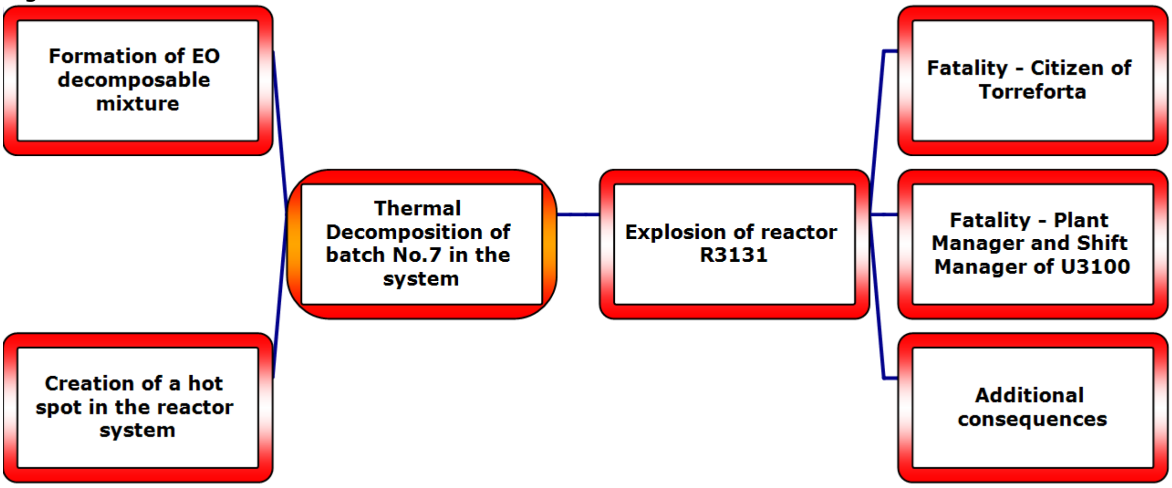


Figure 4-21



DNV GL assessed a number of potential causes on the basis of gathered information. The below tables show the high likelihood and medium likelihood causes, excluding the causes considered to have a low likelihood.

Potential causes for "Formation of EO decomposable mixture"

No.	Potential cause	Evaluation
EO/1	A fault in the nitrogen pressure control	High likelihood
EO/3	An external leak would release a mixture of nitrogen and EO but be replaced by pure EO if addition continued	High likelihood
EO/2	EO accumulation in the reused nitrogen between batches	Medium likelihood
EO/5	Opening, or passing, of the reactor vent valve (31XV332) to the vent header	Medium likelihood

Potential causes for "Creation of a hot spot"

No.	Potential cause	Evaluation
HS/3	A fire impinging on part of the attached process	High likelihood
HS/1	Runaway reaction reaching the decomposition temperature	Medium likelihood
HS/4	A fire impinging on the vent system connected to the reactor	Medium likelihood
HS/9	Heat from unintended reaction catalyzed by contaminant	Medium likelihood

The above tables are an excerpt from Figure 4-21 Summary of hypotheses

The investigation has not yet been able to identify the actual causes or the common cause for the two events leading to the thermal decomposition, due to the previously mentioned constraints.

From this point the investigation focused on the identification and analysis of safety barriers for this chain of events. Safety barriers are physical and/or non-physical means planned to prevent, control, or mitigate undesired events or accidents. The terms "risk control" or "safeguard" are similarly used.

The identification and analysis of safety barriers (or similar terms) has been done on the basis of good industry practice and guidance from sources including the American Chemistry Council ethylene oxides guide and was not directed by consideration of legal compliance. Thus, the barrier state definition "missing", "failed", "inadequate", etc. as outlined in Section 4.5 of this report (and in the table below in this summary) should be understood in its technical sense rather than any comment on legal compliance.

DNV GL assessed a number of barriers, which are below clustered in groups 1-4.

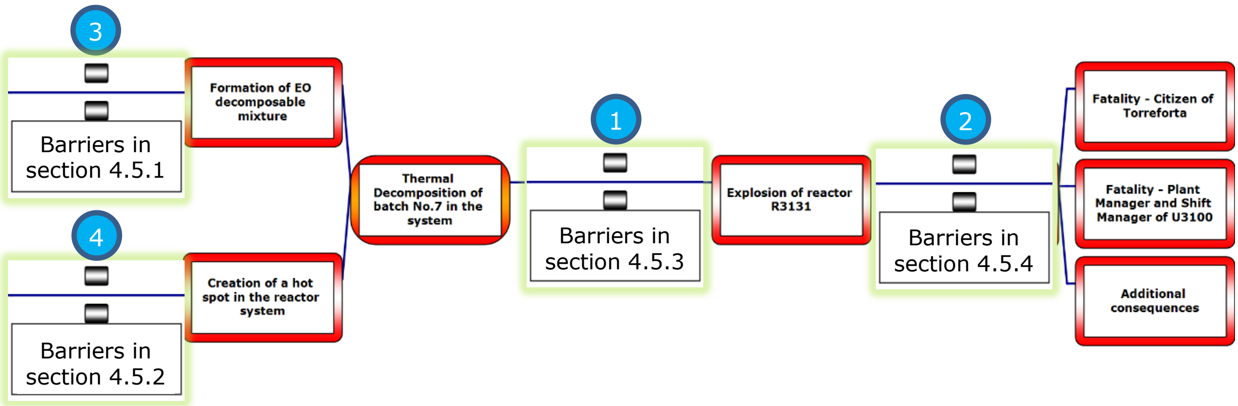


Figure 4-22

The following table provides an overview of the barrier status and their identified deficiencies.
Note about barrier state definitions:

- Missing: The barrier was described in the organisation's safety management system or was considered an industry standard, but was not successfully implemented
- Failed: The barrier was implemented, but did not function according its intended design
- Inadequate: The barrier functioned as intended by its design (envelop), but was unable to stop the sequence of events
- Unreliable: The barrier stopped the next event in the incident sequence, but the organisation is uncertain, if it will do so in the future
- Effective: The barrier functioned as planned and stopped the next event in the incident sequence.

Group No.	**Barrier assessment** (for details on the barrier assessment ref. is made to section 4.5)
1	**Barriers to prevent the event "Explosion of reactor R3131" after the event "Thermal Decomposition of batch No.7 in the system" occurred** Once the thermal decomposition has started, it will immediately result in a major event. There are no preventive barriers known by DNV GL, that could effectively stop the thermal decomposition from progressing to an explosion. Existing barriers, such as 3.1 "Pressure Safety Valve 31-RV-323", or 3.2 "Design of the system to contain a thermal decomposition" were inadequate for this event. The barrier 3.2 could cope with thermal decompositions not reaching more than 45barg.

2	**Barriers to prevent or mitigate the consequences from the event "Explosion of reactor R3131"** There are only very few mitigating barriers to reduce the consequences from the major event. The barrier 4.1 „Local Planning Controls" to protect external parties is regarded as inadequate to stop the sequence of events in this particular accident where the serious consequences of the atypical projection of a fragment would have had a very low predicted likelihood. The barrier 4.1 „Local Planning Controls" may be adequate for managing the predicted risks to a normally acceptable level, but this aspect was not part of the investigation. The second identified barrier to protect people working on site in the control room, 4.2 „Design and location of the control room" failed, as there is no evidence that the risks to the persons in the control room from the new unit U3100 had been fully assessed, neither by management of change, nor by occupied building risk assessment. As it becomes obvious from the limited prevention and mitigation barriers, an incident like this must be prevented by all means before a thermal decomposition is initiated.
3	**Barriers to prevent the event "Formation of EO decomposable mixture"** The barrier 1.1„Verification of correct gas composition in the reactor head space" is not in place (missing), however, currently it is not standard practice in ethoxylation reactor design to provide a gas analyser on the head space. There would be a number of practical difficulties in providing such analysis including the impact of polymer contamination on the analyser. The barrier 1.2 „Leak detection system" has been regarded as inadequate. The leak detection provided in the facility appears to be insufficient. No evidence has been seen that relevant safe studies were performed and that relevant guidance was applied in selection or location of leak detection.
4	**Barriers to prevent the event "Creation of a hot spot in the reactor system"** Barrier 2.1 „Fire detection and fire fighting system" is considered inadequate. The installed sprinkler system only protected the reactor vessel, but not the entire EO connected system in U3100. No evidence was seen of safety studies to identify possible fire sources in U3100, that might affect the EO-connected system, nor was evidence seen of identification of required active or passive fire protection other than a design document based on industrial building regulatory requirements. Barrier 2.2 „Heat insulation of R-3131", Barriers: 2.3 „Temperature and Pressure Control System", 2.4 „ESD Emergency Shutdown System" and 2.5 „Manual ESD: emergency full cooling": Due to the extent of damage to the unit and the lack of data or witness information, it is not possible to determine if there was a failure of the systems or the manual ESD activation. However, such a failure is credible but low likelihood.

The detailed assessment of the barriers is section 4.5 have led to the following recommendations, which shall ensure the failed or inadequate barriers are improved on a management system level and thus the likelihood for further incidents will be reduced. The following **recommendations** are proposed and further outlined in section 5:

1. Ensure appropriate risk identification and management
2. Review and improve the management of change process
3. Ensure safe control room or occupied buildings
4. Assess level of prevention barriers/safeguards to take account for limited containment
5. Apply good industry practice for the fire detection and firefighting system
6. Install appropriate gas detection in the unit
7. Assess possibility for reactor gas analysis
8. Review approach for risk reduction from ethylene oxide installations

Moreover, DNV GL looked at a number of hypothetical events proposed as possible causes of either enrichment of the EO concentration or causes of a hot spot. As has been demonstrated in the barrier analysis in Section 4.5, by considering what might have prevented these hypothetical events, the following **expectations** for management systems and operating procedures can be proposed and further outlined in section 5. Expectations are proposed in order that the operator and other stakeholders might be able to verify the management systems and barriers against these expectations which reflect good practice.

1. Reliability of the control system;
2. Competence assurance for critical tasks;
3. Adequate fire resistant insulation of the R-3131 system;
4. Prevention of EO accumulation in the head space;
5. Leak prevention;
6. Prevention of leaks to the vent header;
7. Fire prevention by inspection and maintenance;
8. Prevention of contaminants.

To date, the investigation has not yet been able to reach firm conclusions on the causes of the accident. This has been due to a number of limitations as outlined in Section 2. As the investigation has proceeded, several outstanding questions remain unanswered. A number of additional tests have been identified. The following **future actions** are recommended:

1. Where possible, person to person interviews with key witnesses should be held, recognizing the time that has elapsed since the accident;
2. In conjunction with the interviews, information should be made available by IQOXE to fully answer the outstanding questions;
3. Further assessment of the final stage of the process before the explosion happened, i.e. assessment of the electrical power reduction by 430kW between

18:15 and 18:30 – in order to answer the question of whether the loop pumps were stopped.

4. If possible, information, photographs and data collected by the police and judicial enquiry should be examined;
5. Several fragments of the damaged unit have been identified to GenCat for analysis of surface effects to determine to what extent they have been exposed to heat or have smoke deposits. This analysis should be carried out and the results assessed;
6. Subsequent to the initial thermal stability findings presented by IQS, further tests on the MPEG 500 reaction medium and product should be continued to understand its thermal stability as a function of time and temperature.

DNV GL hopes that the future actions will be able to fully clarify the chain of events and the reasons for it. We would like to continue supporting this process and would like to thank GenCat who helped the investigation to achieve a substantial part of the investigation target.

2 INVESTIGATION

2.1 Investigation by DNV GL

DNV GL was commissioned by the department for Industrial Safety and Mining Safety of the Catalonian Government (GenCat) to investigate the chemical explosion at IQOXE in Tarragona, which happened on 14th of January 2020. The purpose of DNV GL's investigation was to find out:

- What has happened?
- Why could it happen?
- What changes are required, to avoid such an incident from happening again?

Table 2-1: Key investigation steps

9th of April	Kick-off meeting with GenCat, Preparing the investigation and start information gathering from GenCat and public sources.
17th of April	Kick-off meeting with IQOXE via video conference and information gathering from IQOXE by end of May.
May and June	On 13th of May the decision was taken with GenCat to reshape the focus of the investigation to provide assurance rather than to investigate the root causes, subject to limited information made available to the investigation team. Based on this the team proceeded with event and hypothesis identification and evaluation, barrier identification and assessment, and causal analysis for the high and medium likelihood hypotheses.
29th of May	Site visit to IQOXE plant after approval was given by the responsible authorities. One DNV GL investigator was present on site and others including fire and explosion experts were connected via a remote inspection application to the mobile device of the person present at site.
Beginning of June	Selection of fragments and missiles, as well as advice on scope for forensic examination to find out whether fire damage can be allocated to prior or after the explosion.
During June	Development of recommendations and expectations to verify and improve the barriers in place at IQOXE, as well as completion of draft investigation report.
2nd of July	Exchange on investigation findings with GenCat, IQOXE and their contracted investigator from IQS university of Barcelona
13th of July	Provision of investigation report to GenCat for review
9th of October	Release of investigation report to GenCat

The investigation was hampered by several limitations, which affected negatively the investigation:

- Secrecy of the judicial police investigation;
- Because of the judicial enquiry, IQOXE was advised by its legal representative not to hold interviews with DNV GL but instead to communicate information via written and translated questions and answers;
- Absence of process record data due to destruction by the explosion;
- Prevention by the court of access to the site of the damaged unit (until the end of May);
- Restrictions on travel and physical meetings due to COVID-19;
- Non-exclusion of DNV GL report for judge purpose;
- Engagement of DNV GL three months after the incident.

On the other hand, the work has continued and been very well supported by the responsible GenCat team who helped the investigation team to achieve a substantial part of the investigation objectives.

For the terms of reference for the investigation, as well as the investigation team, please see 7.1.

2.2 Parallel investigation by IQS

In parallel with the investigation by DNV GL, a team at the School of Engineering at IQS in Barcelona led by Prof. Julia Sempere has been carrying out a separate investigation on behalf of IQOXE. Results have yet to be published but there is an early indication that the decomposition of the product, MPEG500, is itself highly energetic. One hypothesis for the event is the decomposition of the liquid product in the reactor, which liberates gaseous decomposition products leading to overpressure of the vessel. At the time of writing further tests are to be carried out on the product. The cause of the initiation of the product decomposition is still being investigated. This report should be read in conjunction with any publication on the investigation by IQS.

3 INCIDENT DESCRIPTION

The incident on 14th of January 2020 at IQOXE is described in the below sections. Basic information is provided on the plant in general, the incident location, the normal operation process, as well as the actual operation process undertaken on the day of the incident. The consequences from the incident are described and a timeline is drawn up for the course of the incident.

3.1 General information about affected Unit and incident location

Industrias Quimicas del Óxido de Etileno (in the following "IQOXE") is a petrochemical company established in 1964. It has been recently acquired by CL Grupo Industrial in 2014 when it got its current name.

The main activity of IQOXE is the production of ethylene oxide. Additionally, it produces derivative products from the ethylene oxide such as MEG, DEG and PEG. Facilities are located in Tarragona, Catalonia, Spain within an industrial complex at 2km from the sea.

Figure 3-1: Tarragona area with IQOXE plant location (blue frame) and U3100 (red frame)

The facilities are composed of one production plant used to produce ethylene oxide and glycols continuously as well as production plants used to produce derivatives by batch.

Among these batch type plants there is the unit U3100 where the explosion occurred during the production of the 7th batch of MPEG 500. MPEG 500 is used as additives for cement.

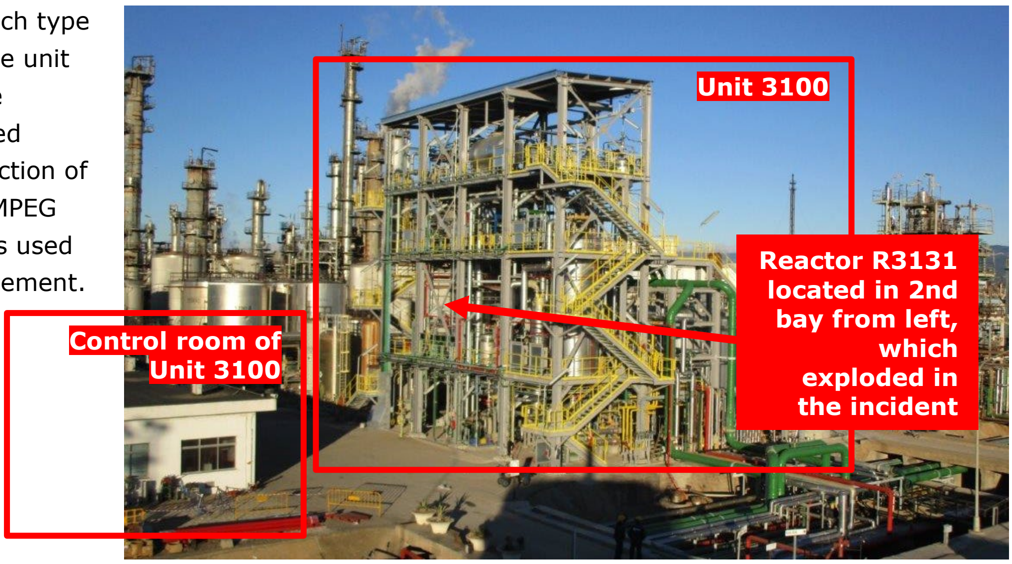


Figure 3-2: Unit 3100 prior to the explosion

3.2 Work order and basic operational aspects for production of MPEG 500 batch No7

A batch of MPEG 500 was planned to be produced on the incident day in the derivates plant U3100.

MPEGs are manufactured by reacting methanol with ethylene oxide plus a catalyst, which in this case is 30% sodium methylate in methanol and subsequent neutralization with acetic acid.

The planned recipe for the MPEG 500 production Batch 7 contained:

- Methanol 1341.2kg raw material.
- Sodium methylate 47kg, catalyst.
- EO 19104 kg
- acetic acid 16.4kg

The batch on the incident day was the 7th batch of that type since first production was made in June 2019. The batch process runs basically automatically with little operator action, and consists of the following steps:

1. Raw material and catalyst are charged to the reactor
2. Heating to reaction temperature
3. Continuous feeding of ethylene oxide (EO) to the loop reactor which reacts with the raw material in the presence of the catalyst. Cooling is required to remove reaction heat
4. Heating to complete the reaction
5. Postreaction and Filtration

Whilst a pre-reactor is available for carrying out steps 1 and 2, the recipe indicates that for MPEG 500, steps 1 and 2 are carried out in the loop reactor 31-R-3131. Step 3 takes place in the reactor R3131 and for step 4 the material is transferred to the post-reactor vessel V-3141. Details about the process, normally using also the pre-reactor can be obtained from the basic process description in 7.3 and the process flow charts in 7.4.

Operators are running the process, which is divided into blocks:

Table 3-1: Operation sequence by blocks

Block	Description
1 Recipe	Recipe load
2 Charge raw material	Loading the raw material using the small reaction loop
	Loading the raw material using the large reaction loop
2ª Elimination air	Air removal with vacuum of the raw material, as applicable
3 Charge catalyst	Addition of catalyst
4 Elimination water	Elimination of water with vacuum of the raw material, as applicable
5ª Adjustment reaction cond.	Adjustment to reaction conditions
5 Reaction	Adding EO using the small reaction loop
	Adding EO using the large reaction loop
6 Exhaustion	Exhaustion (or cook down) of unreacted EO at 140 degC for 30 mins
7 Transfer	The batch is transferred by pressure to the post-treatment vessel V-3141

3.3 Incident and damage description

The incident occurred in the U3100 on the 14th January of 2020 at approx. 18:40.

Comparing the damage to the steel structure of U-3100 with the unit prior to the accident indicates a centre of an explosion located in the upper part of the reactor bay. The vertical structural steel has been forced away from the centre of the explosion.

Figure 3-3: U3100 directly after the explosion

Figure 3-4: plate from reactor found in household in Torreforta

Sadly, two workers of IQOXE, who were working at U3100 died. Furthermore, one person living in the nearby village Torreforta also died, when a plate from the reactor hit his household 2.5km away from plant. Several workers were physically and psychologically injured.

3.3.1 Damages at IQOXE plant

The explosion resulted in overpressure effects, resulting in total destruction of the plant unit U-3100 and the adjacent control room (approximately 25m from the unit boundary to the control room wall.). The preceding fire and the subsequent explosion led to severe distortion of U-3100's structural steel and displacement of main vessels. Lighter damage was caused to buildings

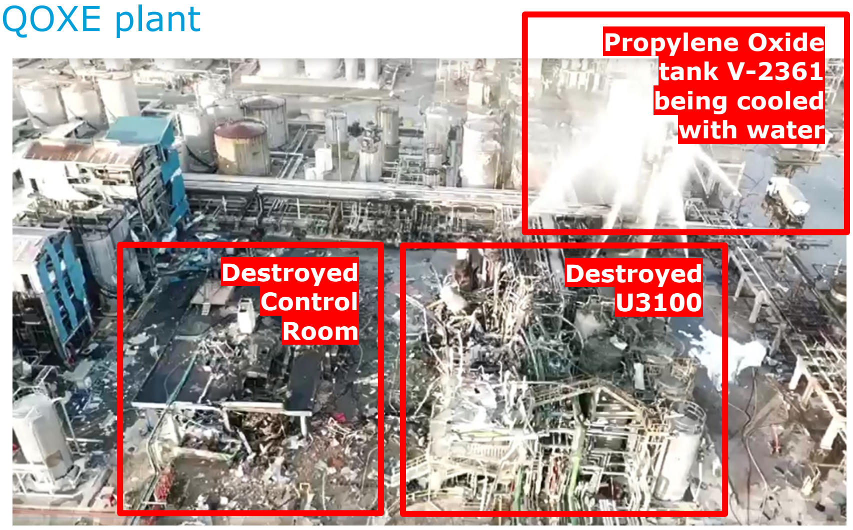


Figure 3-5: Excerpt from video showing the destroyed U3100 and surrounding facilities

located further away, examples being that a proportion but not all cladding panels were blown from buildings located at a distance of approximately 50m from U-3100. Windows in the office building located approximately 200 m away from the affected unit shattered due to overpressure. A large number of the unit fragments fell on adjacent parts of the IQOXE site.

A fragment pierced the walls of the Propylene Oxide tank V-2361 leaking fuel which subsequently ignited leading to a jet fire that was mitigated by fire-water cooling on the walls of the tank and adjacent tanks.

Burning material projected by the explosion, in combination with the subsequent fireball, led to the outbreak of secondary fires around the affected unit U-3100.

A different manufacturing unit known as the Ethylene Oxide plant (Unit U-2000) is located approximately 150m from U-3100. Unit U-2000 manufactures Ethylene Oxide and derivatives. It was not seriously damaged following the explosion and it is intended to restart production.

3.3.2 Damages at the surrounding plants

Several fragments projected from the explosion center hit the industries located around IQOXE. Some of them have reported the damages, but not all of them have provided their plant layouts with the projectiles and fragments found. The next figure shows a map in which the reported fragments have been plotted.

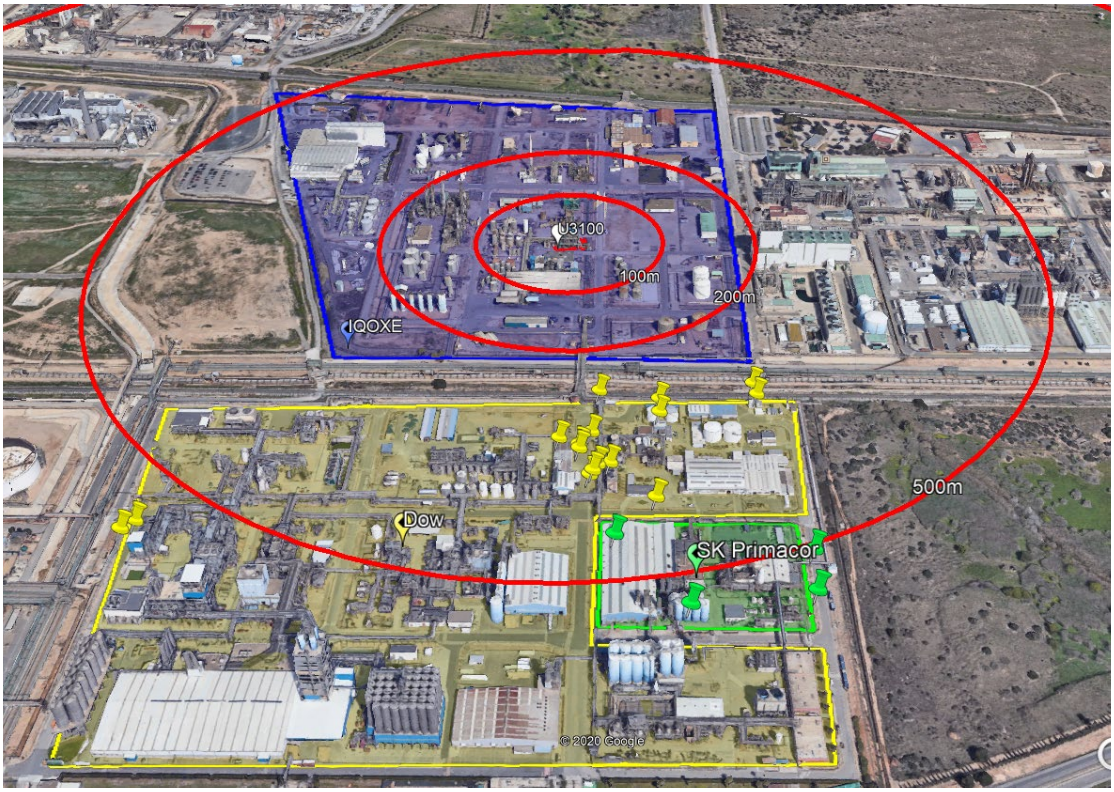


Figure 3-6: Plotted missile fragments to IQOXE and surrounding plants

Most of the fragments are located at the east of the plants. This happens because other directions were blocked by buildings in the IQOXE site itself. Around 40 fragments have been reported, some of them up to 400kg. Most of them were parts of the U3100 structure.

Only a small surface around IQOXE has been scanned for fragments, other industries or lands have not reported the fragments and thus there is no information about them.

3.4 Time Line: Course of activities and processes prior to the explosion

Table 3-2: Course of activities and processes prior to the explosion

Date, Time:	**Description of events/activity incl. key information:**	**Reference to evidence:**
13th of January		
Night Shift	22:00 – 06:00 (staff present: Shift manager, two operators)	
05:24	Work order 67924 was issued on 13-01-2020 for removal of the pump P3132 (wrongly numbered) insulation to locate the leak and change burnt fiber glass of the pump with the priority to finish the works at the same day. The burnt fiberglass was detected on the 12th of January.	PAP_013, Interview IQOXE
	67.957-Repair 31_X_320 Y 31_X_329 – ACCESORIOS (valves of the catalyzer). Works were finished on at the same day	PAP_013, Interview IQOXE
Afternoon Shift	14:00 – 22:00 (staff present: Shift manager, two operators, additionally from 8:00 -17:00 Plant manager and one operator)	
	Work order 67924: Maintenance was called to check the P-3132 pump (small loop). The pump P3132 is used for circulation of the mixture of raw material and catalyst through external tubular exchangers (E-3131 and E-3132) to raise the temperature to around 100 ° C. It is located next to R3131. Together Plant (operation) and Maintenance observed that it had no problems, and actually the work order named the wrong pump. The right pump was identified as P3152.	PAP_015, Interview IQOXE
14th of January		
	Verbal work instruction was given to reconnect the washing system of the pump seal of P3132 (it was out of service after the seal model was changed by the manufacturer on 28th Nov 2019 as it was not needed anymore in this new model). During this work a probable leak was identified in the seal housing. Repair works were postponed by the responsible person. The site visit of DNV GL on the 29th of May did not indicate any fire damage at or around that pump.	PAP_015, Interview IQOXE
	Work Order 67.993: Calibrate level indicators 31-L511, 521, 541 AND 551 FOR MPEG-1000 at the intermediate tanks, finish within 72h. The work order is for a periodic change due to product change.	PAP_015, Interview IQOXE
Morning Shift	06:00 – 14:00 (staff present: Shift manager, two operators, additionally from 8:00 -17:00 Plant manager and one operator)	
Approx. 12:40	The batch 423 of MPEG1000 was finished and the batch 7 of MPEG500 was started. It is assumed, that raw material, methanol and the catalyst were introduced to the reactor R3131. However, no process data or documentation of raw material could be gathered.	Interview IQOXE, IT_03

Afternoon Shift	14:00 – 22:00 (staff present: Shift manager, two operators, additionally from 8:00 -17:00 Plant manager and one reinforcement operator)	
15:00 - 16:00	EO of 1.014tn was withdrawn from EO tank to derivates unit 3100.	IT_02
16:00 - 17:00	EO of 6.323tn was withdrawn from EO tank to derivates unit 3100.	IT_02
17:00 - 17:58	EO of 9.876tn was withdrawn from EO tank to derivates unit 3100. The feed stopped at 17:58.	IT_02, IT_01
Between 18:15 and 18:30	Electrical consumers of approx. 430kW belonging to U3100 were shut-off. As there is no further information or data available, it is presumed that the big circulation pump together with other electrical consumers (pump and fan of cooling water tower, possibly even the small loop pump) were switched off, either by manual operation or by an automated safety process. As per the operation manual both loop pumps should have been running throughout the entire exhausting phase of the batch.	IT_03, IT_04, IT_05, IT_06, PAP_04
Between 18:10 and 18:40	Steam was applied to the system to conduct exhaustion of unreacted ethylene oxide at an intended reaction temperature at 140 ° C for 30 minutes. The related steam graph is actually for the entire facility incl. the derivates plant. As no other consumers were operating at this time, the rise in steam was allocated by IQOXE to the MPEG 500 production.	IT_07, Interview IQOXE
Approx. 18:30	The plant manager, who was supposed to work from the U3100 control room building, sent an email. The content of the email was not related to the running MPEG 500 production.	Interview IQOXE
	A witness inside the IQOXE main office on site heard the sound of a loud depressurisation noise estimated to have lasted about 10-15 secs, before the explosion.	Interview IQOXE, PAP_01
Approx. 18:40	The reactor R3131 in unit 3100 exploded, Severe damage caused by the explosion The explosion is further described in detail: An initial fire lasting for minimum 20ms followed by two fireballs within a timeframe of less than 2 seconds. The second fireball is several times bigger than the first fireball.	Interview IQOXE, IT_10, IT_13, IT_14

4 INCIDENT ANALYSIS

For the subsequent analysis the DNV GL BSCAT methodology was applied. BSCAT stands for "barrier based systematic cause analysis technique". It is scalable, which allows its application to any incident complexity, and provides a minimum structure with reasonable flexibility to support the creative thinking process.

Based on the information received the chain of events are identified backwards from the final consequences, in this case the explosion in U3100. The chain of events in chronological order represents the increasing risk towards the top event (e.g. loss of control over …, or loss of containment) and the final consequences, which can be related to different damage related to personnel, environment, production, asset, and reputation.

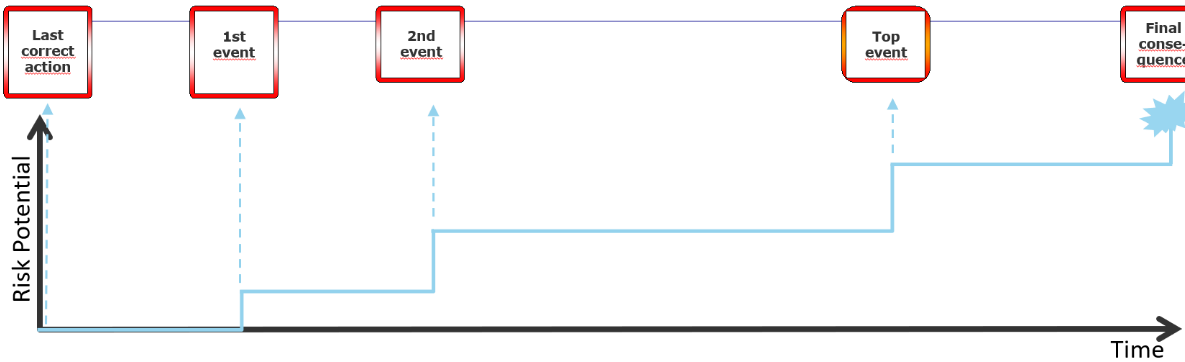


Figure 4-1: BSCAT systematic –Several events leading to the incident

In-between the events the BSCAT methodology identifies **barriers** which shall be able to prevent the occurrence of the next event. After identification follows the analysis of the barriers. The barriers that were missing, have failed or were inadequate are further analysed for the direct causes and the root causes. To avoid barrier failures in the future in similar cases respective recommendations are given. See Figure 4-2

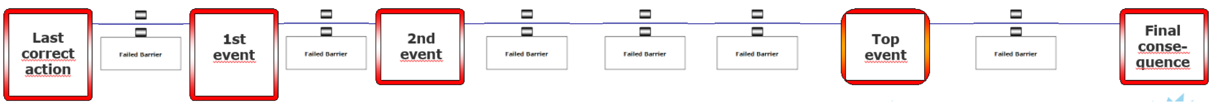


Figure 4-2: BSCAT systematic - Identification of barriers to prevent the events from occurring

In several cases it was not possible to identify all events leading to an incident, as well as the full analysis of barriers, due to several restrictions in information gathering. In that case hypothesis and different scenarios are developed.

4.1 Understanding the type of event by assessing the consequences

The characteristics of the event, i.e. the explosion itself, will be important to identify the potential causes for its occurrence. Therefore, the investigation team collected the following evidence from observations.

Videos and photographs of the accident taken from outside the site indicate that a highly energetic event took place at 18:40. This was followed by an initial rapid release of burning material in the location of the unit including a projection of incendiary items. This was further followed (approximately 2 seconds later) by a larger release of burning material forming a fireball above the site that lasted longer than 10s.

Figure 4-3: Initial scene from external video

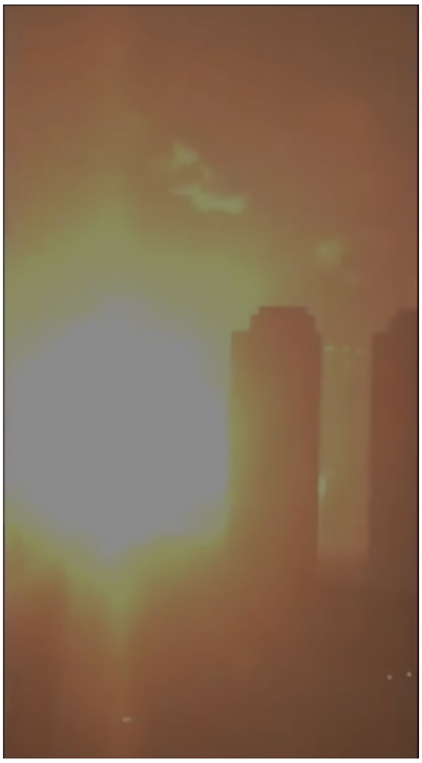


Figure 4-4: 1st explosion 20ms later

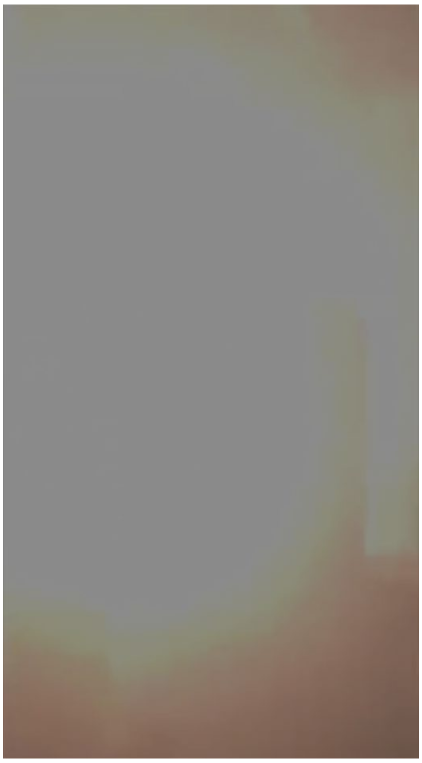


Figure 4-5: 2nd explosion 2s later

It is not possible to ascertain from the short video whether these are separate moments of loss of containment or 3 stages of the failure of the reactor. Other than the reactor R3131, no vessels showed signs of an explosion.

The damage caused by the explosion indicates a very high energy release within a very short time. Damage samples are for example:

Damage by missiles and fragments travelling

Figure 4-6: Zone 0 and 1 at IQOXE plant

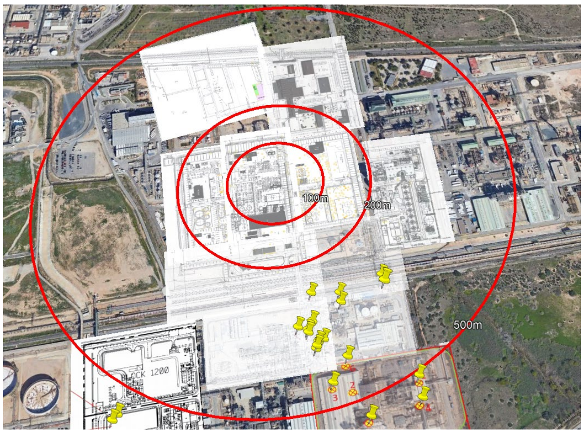


Figure 4-7: Zone 2 covering neighbouring plants

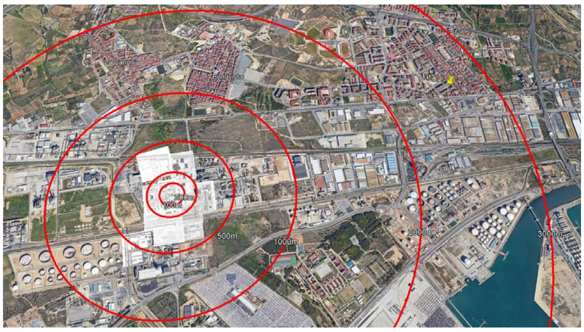


Figure 4-8: Zones 3-5 covering the missile lacation in Torreforta

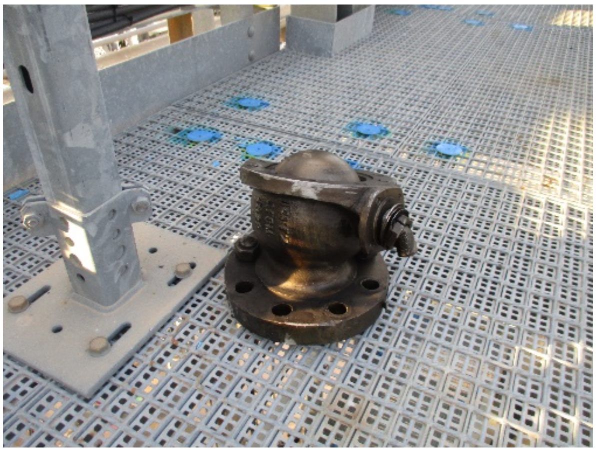
The missile with the largest travel distance belongs to the lower section of the reactor R3131 and travelled about 2.5km.
However, most of the missiles and fragments are located within a radius of 200m, to the north and west of the plant. This is because to the east and south of the unit, there were surrounding buildings that stopped the fragments. The nature of the fragments located in this range are of all kinds, mostly metal parts coming from the reactor surroundings.

Several fragments in an industrial zone around 400-500m away. In total around 40 fragments up to 200kg were identified in these areas. These circular sector accounts for around 25% of the surface between 400 and 500m. These fragments are mainly structure sections, valves and vessel parts.

It has to be taken in mind that only fragments that landed in private areas were reported. There is not information about fragments found in the rest of the circular sector. From videos and photographs obtained by members of the public it can be seen that fragments reached other places that have not been documented and thus provided to DNV GL.

Lastly the fragment that impacted the victim’s house, located over 2.5km away from IQOXE weighted around 750-1000kg. The house was located at the east of the facility.

Figure 4-9: Missile fragment of the reactor R3131 landed in Torreforta

Damage by blast wave	**Damage by energy release**
The blast wave “cut-off” the upper two levels of the U3100. Figure 3-5: Excerpt from video showing the destroyed U3100 and surrounding facilities  It further partially destroyed the control room 25m next to the U3100.  **Figure 4-10: destroyed control room building** Windows were shattered in the office building located approx. 200m away.  **Figure 4-11: Distance from incident site to IQOXE office building**	Many of the fragments which are process fittings such as flanges and valves have broken bolts indicating a very high force wrenched them from their installed location. Examples are provided below:  **Figure 4-12: FOTOGRAFIA 200**  **Figure 4-13 : FOTOGRAFIA 122B**  **Figure 4-14:**

4.2 Understanding the type of event

The maximum design pressure of the reactor R-3131 is 45 barg, which is the setpoint of the pressure relief. The maximum design temperature of the reactor R-3131 is 220°C.

There are several different event types that should be considered for possible events that might rupture the reactor:

1. Loss of control of exothermic reaction leading to overpressure of the reactor;
2. Loss of temperature control leading to overheating of the batch, increase in vapour pressure and causing overpressure of the reactor;
3. High pressure caused by connected feeds or services;
4. Overpressure due to fire engulfment, leading to a BLEVE;
5. Thermal decomposition inside the reactor leading to overpressure.

No1	**Loss of control of exothermic reaction leading to overpressure of the reactor**
Description	The ethoxylation reaction is very exothermic, approximately 100 kJ/mole of EO. In an uncontrolled situation, the rise in temperature would raise the vapour pressure in the reactor to a level where it could, if not relieved, result in failure of the vessel. An additional hazard is presented by the presence of unreacted EO in the reactor at the time of a runaway reaction. EO vapour decomposes explosively at 560°C with an energy release of 133760 kJ/Kg.mol (Burgoyne). This decomposition is addressed in event type 5.
Supporting indication	a) Theoretically, there is enough energy released when 23360kg [Note 1] EO reacts to raise the temperature by about 850 °C. b) There are several failures that could lead to an uncontrolled reaction: b.1 Failure of temperature control on the cooling loop; b.2 Failure of cooling medium supply to the reactor loop heat exchangers; b.3 Late addition of the catalyst; b.4 Accumulation of unreacted EO due to low temperature or poor mixing; b.5 Error in quantities of reactants. c) It is theoretically possible that an uncontrolled runaway reaction could reach the temperature of EO decomposition and cause the reactor explosion. d) The reactor R-3131 is fitted with a 3inch pressure relief valve 31-RV-323. However, this is sized for relief of methanol vapour during a fire event with heat only provided by the external fire. It is not sized for 2-phase flow runaway reaction relief.
Disregarding indication	a) There are a number of safeguards against a runaway reaction: a.1 Independent high temperature measured in the reactor will cause the EO feed to stop via the safety instrument system. a.2 On observing a rising temperature, the operator can initiate stopping the EO feed and apply full cooling. a.3 On high pressure measured in the reactor, the EO feed is stopped via the safety instrument system. a.4 Catalyst quantity is measured by mass flow meter and the programme will not advance to allow introduction of EO until the correct mass has been added. The recipe control provides safe-window limits for new quantities being entered. a.5 Semi-batch addition of EO minimizes the accumulation of unreacted EO in the reactor. The full quantity of reactants cannot be present in the reactor simultaneously. a.6 The design of the venturi jet for mixing the gaseous EO with the liquid reaction mixture ensures rapid reaction and minimises the accumulation of unreacted EO in the reactor. Loss of circulation through the venturi, for example if the loop circulation pump failed, leads to a significant slowing of the reaction since the gas-liquid mass transfer would be reduced. a.7 Whilst process data is not available for the batch involved in the accident,

	due to the destruction of the control room and the presumed loss of the data storage, it was understood that the reaction had reached completion. This reduces the likelihood that the reaction heat was still to be released immediately before or at the time of the accident. This deduction is made based on: • The time that had elapsed from the start time of the reaction (verbally reported as 14H00); • Measurements from the EO plant supplying EO to U-3100, that the feed had stopped after having delivered the correct quantity; • Electrical power consumption decreasing rapidly just before the explosion, consistent with stopping the main loop circulation pump P-3131 and consistent with electrical power data from a previous batch.	
Evaluation	Medium likelihood	This scenario is possible, but does not explain the fire that was observed shortly prior to the explosion. This large fire observed less than a second before the explosion may have been a consequence rather than a cause of the overpressure.

No2	**Loss of temperature control leading to overheating of the batch, increase in vapour pressure and causing overpressure of the reactor**	
Description	If the temperature control of the reactor had malfunctioned, heating by the external heat exchanger(s) could have continued beyond the intended set temperature. The vapour pressure of materials in the reaction mixture would have increased with the temperature. If methanol was assumed to represent the liquid contents of the reactor, the temperature would need to reach 210 °C in order to reach a vapour pressure of 45 barg. The maximum design pressure of the reactor R-3131 is 45 barg, which is the setpoint of the pressure relief. The maximum design temperature of the reactor R-3131 is 220°C.	
Supporting indication	a) Measurement of steam supply to the IQOXE site indicates an increase in consumption at the time prior to the accident. It is not known if unit U-3100 was consuming this steam.	
Disregarding indication	a) The heating system for the reactor is unlikely to be able to reach a temperature that might overpressurise the reactor. The heat is provided during the exhausting or "cook down" phase via a secondary tempered water circuit which is heated by steam in a separate heat exchanger. Heat could also have been abnormally applied during the batch. The water circuit has a pressure relief which would limit its maximum temperature and vapour pressure. HH Technology suggests that a maximum temperature of about 195 °C could be reached in the steam-fed exchanger which would lead to a vapour pressure of methanol below the design pressure. b) The safety instrument system includes two high-high temperature switches which stop the EO feed an initiate full cooling. c) The massive fireball observed after the explosion would not be expected following a release of methanol raw material or MPEG 500 product.	
Evaluation	Low likelihood	This scenario is unlikely to be a cause of the accident.

No3	High pressure caused by connected feeds or services	
Description	At the time of the explosion, the two main feeds connected to the reactor were EO and nitrogen. The maximum delivery pressure of the EO feed pump is stated as being 16 barg. Nitrogen system mains pressure is 16 barg then controlled down. The design pressure of the reactor R-3131 is 45 barg, which is the setpoint of the pressure relief.	
Supporting indication	a) None	
Disregarding indication	a) None of the connected feeds have sufficient pressure to exceed the design	
Evaluation	Low likelihood	It is difficult to see how these feeds could lead directly to the overpressure and rupture of the reactor. This scenario is unlikely to be a cause of the accident.

No4	Overpressure due to fire engulfment, leading to a BLEVE	
Description	A Boiling Liquid Expanding Vapour Explosion (BLEVE) is possible for vessels containing liquids that are held above their boiling points by pressure. A BLEVE usually requires flame impingement on the vessel, above the liquid level, so that the metal walls reach a temperature at which they fail (typically above about 650 °C). The vapour pressure in the vessel increases with the temperature until the pressure relief activates or the vessel wall fails. Continued heating will weaken the vessel walls until they might fail. During a BLEVE event, when the metal of the vessel walls fail, a number of fragments are projected by the release and the vessel contents (which are at a temperature considerably above its boiling point at atmospheric pressure) expand rapidly and, assuming ignited, will form a rising fireball with intense heat radiation and produce a blast wave.	
Supporting indication	a) A sound was heard for approx. 10 seconds before the explosion, identified by the witness as a depressurisation sound. The reactor R-3131 is fitted with a 3inch pressure relief valve 31-RV-323 and an upstream burst disc. This is sized for relief of methanol vapour during a fire event with heat only provided by the external fire. b) The video evidence shows a sudden release of burning material from the vessel followed by a fireball as would be expected following a BLEVE. c) A CCTV camera located at a shopping centre at (approximately 3.2 km) from the explosion was shaken by the blast wave shortly (approximately 9 seconds) after the appearance of the most intense flash from the accident location. d) Damage on site is also consistent with this blast wave effect.	
Disregarding indication	a) However, whilst there are indications, from the videos and from the images of fragments, that there was an intense fire preceding the explosions, parts of the reactor which are observed as fragments appear to not have been exposed to fire. Part of the reactor wall became one of the fragments and appears to have not been exposed to intense fire. b) The extent and duration of the type of fire needed for a BLEVE would have most likely meant that the fire would have been observed by operators on the site. However, the site emergency alarm was not activated before the explosion. c) It has been stated that the firefighting deluge system around the reactor did not activate. It is understood that this is activated by the bulbs melting on the nozzles around the reactor. d) The reactor is shown in P&IDs as having insulation at least around the main body, although it is not known at this stage if this is intended as fire insulation. The insulation would have slowed the increase in pressure and temperature of the vessel contents such that the pressure relief system would be able to prevent overpressure. e) Many fragments such as process fittings have been damaged by a very high force of explosion as described in Section 4.1. This damage is not consistent with a solely BLEVE mechanism.	
Evaluation	Low likelihood	Whilst the outcome of the reactor vessel failure (fireball, vessel shell fragments) has some similarity to a BLEVE, it would appear that the reactor was not engulfed by fire for a period long enough to be the sole cause of the rupture.

No5	Thermal decomposition inside the reactor leading to overpressure	
Description	EO vapour decomposes explosively at 560°C with an energy release of 133760 kJ/Kg.mol (Burgoyne). The temperature may be affected by impurities and the geometry of the vessel. Onset temperatures as low as 450°C have been reported. The decomposition event can be very rapid since it does not rely on mass transfer/mixing like combustion. Heat transfer from one part of the decomposing EO to another part is sufficient for it to propagate at a very high rate. Experiments to measure typical rates of pressure rise of the decomposition of EO 60% in nitrogen indicate that 25 bar/sec is possible (Braithwaite and Pekalski).	
Supporting indication	a) The energy release would be sufficient to cause the effects observed at the time of the explosion. b) The 3 inch pressure relief device 31-RV-323 fitted to the reactor would not be able and is not sized to vent such a rate of pressure rise. c) The high rate of pressure rise is consistent with the fracture of the reactor body and the damage observed to bolted process valves and flanges. d) The products of decomposition of EO are methane, hydrogen, ethylene and carbon monoxide (Burgoyne) as well as residual EO all of which are highly flammable. Along with the liquid contents of the reactor, they would likely be able to create the intense burning release and fireball that was observed. e) Ethylene Oxide has a very low minimum ignition energy for mixtures with air, in the order of 0.06 mJ. If it leaks into the air, it is very likely to ignite. f) At the start of the reaction there was a free space of approximately 35000 L, of which 50%vol could have been EO vapour. If for some reason, such as a lack of reaction, this free space volume remained the same at the end of the reaction when the pressure reached 11 barg, the head space would have contained approximately 8.8 kg.mol of EO with a potential decomposition energy of about 1170 MJ. Release of this energy would have been sufficient to rupture the reactor. See Section 7.7 for more detail. g) The damage caused by the explosion as well as the distance several fragments traveled are consistent with the calculation of explosion energy for isothermal and thermal decomposition. See Section 7.7. h) A research of the French ARIA accident database reveals a number of ethylene oxide explosions. An accident at Zwijndrecht, Belgium on 03/07/1987 describes a fireball following the explosion, which initiated secondary fires in neighbouring units whilst the unit itself suffered major damage due to missiles and the blast wave. The explosion was thought to have been due to thermal decomposition of the EO vapour inside a distillation column, leading to rupture and release of flammable vapour. These observations are very similar to the IQOXE	
Disregarding indication	a) To have a complete thermal decomposition of the EO in the reactor, the concentration of ethylene oxide in the gas phase would need to be decomposable, that is, sufficiently concentrated that a decomposition could propagate through the gas phase. In the normal process, the control system ensures that the gas phase is a minimum 50% nitrogen throughout the reaction to prevent propagation. This is achieved through pressure control and is explained further below. However, there are scenarios where a deviation in this control of EO concentration could occur and has occurred in previous accidents. b) The decomposition has to be initiated which would require a source of heat sufficient to reach the decomposition temperature. NB It would not be necessary to raise the temperature of the whole reactor or the reaction mixture to the decomposition temperature. It would be sufficient for a hot spot to occur on pipework or the reactor system wall in contact with EO and for the decomposition to be initiated locally. The high energy release from the initiation will allow the decomposition reaction to propagate throughout the gas phase. Possible sources of heat are discussed further below. Following the explosion, it would be difficult to identify the exact location of the hot spot without additional clues such as previous operational problems.	
Evaluation	High likelihood	Thermal decomposition of ethylene oxide is considered to be the most likely cause of overpressure.

To summarise the above cause assessment the potential causes are sorted from high likelihood to low likelihood. Cause No. 5 will be further assessed for potential causes leading to the thermal decomposition in the following chapter. Cause No1 will be one of these potential causes, as described in the above assessment, but will not be considered, such as the potential causes rated with low likelihood, as direct cause of the explosion.

No.	Cause	Evaluation
5	**Thermal decomposition inside the reactor leading to overpressure**	**High likelihood**
1	Loss of control of exothermic reaction leading to overpressure of the reactor	Medium likelihood
2	Loss of temperature control leading to overheating of the batch, increase in vapour pressure and causing overpressure of the reactor	Low likelihood
3	High pressure caused by connected feeds or service	Low likelihood
4	Overpressure due to fire engulfment, leading to a BLEVE	Low likelihood

4.3 Discussion of potential causes for a thermal decomposition in the U3100

4.3.1 Causes of formation of a decomposable gas phase

In normal operation, the reactor control algorithm ensures that the gas phase does not become decomposable (meaning a decomposition can self-propagate through the gas phase once initiated). This is achieved by:

1. Ensuring an initial minimum pressurisation with nitrogen, normally to 3 barg = 4bara.
2. Measurement of the total pressure during the reaction. The pressure rises due to the compression of the gas space as the level of product liquid increases.
3. During the reaction, control of the EO addition so that the partial pressure of EO is kept below 50% of the total pressure.
4. Independent pressure safety trips will close the EO feed if the pressure is too low at the start (not enough nitrogen) or if the total pressure exceeds 14 barg (According to HH Technology). The higher pressure must be prevented because reaching this pressure would mean the EO proportion of the gas phase has reached 50% and will become decomposable.

The following graph in Figure 4-15 demonstrates the profiles of the measured and calculated partial and total pressures. It is important to note that the partial pressure of EO remains flat during the reaction and does not reach 50% of the total pressure.

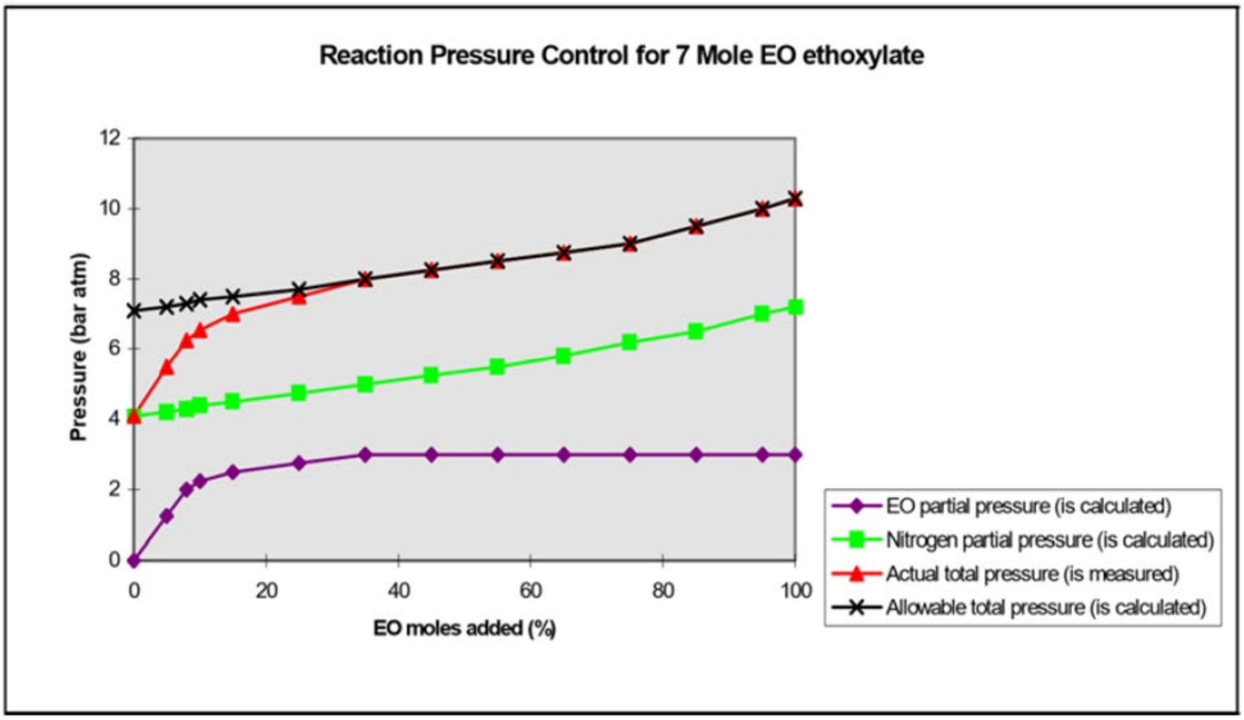


Figure 4-15

It is possible that this control of EO concentration could be at fault. There is no chemical analysis of the gas phase so if part or all the initial nitrogen were replaced by EO, this would not be detected by the control system and its algorithm whilst the pressure is maintained. Possible scenarios are:

1. A fault in the nitrogen pressure control which is also integrated with the EO feed flow control, at the start or during the batch;
2. EO accumulation in the reused nitrogen between batches;
3. An external leak would release a mixture of nitrogen and EO but be replaced by pure EO if addition continued.
4. Venting through the pressure relief system would release a mixture of nitrogen and EO but be replaced by pure EO if the feed were continued, possibly with no drop in pressure.
5. Opening, or passing, of the reactor vent valve (31XV332) to the vent header
6. Presence of liquid EO in the reactor.

In the following these scenarios are described and evaluated. Supporting indication or disregarding indication, as employed in the previous Section 4.2, is not possible here, due to missing information.

1	A fault in the nitrogen pressure control	
Description	A fault in the nitrogen pressure control, allowing EO feed to start below the minimum starting pressure or adding EO at a rate above the correct rate as calculated by the algorithm. Note the way that the nitrogen and EO concentrations are controlled is explained in Section 0	
Evaluation	High likelihood	In Layer of Protection Analyses, typically a failure rate of a process control system loop is taken to be once in 10 years.

2	EO accumulation in the reused nitrogen between batches	
Description	The nitrogen is reused from one batch to another. Additional nitrogen is added to make up for losses of nitrogen that dissolved in the product of the previous batch. EO could gradually accumulate, possibly over several batches, in the nitrogen buffer. A batch of MPEG 1000 had been completed on the morning of the accident. There is no evidence that the head space had been completely purged of EO before the accident batch was started.	
Evaluation	High likelihood	

3	An external leak of gases.	
Description	An external leak would release a mixture of nitrogen and EO but be replaced by pure EO if addition continued. This is thought to have been the cause of enrichment during an historic accident case. To detect such a leak from the flange connections on the top of the reactor a gas detector is provided. Other leak locations not furnished with gas detection might not be detected. Note that EO will very easily ignite so a leak could also be a source of hot spot. This is addressed separately in the next Section 0.	
Evaluation	High likelihood	

4	Venting through the pressure relief system.	
Description	Venting through the pressure relief system would release a mixture of nitrogen and EO but be replaced by pure EO if the feed were continued. There is pressure detection between the pressure relief valve and the rupture disc to detect leaks.	
Evaluation	Low likelihood	

5	Opening, or passing, of the reactor vent valve (31XV332) to the vent header	
Description	Opening, or passing, of the reactor vent valve to the vent header. Normally the vent valve 31-XV-332 and control vent valve 31-PCV-321 are kept closed during the reaction. They might be opened due to a control system fault, operator decision to vent or they might leak. The vent valve is interlocked with the EO feed inlet, to prevent both being opened at the same time, but it is possible that the feed could be restarted shortly after venting nitrogen/EO mixture and so the EO concentration could be enriched. The vent header is supplied with a low flow of nitrogen to prevent oxygen ingress from the atmosphere. Rapid venting might have overwhelmed this nitrogen flow, or it might have been accidentally left closed, and the vent header become decomposable	
Evaluation	Medium likelihood	

6	Presence of liquid EO in the reactor	
Description	Presence of liquid EO in the reactor. Liquid EO is normally pumped to the reactor but will flash into the gas phase at the temperature of the reaction. The normal boiling point is about 10°C. The saturated vapour pressure at the reaction temperature 125°C is approximate 24 bara so it will be in the gas phase. However, according to the American Chemistry Council guide, if the temperature is significantly lower, EO can accumulate in the liquid phase. HH Technology has indicated that expected reaction temperatures are usually in the range 150-170°C. Temperature control and an independent low temperature trip are provided to protect against this scenario. At the end of the reaction the liquid addition feed line is blown clear with nitrogen towards the reactor, adding additional EO to the head space.	
Evaluation	Low likelihood	

To summarise the above cause assessment, the potential causes are sorted from high likelihood to low likelihood. The cause evaluated with high and medium likelihood will be taken further to the barrier identification and assessment in Section 0.

No.	Cause	Evaluation
1	A fault in the nitrogen pressure control	High likelihood
3	An external leak would release a mixture of nitrogen and EO but be replaced by pure EO if addition continued	High likelihood
2	EO accumulation in the reused nitrogen between batches	High likelihood
5	Opening, or passing, of the reactor vent valve (31XV332) to the vent header	Medium likelihood
4	Venting through the pressure relief system would release a mixture of nitrogen and EO but be replaced by pure EO if the feed were continued	Low likelihood
6	Presence of liquid EO in the reactor	Low likelihood

It is clear from the energy of the explosion that the EO concentration would have to have increased beyond 50% and a decomposable mixture formed. To date, the causes of the increased EO concentration have not been identified. The level of destruction of the equipment, the destruction of recorded process data and the absence of witnesses from the unit will make this identification very difficult.

The next section considers the causes of the initiation of the decomposition.

Initiation of the decomposition

As noted earlier, for decomposition of EO to start, it requires part of the EO to be heated to its decomposition temperature (nominally 560 °C , but can be as low as 450°C). Also, as noted earlier, it would **not** be necessary to raise the temperature of the whole reactor or the reaction mixture to the decomposition temperature. It would be sufficient for a hot spot to occur on pipework or the reactor system wall in contact with EO and for the decomposition to be initiated locally. The high energy released from the initiation will allow the decomposition reaction to propagate throughout the gas phase. This scenario of a small initial heat source leading to catastrophic explosion has been the causes of several historical ethylene oxide explosions.

Possible causes of a hot spot are:

1. Uncontrolled exothermic reaction reaching the decomposition temperature (See event type 1);
2. A fire impinging on the reactor vessel: it is only necessary for a hotspot of the reactor wall to reach 560°C to initiate the decomposition;
3. A fire impinging on part of the attached process, for example the EO feed inlet, which initiates the decomposition and is then propagated into the reactor;
4. A fire impinging on the vent system connected to the reactor;
5. A mechanical fault in a pump connected to the reactor system e.g. one of the two circulation pumps P-3131 or P-3132 or one of the EO feed pumps. The decomposition would then propagate toward the reactor;
6. Maloperation (for example pumping against a closed valve on the discharge or cavitation due to a closed suction) of a pump connected to the reactor system e.g. one of the two circulation pumps P-3131 or P-3132 or one of the EO feed pumps. The decomposition would then propagate toward the reactor;
7. A fault in the electric heat tracing positioned adjacent to some of the pipework connected to the reactor.
8. Hot work such as welding or cutting on a connected system.
9. Contamination of the reactor or its connected system by rust (iron oxide) or other substances that accelerate the polymerisation of EO. The polymerisation is very exothermic and without cooling could reach the decomposition temperature.

1	**Runaway reaction reaching the decomposition temperature**
Description	Uncontrolled exothermic reaction reaching the decomposition temperature (See Section 4.2, Event type No. 1
Supporting indication	a) See Section 4.2, Event type No. 1
Disregarding indication	a) See Section 4.2, Event type No. 1. This scenario would require a failure of the safety instrument system.
Evaluation	Medium likelihood

2	**A fire impinging on the reactor vessel**
Description	A fire (possibly only a small one) which causes at least a spot of the reactor shell reaching the EO decomposition temperature
Supporting indication	a) Evidence of a preceding fire is discussed later in this report. b) Only a small hot spot is required which may not have been noticed by the operators.
Disregarding indication	a) IQOXE states that the firefighting system was not activated prior to the explosion. b) The fragments of reactor shell show no indication of fire impact. c) The reactor was protected by thermal insulation and cladding d) The reactor was protected by water sprays activated by heat sensitive bulbs. A fire in the area of the reactor should have activated the sprays.
Evaluation	Low Likelihood

3	A fire impinging on part of the attached process
Description	A fire (possibly only a small one) which causes part of the system connected to the reactor (pipework, valves, fittings) reaching the EO decomposition temperature.
Supporting indication	a) Evidence of a preceding fire is discussed later in this report. b) Only a small hot spot is required which may not have been noticed by the operators. c) A small fire not in contact with the reactor may not have activated the fire protection water sprays. d) This has been a cause of previous historical ethylene oxide explosions. Often the fire is due to a small EO leak which ignites very easily. e) U-3100 has experienced at least one previous incident of burnt insulation. The example seen related to pump P-3152.
Disregarding indication	a) To date, the location of such a small fire has not been identified. Given the level of destruction of the unit, this will be very difficult.
Evaluation	High Likelihood

4	A fire impinging on the vent system connected to the reactor
Description	A fire impinging on part of the vent header system which is connected to the reactor. If ethylene oxide was vented through this route at the time that part of the system was hot, it may have initiated the decomposition which could have propagated back to the reactor.
Supporting indication	a) Evidence can be seen of a fire in the vicinity of the vent header catchment tank V-3146. The vessel is connected to the reactor process vent. b) Evidence of a preceding fire is discussed later in this report. c) Only a small hot spot is required which may not have been noticed by the operators. d) A small fire close to V-3146 may not have activated the fire protection water sprays. The sprays are not positioned to counter a fire in the location of V-3146.
Disregarding indication	a) Whilst there was clearly a fierce fire next to V-3146, to date it has not yet been confirmed by forensic examination whether some of the fire damage had occurred before the explosion.
Evaluation	Medium Likelihood

5	A mechanical fault in a pump connected to the reactor
Description	A mechanical fault in a pump such as a seal failure, overheating bearing or impeller damage could lead to high temperature in the pump. If the pump contains ethylene oxide and if this temperature were high enough it could reach the EO decomposition temperature. The decomposition could have then propagated to the reactor.
Supporting indication	a) Previous accidents have implicated the EO or propylene-oxide feed pumps.
Disregarding indication	a) Previous accidents have implicated the EO or propylene-oxide feed pumps. Inspection after the accident of the IQOXE EO feed pumps 31-P-3135A and 31-P-3135B shows them to be unaffected. b) Small reactor loop pump 31-P-3132 was displaced by the blast but does not appear to have ruptured its casing nor is there evidence of fire around the pump. c) Large reactor loop pump 31-P-3131 was pulled apart and displaced by the blast but does not appear to have ruptured its casing nor is there evidence of fire around the pump. Some sticky material was observed around the pump after the accident, but this may be product that leaked from the pump following the explosion. d) No other pumps handle EO. e) It has not been confirmed for the IQOXE loop pumps but normally these pumps would be protected by high temperature trips.
Evaluation	Low likelihood

6	Maloperation of a pump connected to the reactor
Description	Maloperation of a pump connected to the reactor, such as running the pump against a closed valve or starving the pump of feed could lead to high temperature in the pump. Maloperation could have been due to an operator error or a control system failure. If the pump contains ethylene oxide and if this temperature were high enough it could reach the EO decomposition temperature. The decomposition could have then propagated to the reactor.
Supporting indication	a) Previous accidents have implicated the EO or propylene-oxide feed pumps.
Disregarding indication	a) Previous accidents have implicated the EO or propylene-oxide feed pumps. However, inspection after the accident of the IQOXE EO feed pumps 31-P-3135A and 31-P-3135B shows them to be unaffected. b) Small reactor loop pump 31-P-3132 was displaced by the blast but does not appear to have ruptured its casing nor is there evidence of fire around the pump. c) Large reactor loop pump 31-P-3131 was pulled apart and displaced by the blast but does not appear to have ruptured its casing nor is there evidence of fire around the pump. Some sticky material was observed around the pump after the accident, but this may be product that leaked from the pump following the explosion. d) No other pumps handle EO. e) It has not been confirmed for the IQOXE loop pumps but normally these pumps would be protected by high temperature trips.
Evaluation	Low likelihood
7	**A fault in the electrical heat tracing positioned adjacent to some of the pipework connected to the reactor.**
Description	Electrical heat tracing was fitted to pipework connected to the reactor, including the EO feed line. An electrical fault such as a short circuit causes a local hot spot under the insulation. If this temperature were high enough it could reach the EO decomposition temperature. The decomposition could have then propagated to the reactor.
Supporting indication	None. The damage to the unit prevents easy identification of such a fault.
Disregarding indication	a) It has not been verified for unit U-3100, but electrical tracing is normally protected by fuses or similar. b) The heat tracing is intended only to compensate for heat loss through the insulation so is normally not very powerful.
Evaluation	Low likelihood

8	Hot work such as welding or cutting on a connected system
Description	Hot work being carried out on the live reactor system which causes a hot spot on the reactor of any of the connected pipework.
Supporting indication	None
Disregarding indication	a) No known work was underway b) The site has a permit to work system that would normally prevent this circumstance c) Anyone carrying out hot work and initiating the decomposition would have been severely injured or killed by the explosion.
Evaluation	Low likelihood

9	Heat from unintended reaction catalyzed by contaminant
Description	EO can undergo an exothermic self-polymerisation. The generates heat locally and depending on the location of the unwanted reaction, the heat may not be removed by the loop cooling exchangers. If this temperature were high enough it could reach the EO decomposition temperature. The decomposition could have then propagated to the reactor. This polymerisation is catalyzed by the presence of one of a range of contaminants including: • Ferric oxide, in the form of rust; • Bases, such as potassium hydroxide or sodium methylate which are both

	reactants connected to the reactor; • Water. Contact between EO and the contaminant could occur in several locations: • Back-flow of catalyst from the reactor into the EO feed line; • A leak of EO into wet or contaminated lagging; • EO reaching the reactor vent header, part of which is mild steel and will contain rust. • Contamination of process pipework following maintenance intervention.
Supporting indication	a) Some of these scenarios have been the causes of historic accidents. b) These scenarios would not normally produce any external sign of an anomaly. The explosion would occur unannounced as observed at the time of the accident. c) Back-flow of catalyst from the reactor into the EO feed line has been a cause of historic accidents. To date, evidence has not been found of a ruptured EO feed line which might be expected in such a scenario. Given the level of destruction of the unit, this will be very difficult to verify. The video of the accident suggests a significant release of EO occurred shortly before the explosion. d) To date, evidence has not been seen of an unignited EO leak. Given the level of destruction of the unit, this will be very difficult to verify.
Disregarding indication	a) Check valves and a pressure difference across the inlet valves are used to prevent backflow of catalyst into the EO feed line. Check valves are notorious for failing in the presence of polymeric contamination. However, a failure of the pressure difference would be required to permit the backflow. b) A gas detector was positioned adjacent to some of the flanges where an EO leak might be expected to occur, at the dome of the reactor. If the leak occurred in this location, it should have activated the detector and alerted the operators. However, the reactor dome detector is positioned on the opposite side of the dome from flanged inlets to the small jet head assembly so might not have been able to detect a leak in this location. There does not appear to be a gas detector provided adjacent to the ground floor EO manifold, where there are several flanges. A leak here may have been undetected. c) Normally the vent valve 31-XV-332 and control vent valve 31-PCV-321 are kept closed during the reaction so there is normally no flow of EO into the vent header and catch tank 31-V-3146. They might be opened due to a control system fault, operator decision to vent or they might leak.
Evaluation	Medium likelihood

To summarise the above cause assessment, the potential causes are sorted from high likelihood to low likelihood. The cause evaluated with high and medium likelihood will be taken further to the barrier identification and assessment in Section 0.

No.	Cause	Evaluation
3	A fire impinging on part of the attached process	High likelihood
1	Runaway reaction reaching the decomposition temperature	Medium likelihood
4	A fire impinging on the vent system connected to the reactor	Medium likelihood
9	Heat from unintended reaction catalyzed by contaminant	Medium likelihood
2	A fire impinging on the reactor vessel	Low likelihood
5	A mechanical fault in a pump connected to the reactor	Low likelihood
6	Maloperation of a pump connected to the reactor	Low likelihood
7	A fault in the electric heat tracing positioned adjacent to some of the pipework connected to the reactor.	Low likelihood
8	Hot work such as welding or cutting on a connected system	Low likelihood

4.3.2 Fire preceding the explosion

Examination of photographs of missile fragments as well as photographs from the incident scene suggests that fire damage had been caused prior to the explosion. Therefore, in this section we examine the possibility that a fire occurred before the explosion. Two types of fire are discussed:

- A short-lived intense fire very shortly before the explosion;
- A small fire that may have produced the hot spot that initiated the decomposition.

Moreover, a forensic examination of several missile fragments as well as pieces from the incident scene will be conducted. The results will support and disregard hypothesis of the prior sections.

Example for fire damage in U3100	Missile fragments indicating a fire damage
 **Figure 4-16 IMG_00018_A_1.jpg Fire damage around V-3146 catchtank in centre**	 **Figure 4-18 - FOTOGRAFIA 26**  **Figure 4-19 - FOTOGRAFIA 18**
 **Figure 4-17 IMG_00017_A_1.jpg Damage around V-3146**	 **Figure 4-20 - FOTGRAFIA 59** FOTOGRAFIA 59 shows surface fire damage to the structural member at one end but the surface nearest the camera shows an inside surface that would have been unexposed to fire in its original bolted location. This still has a clean surface following its ejection by the blast.

4.3.2.1 The Intense Fire

Distant observers were able to capture the moment of the explosion on mobile phone video recordings, suggesting that a significant event have been already drawing their attention to the IQOXE site shortly before the explosions. One video (20200114-WA0074) shows an intense fire was in progress but the video clip lasts a very short period less than a second, before the explosion. It is not possible to know from the video how long this fire endured prior to the explosion. Another video (20200114-WA0030) observes the start of the fireball. Two sounds of explosion are heard, approximately half a second apart, but the reason for being able to capture the sound may be due to the time delay for sound to travel to the observer's location (not known).

Witness reports from the site indicate that 10 minutes before the explosion there had been no report of such a major fire. Is was stated that the site firefighting system had not activated automatically as would be expected in such an event. Activation would also have initiated an alarm.

The above observations may just suggest that the intense fire lasted only a short period, perhaps only a few seconds, before the explosion.

4.3.2.2 What started the Intense Fire?

The intense fire needed a fuel with a high heat output. The main highly flammable materials in the unit were:

- Methanol,
- Ethylene Oxide,
- Propylene Oxide.

Methanol burns with a near invisible flame and this is not consistent with the video observation. Propylene oxide and ethylene oxide would have been more likely fuels. Since the ethylene oxide was the material in use at the time, under pressure from the pumping feed, this is the most likely fuel.

The most likely cause of a large release of ethylene oxide is that the decomposition had already been initiated. This may have ruptured part of the reactor system, such as the EO feed line leading to the visible flare. The intense fire may have exacerbated the propagation to the reactor or may have occurred in parallel to the reactor explosion.

4.3.2.3 Evidence for an initial small fire

As explained in Section 0, one of the hypotheses for the hot spot that initiated the decomposition is the presence of a fire before the explosion. This need only have been a small fire. It would not be necessary to raise the temperature of the whole reactor or the reaction mixture to the decomposition temperature. It would be sufficient for a hot spot to occur on pipework or the reactor system wall in contact with EO and for the decomposition to be initiated locally. The high energy released from the initiation will allow the decomposition reaction to propagate throughout the gas phase.

Examination of photographs of missile fragments suggests that fire damage had been caused to many of the missiles prior to the explosion. Following the explosion these missiles would have been projected at high velocity by the blast wave, in advance of the fireball that followed. Observed severe heat damage is therefore likely to have occurred before the explosion.

Apparently, fire-damaged missile fragments are shown in Figure 4-18 - FOTOGRAFIA 26, Figure 4-19 - FOTOGRAFIA 18, Figure 4-20 - FOTGRAFIA 59, and Figure 7-6: FOTOGRAFIA 182. Figure 7-6: FOTOGRAFIA 182 shows a piece of distorted welded metal plate. At the time of writing it has not been identified. It appears to have been fire damaged prior to ejection by the blast. This fragment could be significant if it is part of the reactor R-3131, since it would imply at least partial exposure of the reactor to fire. However, assessing fire damage from the photographs is subject to error. To validate the observations, forensic analysis of selected missile fragments is needed.

On 29th May 2020, a visit was made to the wreckage of the unit U-3100. Significant fire damage was observed around the area of vent header catchtank 31-V-3146. The fire had involved several electrical power cables which had fallen from a horizontal cable tray at the 5m level and from a vertical cable tray at the south-west corner of the bay containing 31-V-3146. The heat of the fire appeared to have impacted on the surface of 31-V-3146. Photographs of this damage are shown in Figure 4-16. The cables have been severely burnt and would have formed an intense fire in this area. The main fire could have occurred after the explosion when the cables were displaced to this location from the cable trays. In the photograph, there are many pieces of debris intermingled with the burnt cable but which appear to have not suffered heat damage.

Figure 4-17 shows another view of the damage around catchtank 31-V-3146. The fire around 31-V-3146 appears to have blackened steelwork above, around the 5m level on the south side of the structure. It is not clear whether this damage occurred before or after the explosion. It is worth noting that a section of vertical drainpipe still attached to the lower part of the steel vertical column is apparently severely burnt. However, the metal perforated strip lying against it, and presumably projected there by the blast, appears to be not fire-damaged. Photographs can be deceptive, however, and a forensic analysis is need to the validate this.

It is concluded that there is a suggestion, but not firm proof, that a fire, involving the electrical cables, may have been under way before the explosion. At this stage it is not possible to determine if such a fire might have had its origins in an electrical fault, or some other exterior heat source. Both hypotheses should be retained as possibilities.

4.3.2.4 Why was a small fire not observed?

If a small fire had started, it may not have been observed for the following reasons:

- Overheated electrical cable forms a smoky fire rather than intense flame. This may not have been observed in the dark. There are no smoke detectors on U-3100.
- The control room windows are high level. Personnel in the control room may not have had a clear view of the plant from desk locations
- There is a fire sprinkler system around the reactor in the next bay to 31-V-3146 which relies on activation by melting heat sensitive bulbs. Fires away from the reactor R-3131 may not activate these bulbs and therefore not activate the fire sprinklers around the reactor.
- From the information supplied it appears that no other fire detection or sprinkler system was installed in U-3100. Operators would not have been alerted to activation of such systems.

4.3.3 Summary of hypotheses for thermal decomposition of batch No7

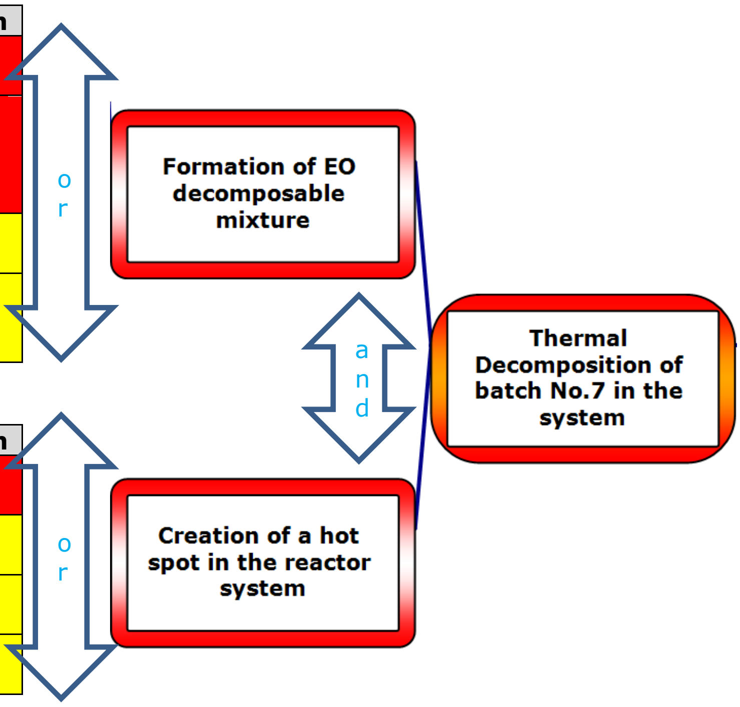
Figure 4-21 summarises the different combinations of causes leading to the two requirements for the decomposition: a heat source and formation of a decomposable mixture in the reactor. In this summary, potential causes have been omitted where the likelihoods are considered low for this particular accident.

Certain causes in the two branches may have a common origin. For example, a leak of EO is likely to ignite and provide the heat source as well as provide a mechanism for enrichment of the gas mixture in the reactor.

Figure 4-21 Summary of hypotheses

No.	Potential cause	Evaluation
EO/1	A fault in the nitrogen pressure control	High likelihood
EO/3	An external leak would release a mixture of nitrogen and EO but be replaced by pure EO if addition continued	High likelihood
EO/2	EO accumulation in the reused nitrogen between batches	Medium likelihood
EO/5	Opening, or passing, of the reactor vent valve (31XV332) to the vent header	Medium likelihood

No.	Potential cause	Evaluation
HS/3	A fire impinging on part of the attached process	High likelihood
HS/1	Runaway reaction reaching the decomposition temperature	Medium likelihood
HS/4	A fire impinging on the vent system connected to the reactor	Medium likelihood
HS/9	Heat from unintended reaction catalyzed by contaminant	Medium likelihood

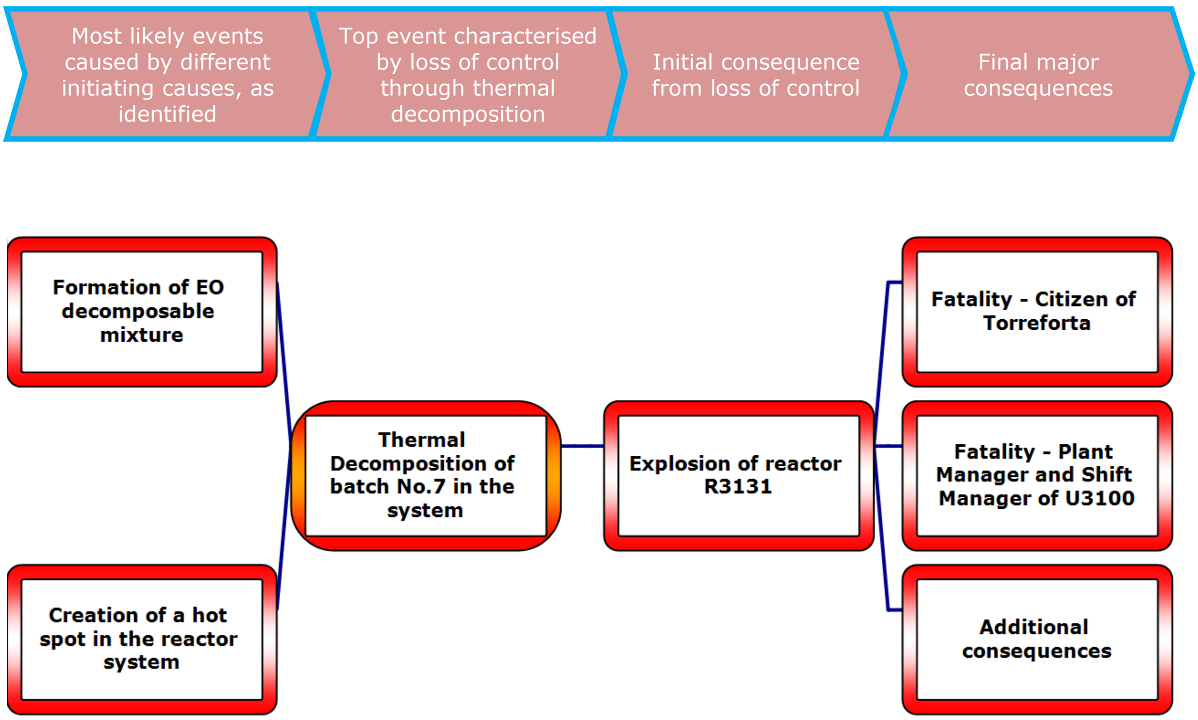


4.4 Summary of key events leading to the incident

The purpose of this step is to build a chain of key events, from the first deviation of the normal and safe operation via the further escalation towards the final consequences of the incident. It prepares the next step, which is the Identification and Assessment of barriers and subsequently the root cause analysis. These barriers shall be able to prevent the occurrence of the next event and hence stop the chain of events from progressing.

In the prior incident analysis, the identification of the type of event by assessing the consequences derived the explosion of the reactor R3131, in which the incident batch No7 of MPEG 500 was produced. In a second step the Thermal decomposition of the batch No7 was assessed, to be the most likely cause for the severe explosion. In a third step the potential causes for a thermal decomposition was assessed and led to the assumption of two parallel events – one is the Formation of an EO decomposable mixture and the second is the Creation of a hot spot in the reactor system. The investigation could unfortunately not identify further, the actual causes or the actual common cause for the two events leading to the thermal decomposition.

This chain of events is visualised in the below diagram and the events are described.



4.5 Identification and assessment of barriers and Root Cause Analysis

In this section the barriers which shall be able to prevent the occurrence of the next event and hence stop the chain of events from progressing are identified and analysed and root cause analysis is performed for the barrier failure.

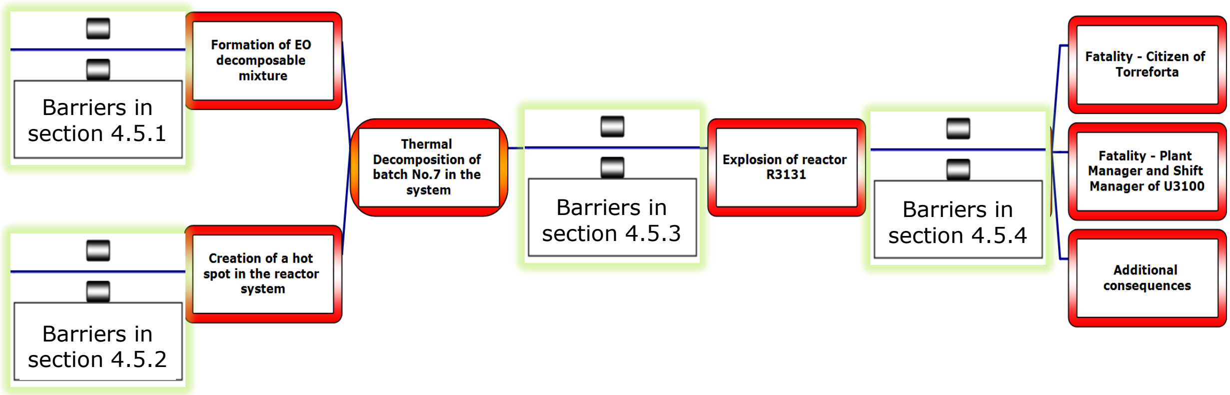
For a better overview, this activity is broken down in four different chapters, e.g. the barriers, which shall prevent from formation of EO decomposable mixture are described and analysed in section 4.5.1.

According to the BSCAT methodology for each barrier,

1st - the desired intention and the actual performance during the incident are described

2nd - the barrier state (effective, unreliable, inadequate, failed, or missing) is derived by comparing desired intention and actual intention.

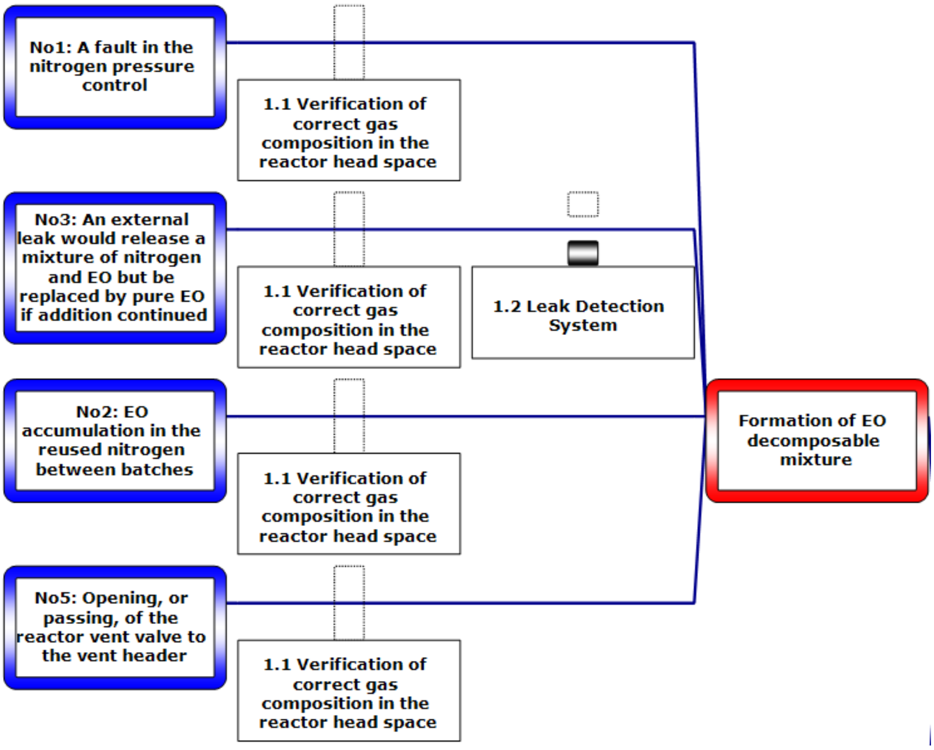
3rd – the root cause analysis is conducted for each barrier, to the extent possible.



No barriers are identified between the initial two events (Formation of EO decomposable mixture and Creation of a hot spot in the reactor system), as once this stage is reached and both events occur, a Thermal decomposition cannot be prevented anymore.

Barrier state definitions:
- *Missing*: The barrier was described in the organisation's safety management system or was considered an industry standard, but was not successfully implemented
- *Failed*: The barrier was implemented, but did not function according its intended design
- *Inadequate*: The barrier functioned as intended by its design (envelop), but was unable to stop the sequence of events
- *Unreliable*: The barrier stopped the next event in the incident sequence, but the organisation is uncertain, if it will do so in the future
- *Effective*: The barrier functioned as planned and stopped the next event in the incident sequence.

4.5.1 Barrier description and Root Cause Analysis between potential causes and the event "Formation of EO decomposable mixture"



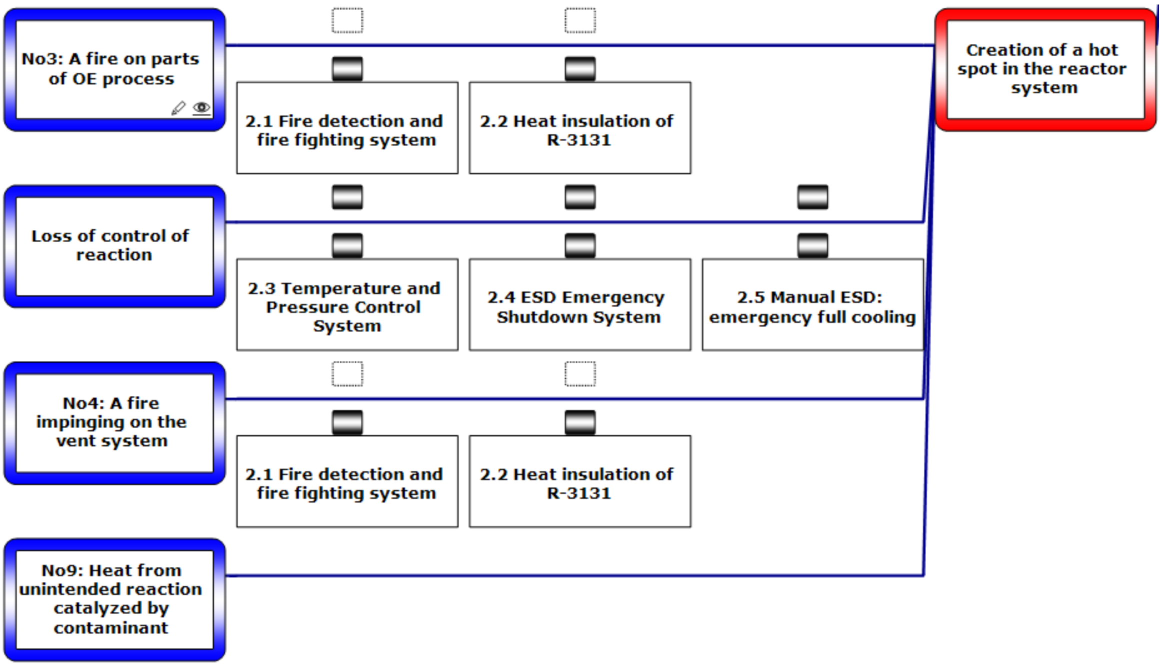
Barrier 1.1„Verification of correct gas composition in the reactor head space"

Barrier Analysis -	
Intention of the barrier	To measure the concentration of EO in the head space of the reactor. If the concentration exceeds a defined safety level, to activate an alarm to warn the operators and automatically stop the EO feed pump and close the EO feed valves.
Actual barrier behaviour	**Missing barrier** The EO concentration in the reactor head space is not measured. However, to ensure the correct gas composition, the system is pressurised nitrogen prior to the EO supply and the system continuously controls EO partial pressure with an algorithm. Currently it is not standard practice in ethoxylation reactor design to provide a gas analyser on the head space. There would be a number of practical difficulties in providing such analysis including the impact of polymer contamination on the analyser. There will be no further analysis of this barrier except to recommend that IQOXE liaises with other ethoxylation operators to review developments in this area and adopt new technology if appropriate. **(Recommendation 7)**

Barrier 1.2 „Leak detection system“

Barrier Analysis -			
Intention of the barrier	To detect a low concentration of EO at the exterior of flanged pipework, caused by a leak. If the concentration exceeds a defined safety level, to activate an alarm to warn the operators and automatically stop the EO feed pump and close the EO feed valves.		
Actual barrier behaviour	**Inadequate barrier** A gas detector is located at the top of the reactor, positioned next to a flange on the 20 inch return loop. There is no data or evidence to confirm whether or not the detector was activated prior to the explosion. The gas detector 31-AT-103 had been tested and calibrated in Nov 2019. There are other potential leak points on the EO pipework, which are not covered by the gas detector 31-AT-103, such as: - flanges on the small loop return pipework which are on the opposite side of the reactor from the detector. - several flanges on the EO feed manifold on the ground floor level, where there does not appear to be any gas detection. - the reactor loop circulation pumps. - the sampling system on the small loop return line where a leak could occur.		
Causal Analysis			
Specific Description		**Reference DNV GL SCAT Classification**	
Direct Cause:	Insufficient EO detection	35	Inadequate warning system
Basic Cause(s):	The responses to the request for information on process safety studies undertaken lead to the assumption that insufficient detail and time was spent on identifying leak sources and determination of location of detection. The EO User Guide suggests applying NFPA 58 and API 2510 and 2510A to the design of fire protection systems for EO storage and processing areas. Moreover, it informs about different types of leak detection systems. Furthermore, the basic design documents specify that gas detection in the neighbour-hood of sources of possible leakage shall be installed. Dilution of leakage and control of fire will result if automatic operation of a water spray system is triggered by the gas detection system. The leak detection provided in the facility appears to be insufficient. No evidence has been seen that relevant safe studies were performed and that relevant guidance was applied in selection or location of leak detection.	14.1	Inadequate assessment of needs and risks
Improvement area in management system	Process Hazard Analysis to determine risks and needs and location for gas detection. **(Recommendation 6)**	3.8	Process Hazard Analysis
References			
PAP_005	P15 Pruebas de Puesta en Parcha y Proyectoyecto de Instalacion U-3100, Nov 2016 includes test certificates.		
PAP_043	ACC OE guide		
PAP_018	Safety Concept		

4.5.2 Barrier description and Root Cause Analysis between potential causes and the event “Creation of a hot spot in the reactor system”



Barrier 2.1 „Fire detection and fire fighting system“

Barrier Analysis -	
Intention of the barrier	To detect the onset of fire, including small fires that produce mainly smoke. Once activated, an alarm is initiated to warn the operators and start emergency procedures. On confirmed detection, fire extinguishing media are started automatically (e.g. fire pumps and water sprinklers).
Actual barrier behaviour	**Inadequate barrier** According to photographs and design documents provided, the unit U-3100 was provided with a sprinkler system located around the reactor R-3131 designed to cool the reactor surface in the event of fire impingement. The sprinkler system extends also to the post-treatment vessel. The sprinklers are activated by heat sensitive bulbs fitted to the sprinkler heads. The fire detection and firefighting systems have been designed and installed in line with Spanish regulations for industrial buildings. The process area is classified for intrinsic risk with Ci=1.6 (high risk) and Type D according to Annex I of the Fire safety Regulations for Industrial Establishments (Real Decreto 2267/2004, de 3 de diciembre, por el que se aprueba el Reglamento de seguridad contra incendios en los establecimientos industriales.). Accordingly, a manual fire alarm system and fire extinguishers have been selected as protection measures. Automatic fire detection systems as well as automatic water sprinkler systems were not selected, as they are not required for type D and E installations by the stated regulation. Whilst smoke detectors have been installed in the technical room and control room buildings, no evidence has been seen of any additional fire, heat, flame or smoke detection in the process building. Photographs show some fire monitors located around the unit U-3100.

	Presumably these are activated manually. The installed system in U-3100 is not able to detect fires located away from the reactor or post-treatment vessel sprinkler heads. The sprinkler system would only be effective against a fire impinging directly on the reactor. The sprinkler system would not be capable of combatting fires in other areas. It is common to have no smoke detection in such an open structure. Detectors can be affected by dust and moisture. However, risk assessment might encourage the use of smoke detection in cable ducting to detect electrical fires. No evidence has been seen of fire detection or firefighting systems around vulnerable areas of the EO feed line, particularly the feed manifold.		
Causal Analysis			
Specific Description		**Reference DNV GL SCAT Classification**	
Direct Cause:	Insufficient fire detection system. Inadequate firefighting systems.	35 26	Inadequate warning system Inadequate equipment
Basic Cause(s):	The installed sprinkler system only protected the reactor vessel, but not the entire EO connected system in U3100. No evidence was seen of safety studies to identify possible fire sources in U3100, that might affect the EO-connected system, nor was evidence seen of identification of required active or passive fire protection other than a design document based on industrial building regulatory requirements. The EO User Guide suggests applying NFPA 58 and API 2510 and 2510A to the design of fire protection systems for EO storage and processing areas. Moreover, it suggests using process hazards analysis methods that examine the severity of the consequences of a fire scenario for identification areas appropriate for deluge protection. Furthermore, the basic design documents specify that gas and fire detection in the neighbourhood of sources of possible leakage shall be installed. Dilution of leakage and control of fire will result if automatic operation of a water spray system is triggered by the gas detection system.	14.1	Inadequate assessment of needs and risks
Improvement area in management system	Determination of risks and needs and location for fire detection and types of firefighting systems. **(Recommendation 1, 5)**	3.8	Process Hazard Analysis
References			
PAP_027	Design of Fire Fighting "CHANGE OF THE U-350 UNIT PER UNIT U-3100 FOR THE MANUFACTURE OF PRODUCTS ETHYLENE OXIDE DERIVATIVES"		
PAP_057	PAP_057 ISOS PROTECCION CONTRA INCENDIOS		
PAP_043	ACC OE guide		
PAP_018	Safety Concept		

Barrier 2.2 „Heat insulation of R-3131"

Barrier Analysis -			
Intention of the barrier	To prevent external fire impingement (on the reactor or critical reactor connected systems such as the EO feed line) reaching the EO decomposition temperature.		
Actual barrier behaviour	**Inadequate barrier: hypothesis** The reactor R-3131 and much of the connected systems are protected by a layer of foam glass and metal cladding. This has a low thermal conductivity and has good fire resistance. To date we have been unable to verify if all valves and fittings were protected or if all relevant pipework was insulated.		
Causal Analysis			
Specific Description		**Reference DNV GL SCAT Classification**	
Direct Cause:	Inadequate Integrity of Equipment: some areas of reactor system not protected by foam glass.	27	Inadequate Integrity of Equipment
Basic Cause(s):	Inadequate assessment of needs and risks.	14.1	Inadequate assessment of needs and risks
Improvement area in management system	Use Process Hazard Analysis to identify where thermal protection is required.	3.8	Process Hazard Analysis
	Use regular inspection to ensure thermal protection is maintained in place.	10.7	Special Equipment Inspections
	Use permit to work system to ensure any insulation removed for an intervention is immediately reinstalled using foam glass. **(Expectation 3, Recommendation 1)**	9.8	Work Permits
References			

Barrier 2.3 „Temperature and Pressure Control System"

<table>
<tr><td colspan="4">Barrier Analysis -</td></tr>
<tr><td>Intention of the barrier</td><td colspan="3">Temperature Control System: To maintain the temperature of the reaction contents within safe operating limits since:
• Too low a temperature increases the risk of accumulation of unreacted EO which could lead to a runaway reaction;
• Too high a temperature increases the rate of reaction and presents the risk that heat generation rate may exceed the cooling system capacity leading to a runaway reaction. Ultimately, if not controlled, a high temperature could lead to explosive decomposition of the EO gas.
Pressure Control System: To maintain the reactor pressure within safe operating limits since:
• Too low a pressure indirectly indicates there is insufficient nitrogen pad in the reactor leading to the possibility of an EO concentration above 50% vol, which is a decomposable mixture;
• Too high a pressure, in comparison with the limit profile set by the control system algorithm, leads to the possibility of an EO concentration above 50% vol, which is a decomposable mixture</td></tr>
<tr><td>Actual barrier behaviour</td><td colspan="3">Failed barrier: hypothesis
Due to the extent of damage to the unit and the lack of data or witness information, it is not possible to determine if there was a failure of the control system. However, such a failure is credible and the causal analysis is presented below.</td></tr>
<tr><td colspan="4">Causal Analysis</td></tr>
<tr><td colspan="2">Specific Description</td><td colspan="2">Reference DNV GL SCAT Classification</td></tr>
<tr><td>Direct Cause:</td><td>Failure of part of the control system: sensors (pressure or temperature), logic device (DCS, software error) or final elements (control valves).</td><td>29</td><td>Improper Measurement /Signal Conversion</td></tr>
<tr><td>Basic Cause(s):</td><td>Control system loop equipment failure

Errors in programming control software or recipe control: reasons not known

Inadequate inspection and testing of software or hardware</td><td>14

12.9</td><td>Inadequate device(s)

Inadequate inspection method/interval</td></tr>
<tr><td>Improvement area in management system</td><td>Risk assessment should be used to determine the criticality and then the frequency of testing the control loop and inspecting its elements.
(Expectation 1, Recommendation 1)

A management of change process should be in place for changes to process control parameters or software, including requirement for appropriate verification of the changes.
(Recommendation 2)</td><td>3.8

10.13

10.9</td><td>Process Hazard Analysis

Process Safety Inspections

Engineering Change Management</td></tr>
<tr><td colspan="4">References</td></tr>
</table>

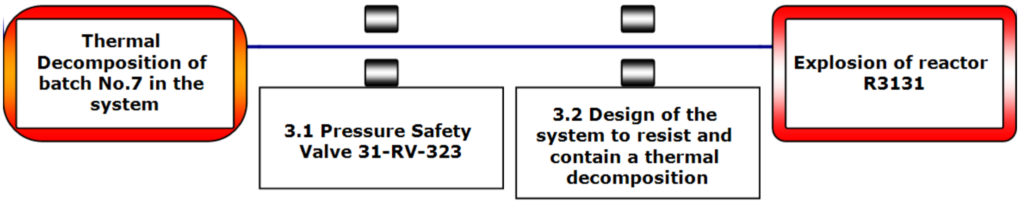
Barrier 2.4 „ESD Emergency Shutdown System“

Barrier Analysis -			
Intention of the barrier	If a parameter such as pressure, temperature, flow or level is detected as being outside the defined safe limit, the Safety Instrument System automatically brings the process to a safe state. The specific actions of each deviation in parameter are defined in a Cause and Effect matrix. Important actions are stopping the EO feed and applying full cooling.		
Actual barrier behaviour	**Failed barrier: hypothesis** A safety instrumented system is installed at U3100 and is activated manually or by the programming based on the configured parameters. Due to the extent of damage to the unit and the lack of data or witness information, it is not possible to determine if there was a failure of the ESD system. However, such a failure is credible but low likelihood and the causal analysis is presented below.		
Causal Analysis			
Specific Description		**Reference DNV GL SCAT Classification**	
Direct Cause:	Failure of part of the safety instrument system: sensors (pressure, temperature, flow, level), logic device (Triconex) or final elements (safety valves).	29	Improper Measurement/Signal Conversion
Basic Cause(s):	Safety instrument system loop equipment failure	14	Inadequate device(s)
	Required reliability of SIS not defined and specified	14.1	Inadequate assessment of needs and risks
	Inadequate inspection and testing of hardware	12.9	Inadequate inspection method/ interval
Improvement area in management system	The safety instrument and ESD systems should be designed, installed, tested, operated and maintained in accordance with IEC 61511. The required reliability is defined by the process hazard analysis. The reliability depends on the architecture of the SIS and its testing interval both of which should be defined. **(Expectation 1, Recommendation 1)**	3.8 10.13	Process Hazard Analysis Process Safety Inspections
References			
PAP_020	Funcionamiento del sistema de seguridad		

Barrier 2.5 „Manual ESD: emergency full cooling"

Barrier Analysis -				
Intention of the barrier	This barrier is similar in its intention to "ESD Emergency Shutdown System". In this case it is the operator who detects an abnormality in a process parameter and activates the emergency shutdown. The specific actions of manual ESD are defined in a Cause and Effect matrix. Important actions are stopping the EO feed and applying full cooling.			
Actual barrier behaviour	**Failed barrier: hypothesis** Due to the extent of damage to the unit and the lack of data or witness information, it is not possible to determine if there was a failure to manually activate the ESD system. However, such a failure is credible and the causal analysis is presented below.			
Causal Analysis				
Specific Description		**Reference DNV GL SCAT Classification**		
Direct Cause:	Hypothesis: Operator did not activate manual ESD to prevent runaway reaction	18?	Failure to identify hazard	
Basic Cause(s):	Error, but reason unknown. Possibly the operator did not have sufficient data to make a decision, or was not aware of the requirement to activate ESD			
Improvement area in management system	For such a hazardous installation, a rigorous competence management system would be expected to operate. Critical tasks such as activation of ESD would be part of training and competence assessment. Regular drills and task observation would be expected. **(Expectation 2)**	7.7 12.9 14.9	Job orientation/ induction Energy Controls Task observation	
References				
PAP_020	Funcionamiento del sistema de seguridad			

4.5.3 Barrier description and Root Cause Analysis between event "Thermal Decomposition" and event "Explosion"



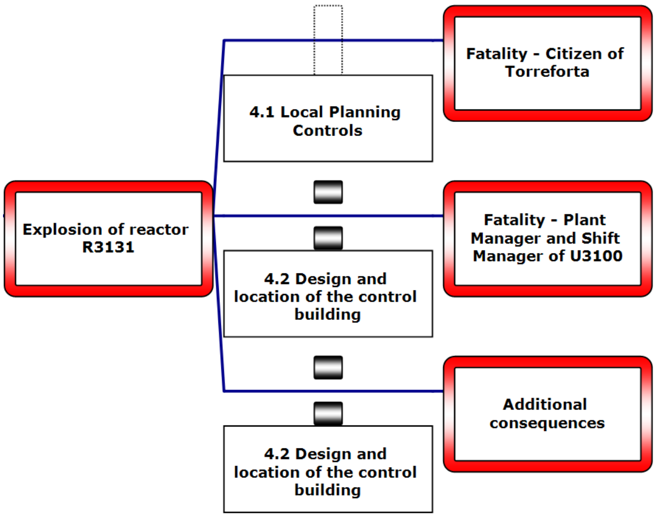
Barrier 3.1 „Pressure Safety Valve 31-RV-323"

Barrier Analysis	
Intention of the barrier	A pressure safety valve (PSV) shall protect the system from rupturing due to overpressure generated from process conditions or exposure to fire heat loads.
Actual barrier behaviour	**Inadequate barrier** The pressure safety valve 31-RV-323 (3 inch) is designed for an overpressure scenario caused by a fire impinging on the reactor building up methanol vapour pressure in the system, without consideration of a runaway reaction or thermal decomposition. For a rapid pressure build-up (25 bar/s for 60% EO according to Braithwaite), as in the case of a thermal decomposition, it will not be able to relieve the pressure from the system. It may be the case that during the accident, the PSV lifted and released gas from the system for a certain time. A witness from the IQOXE plant mentioned a loud noise for approx. 10-15 seconds that sounded like a depressurisation sound, such as from a PSV relief. The function tests, external and internal, are not considered in the barrier assessment, as by design the PSV is considered inadequate for protection against a thermal decomposition. The high rate of pressure rise means that protection using pressure relief would not be possible. No further BSCAT analysis is provided for this barrier, therefore.
References	
PAP_021	Calculation of the PSV received from IQOXE

Barrier 3.2 „Design of the system to contain a thermal decomposition“

Barrier Analysis			
Intention of the barrier	The basic intention of the mechanical integrity is to ensure the content/fluid will be kept inside the mechanical system during operation of the facility. This is required both within the normal operating range but also outside the range up to defined limits. The reactor R-3131 is designed to ASME VIII code. The vessel and the connected pipework are rated to a design pressure of 45 barg and have a test pressure of 150%, 64.35 barg.		
Actual barrier behaviour	**Inadequate barrier** The design basis states, that the mechanical system is designed to withstand an overpressure from a thermal decomposition, estimated to cause an overpressure of maximum 45 barg. This is consistent with the assumption that the starting pressure for the thermal decomposition is approx. 4barg and the pressure multiplication factor is 10, based on the guidance given by the industry. However, as explained in Appendix 7.6, certain process deviations might lead to decomposition starting at higher pressures so that the maximum pressure in the reactor largely exceeds the design or test pressures. Whilst the mechanical strength of the reactor is sufficient for some deviation scenarios, it is inadequate for others. Designing for all possible overpressures presents challenges. The reactor and its fittings would need to be of thicker, heavier steel. Exchange of heat at the loop coolers would then become more difficult. Selection of mechanical resistance has to be a balance between protection and these other factors. Important for ensuring the pressure system has been manufactured correctly and maintains its designed integrity are the initial pressure test, as well as adequate ongoing inspection and maintenance activities. The reactor, but also the entire system has been pressure tested before commissioning the plant in 2016. Construction of the U3100 and respective integrity criteria were confirmed by external verification. To date we have not been able to verify the maintenance or inspection activities performed by IQOXE.		
Causal Analysis			
Specific Description		**Reference DNV GL SCAT Classification**	
Direct Cause:	The system does not protect from all scenarios of decomposition.	27	Inadequate Integrity of Equipment
Basic Cause(s):	Insufficient detail and time spent on identifying scenarios of decomposition that would not be contained by the reactor.	14.1	Inadequate assessment of needs and risks
Improvement area in management system	Identify and assess risks of scenarios of decomposition that would not be contained by the reactor. Ensure levels of safeguards in place are sufficient when the containment is excluded. **(Recommendation 4)**	3.8	Process Hazard Analysis
References			
PAP_018	Safety Concept		
PAP_043	ACC OE guide (regarding theory on thermal decomposition pressure development)		
PAP_005	P15 Pruebas de Puesta en Parcha y Proyectoyecto de Instalacion U-3100, Nov 2016 includes test certificates.		

4.5.4 Barrier description and root cause analysis between the event "explosion" and the consequential events



Barrier 4.1 „Local Planning Controls"

Barrier Analysis	
Intention of the barrier	To ensure that risks are acceptable for: 1. New businesses, residences or public buildings proposed to be developed adjacent to major hazard installations such as U-3100; 2. Proposed new major hazard installations to be developed adjacent to existing businesses, residences or public buildings.
Actual barrier behaviour	Inadequate barrier in in this particular accident where the serious consequences of the atypical projection of a fragment would have had a very low predicted likelihood. Possibly adequate for managing the predicted risks to a normally acceptable level, but this aspect was not part of the investigation. Land use planning controls by the local authorities is assumed to be based on risk or consequence modelling. LUP should evaluate risk acceptability for surrounding locations. Both risk or consequences-based approach include explosion impact assessment where explosion hazards are identified. Explosions related damage may result from overpressure, impulse, missiles and shrapnel. Following international guidelines and standards, overpressure levels are generally considered the most critical measurement since they have a 360 degree effect and pose a higher probability of impacting a specific receptor. No specific LUP report for the Unit 3100 project has been provided to DNV GL but, usually, LUP is based on overpressure level calculation and does not include specific missiles risk assessment and so no definition of mitigation measures is required. Given the number of ethylene oxide explosions that have occurred in history and the incidence of missile fragments, DNV GL would recommend that this approach is reviewed to see whether risk criteria and mitigation of the type used for explosive manufacturing sites should be adopted at least for new installations. This would require joint, international review amongst manufacturers that use ethylene oxide and their regulators. **(Rec. 8)** No further BSCAT analysis is provided for this barrier.

Barrier 4.2 „Design and location of the control room“

Barrier Analysis			
Intention of the barrier	The design and location of the control room should reduce the risk from fires, explosions or toxic releases to a minimal acceptable level. The minimum risk refers both to personnel working in the building as well as the functional integrity of the control and safety systems used for the whole asset. That means, even after incident at the asset, it shall be possible to control the asset from the control room. A safe location is typically enabled by means of enough distance to dangerous / explosive process equipment. Alternatively, the building may use technical and construction measures to withstand the effects of an accident.		
Actual barrier behaviour	**Inadequate barrier** The control room was built in 1965 and later renewed and electrical substation extended. The Unit 3100 was built in 2016 opposite the control room building at approx. 15m distance. The explosion of the reactor R3131 caused severe damage to the control room building, i.e. the first line of rooms located towards the U3100 was completely destroyed by blast effects and by heat damage.		
Causal Analysis			
Specific Description		**Reference DNV GL SCAT Classification**	
Direct Cause:	The control room was not a safe location to work in case of a reactor explosion in Unit 3100.	27	Inadequate Integrity of Equipment
Basic Cause(s):	During and after planning and construction of the derivates plant U3100 in 2016 no evidence has been seen that an Occupied Building Risk Assessment was undertaken to check the new risk profile for working in the control room. Furthermore, no other safety study documentation was provided to the investigation team other than the hazard and operability study (HAZOP) conducted in April 2016 and the quantitative risk assessment of 2019 (when the U3100 was already in operation) submitted to GenCat as part of the notification of a substantial change to a SEVESO site. The reactor R3131 (prior name R-3001) was assessed for leakage, but not for other credible scenarios, such as runaway reactions or a thermal decomposition, which are known to happen from past incidents in EO plants of other EO operators. The HAZOP has been undertaken during the design stage of the U3100 project which is expected to trigger the conduction of an occupied building risk assessment.	14.1	Inadequate assessment of needs and risks
Improvement area in management system	Risk management sets requirements for risk identification, determination of measures and control of risks for occupied buildings on major hazard sites. **(Recommendation 1, 3)** Management of change sets requirements for a response to changes in an existing plant. **(Recommendation 2)**	3.8 10.9	Process Hazard Analysis Engineering Change Management
References			
POS_002	Layout plan derivatives		
POS_007	Layout of the Control room		
PAP_029	HAZOP for U3100		
PAP_038	QRA in 2019 for the major projects:		

4.6 Means to prevent hypothetical events

Earlier in the timeline, a number of hypothetical events have been proposed as possible causes of either enrichment of the EO concentration or causes of a hot spot. These were listed in Figure 4-21 and are repeated in the following table:

No.	Cause EO enrichment
EO/1	A fault in the nitrogen pressure control
EO/3	An external leak would release a mixture of nitrogen and EO but be replaced by pure EO if addition continued
EO/2	EO accumulation in the reused nitrogen between batches
EO/5	Opening, or passing, of the reactor vent valve to the vent header

No.	Cause of Hot Spot
HS/3	A fire impinging on part of the attached process
HS/1	Runaway reaction reaching the decomposition temperature
HS/4	A fire impinging on the vent system connected to the reactor
HS/9	Heat from unintended reaction catalyzed by contaminant

As has been demonstrated in the barrier analysis in Section 4.5, by considering what might have prevented these hypothetical events, the following expectations for management systems and operating procedures can be proposed:

No.	Cause	Proposed expectations
EO/1	A fault in the nitrogen pressure control	This is addressed already in Section 4.5.
EO/3	An external leak would release a mixture of nitrogen and EO but be replaced by pure EO if addition continued	The detection of a leak is already addressed in Section 0. Prevention of a leak requires: • Identification of the failure mechanisms that might lead to a leak: for example vibration, corrosion, degradation of gaskets. The inspection and maintenance system should then ensure monitoring and replacement are carried out with frequency determined by the level of risk. • A periodic pressure test, potentially before each batch, is carried out to test for a leak. This is in addition to regulatory pressure tests. **(Expectation 5)**
EO/2	EO accumulation in the reused nitrogen between batches	The risk of accumulation of EO in the nitrogen reused in the next batch could be managed by either: • Disposing of all the gases at the end of the batch and purging the reactor with nitrogen, or • Analysing the gas mixture at the end of the batch and adjusting the nitrogen partial pressure accordingly. **(Expectation 4)**
EO/5	Opening, or passing, of the reactor vent valve (31XV332) to the vent header	Prevention of unwanted leaks to the vent header requires: • Vent valves should be checked for passing (internal leaks) by carrying out a periodic pressure test, potentially before each batch;

		• Identification of the failure mechanisms that might lead to a leak: for example corrosion, degradation of seats. The inspection and maintenance system should then ensure monitoring and replacement are carried out with frequency determined by the level of risk. **(Expectation 6)**
HS/3	A fire impinging on part of the attached process	Fire detection and firefighting are addressed already in Section 4.5. • A small fire would be very dangerous in this facility. Process Hazard Analysis should be used to identify all types of fire that could occur and the failure modes that lead to them. The inspection and maintenance system should then ensure monitoring and replacement are carried out with frequency determined by the level of risk. For example, observations in the investigation suggest that overheating of electrical cables might have led to a fire, although this has not been confirmed. If this is a realistic failure mode that could lead to a fire, then periodic inspection of the electrical system, possible using thermal imaging, would be expected. • A more inherently safe approach to preventing fire impinging on the process is segregation. An example would be use of fireproof ducting for electrical cables. **(Expectation 7)**
HS/1	Runaway reaction reaching the decomposition temperature	This is addressed already in Section 4.5.
HS/4	A fire impinging on the vent system connected to the reactor	The proposed expectations are similar to HS/3
HS/9	Heat from unintended reaction catalyzed by contaminant	Detailed Process Hazard Analysis should be used to identify all possible contaminants and ensure safeguards are in place for each. Safeguards will need regular monitoring, with frequency determined by the level of risk. Examples of monitoring are: • Internal inspection of the reactor and connected pipework and fittings, looking for contamination or corrosion; • Chemical analysis of materials entering the reactor; • Inspection of non-return valves that prevent catalyst entering the EO system. **(Expectation 8)**

4.7 Conclusions on Barrier Assessment

DNV GL assessed a number of barriers, which are below clustered in groups 1-4.

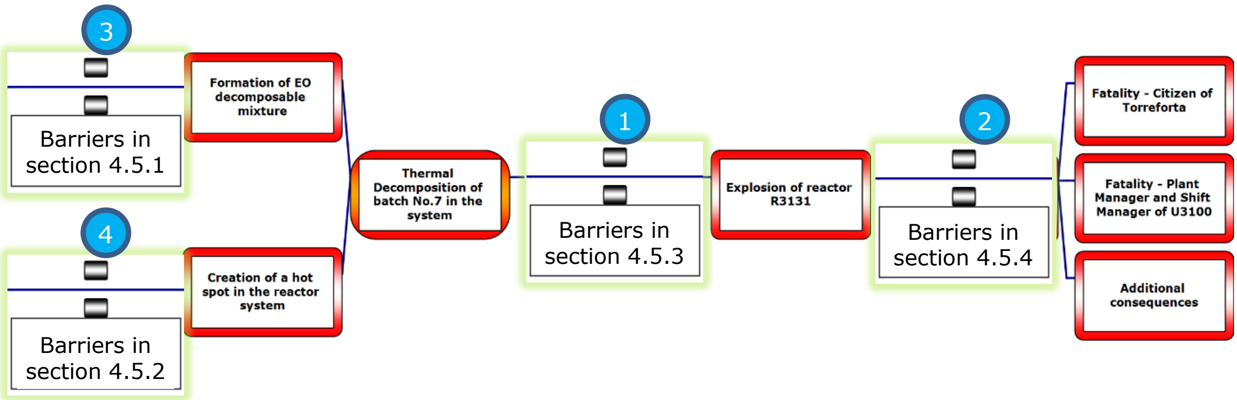


Figure 4-22: Conclusions on Barrier Assessment

Group No.	Barrier assessment
1	**Barriers to prevent the event "Explosion of reactor R3131" after the event "Thermal Decomposition of batch No.7 in the system" occurred** Once the thermal decomposition has started, it will immediately result in a major event. There are no preventive barriers known by DNV GL, that could effectively stop the thermal decomposition from progressing to an explosion. Existing barriers, such as 3.1 "Pressure Safety Valve 31-RV-323", or 3.2 "Design of the system to contain a thermal decomposition" were inadequate for this event. The barrier 3.2 could cope with thermal decompositions not reaching more than 45barg.
2	**Barriers to prevent or mitigate the consequences from the event "Explosion of reactor R3131"** There are only very few mitigating barriers to reduce the consequences from the major event. In this case, the barrier 4.1 „Local Planning Controls" to protect external parties is regarded as inadequate. It would possibly be adequate for managing acceptable risk. The second identified barrier to protect people at IQOXE site working in the control room, 4.2 „Design and location of the control room", unfortunately failed, as the risk from the new unit U3100 have not been dealt with, neither by management of change, nor by risk management. As it becomes obvious from the limited prevention and mitigation barriers, an incident like this must be prevented by all means before a thermal decomposition is initiated.
3	**Barriers to prevent the event "Formation of EO decomposable mixture"** The barrier 1.1„Verification of correct gas composition in the reactor head space" is not in place (missing), However, currently it is not standard practice in ethoxylation reactor design to provide a gas analyser on the head space. There would be a number of practical difficulties in providing such analysis including the impact of polymer contamination on the analyser. The barrier 1.2 „Leak detection system" has been regarded as inadequate. The responses to the request for information on process safety studies undertaken lead to the assumption that insufficient detail and time was spent on identifying leak sources and determination of location of detection.
4	**Barriers to prevent the event "Creation of a hot spot in the reactor system"** Barrier 2.1 „Fire detection and fire fighting system" is considered inadequate. Insufficient detail and time spent on identifying fires that could threaten EO reactor system and specifying detection and firefighting system. Barrier 2.2 „Heat insulation of R-3131", Barriers: 2.3 „Temperature and Pressure Control System", 2.4 „ESD Emergency Shutdown System" and 2.5 „Manual ESD: emergency full cooling": Due to the extent of damage to the unit and the lack of data or witness information, it is not possible to determine if there was a failure of the systems or the manual ESD activation. However, such a failure is credible but low likelihood and the causal analysis is presented below.

5 RECOMMENDATIONS AND EXPECTATIONS FOR PREVENTIVE AND CORRECTIVE ACTIONS

The following tables provides individual recommendations for improvement, linked to the results of the Root Cause Analysis.

Table 5-1: List of Recommendations

No.	Recommendation	Link to barrier	Benefit	Effort
1	**Ensure appropriate risk identification and management** The process for managing risks shall be reviewed to eliminate gaps to international standards, such as ISO 31000 and identify improvement possibilities. Minimum requirements for risk studies, throughout different phases of a plant lifecycle (concept stage to operation and abandonment) shall be defined to ensure risks are adequately identified, assessed and treated. For example, considering the quality of the received HAZOP for U3100, a guideline for conducting a HAZOP should be developed to ensure the right level of detail. The same applies to the QRA in respect to selection of credible scenarios.	2.1 Firefighting System, 2.2, Heat Insulation 2.3, T&P Control 2.4, ESD System 4.2 Design and location of the control room,	H	M
2	**Review and improve the management of change process** The management of change process should be reviewed and revised. This should include its application for extension and modification of plant facilities as well as for changing production recipes or software changes. There should be systems in place for appropriate verification of the changes.	4.2 Design and location of the control room 2.3 Temperature and Pressure control system.	H	L
3	**Ensure safe control room or occupied buildings** Existing and new control rooms and occupied buildings on the site should be assessed to ensure the safety of people within them. The assessment should also include consideration of the building survivability, control systems, safety shutdown systems or use of the location for managing an emergency.	4.2 Design and location of the control room	H	L
4	**Assess level of prevention barriers/safeguards to take account for limited containment** Process Hazard Analysis should be used to identify and assess risks of scenarios of decomposition for which the maximum pressure would not be contained by the reactor. Ensure levels of prevention safeguards in place are sufficient when the containment is not possible.	3.2 Design of the system to contain a thermal decomposition	H	M

5	**Apply good industry practice for the fire detection and firefighting system** Considering the hazardous potential of the U3100 process area, the safety level should be increased beyond the legal requirements and at least be in accordance with good industry practice. Thus, it is recommended to undertake safety studies to examine the severity of the consequences of a fire scenario for identification areas appropriate for deluge protection. The basic design documents (i.e. the Safety concept of the supplier), as well as the EO user manual will provide guidance (Ethylene Oxide Product Stewardship Guidance Manual, prepared by the American Chemistry Council's Ethylene Oxide/Ethylene Glycols Panel). Other plant areas outside the U3100 should be checked for improvement possibilities based on the approach as stated above.	2.1 Fire detection and firefighting system	H	H
6	**Install appropriate gas detection in the unit** Considering the hazardous potential of the U3100 process area, the safety level should be in accordance with good industry practice. Thus, carry out or revise process hazard risk assessments to determine potential sources of EO leak within the unit(s) and determine number and location of gas detectors. Assess and select a detection method.	1.2 Leak detection system	M	M
7	**Assess possibility for reactor gas analysis** Determine if it is reasonably practicable to measure the concentration of EO in the head space of the reactor. If the concentration should exceed a defined safety level, an alarm should be activated to warn the operators and automatically stop the EO feed pump and close the EO feed valves. It is recommended that IQOXE liaises with other ethoxylation operators to review developments in this area and adopt new technology if appropriate.	1.1 Verification of gas composition in the reactor headspace	H	M
8	**Review approach for risk reduction from ethylene oxide installations** Currently the risks zones defined around major hazard plants have their distances determined by overpressure, thermal radiation or toxic dose risks. Given the number of ethylene oxide explosions that have occurred in history and the incidence of missile fragments, DNV GL would recommend that this approach is reviewed to see whether risk criteria and mitigation of the type used for explosive manufacturing sites should be adopted at least for new ethylene oxide installations. This would require joint, international review amongst manufacturers that use ethylene oxide and their regulators.	4.1 Land-Use Planning Controls	M	H

Table 5-2: List of expectations

No.	Expectations	Link to barrier or reference
1	**Reliability of control system** Process risk assessment and SIL assessment should be used to determine the criticality and then the frequency of testing of the reactor control loops and frequency of inspection of its elements. The safety instrument and ESD systems should be designed, installed, tested, operated and maintained in accordance with IEC 61511. The required reliability is defined by the process hazard analysis. The reliability depends on the architecture of the SIS and its testing interval both of which should be defined.	2.3 Temperature and Pressure control system. 2.4 ESD Emergency Shutdown System
2	**Competence Assurance for critical tasks** For such a hazardous installation, a rigorous competence management system would be expected to operate. Critical tasks such as activation of ESD would be part of training and competence assessment and competence demonstration. Regular drills and task observation would be expected.	2.5 Manual ESD: emergency full cooling
3	**Adequate heat insulation of R-3131 system** Use process hazard analysis to identify all critical elements of the reactor and its pipework with regard to fire impingement and ensure fire insulation is provided where practicable. Ensure that maintenance procedures and permit to work system require reinstatement of fire insulation before plant can be put back in service.	2.2 Heat insulation of R-3131
4	**Preventing EO accumulation in the reused nitrogen between batches** Dispose of all the gases at the end of the batch and purge the reactor with nitrogen, or Analyse the gas mixture at the end of the batch and adjust the nitrogen partial pressure accordingly.	Ref. EO/2 EO accumulation in the reused nitrogen
5	**Leak Prevention** Prevention of a leak requires: • Identification of the failure mechanisms that might lead to a leak: for example vibration, corrosion, degradation of gaskets. The inspection and maintenance system should then ensure monitoring and replacement are carried out with frequency determined by the level of risk. • A periodic pressure test, potentially before each batch, is carried out to test for a leak. This is in addition to regulatory pressure tests.	Ref. EO/3 External Leak Prevention
6	**Prevention of leaks to the vent header**	Ref. EO/5

No.	Expectations	Link to barrier or reference
	• Vent valves should be checked for passing (internal leaks) by carrying out a periodic pressure test, potentially before each batch; • Carry out identification of the failure mechanisms that might lead to a leak: for example corrosion, degradation of seats. The inspection and maintenance system should then ensure monitoring of these mechanisms and replacement with frequency determined by the level of risk.	Leaks to vent header
7	**Fire prevention by inspection and maintenance** • Process Hazard Analysis should be used to identify all types of fire that could occur and the failure modes that lead to them. The inspection and maintenance system should then ensure monitoring, for example of overheating components and replacement are carried out with frequency determined by the level of risk. • An inherently safe approach to preventing fire impinging on the process is segregation. An example would be use of fireproof ducting for electrical cables.	Ref. HS/3 Fire prevention
8	**Prevention of contaminants** Detailed Process Hazard Analysis should be used to identify all possible contaminants and ensure safeguards are in place for each. Safeguards will need regular monitoring, with frequency determined by the level of risk. Examples of monitoring are: • Internal inspection of the reactor and connected pipework and fittings, looking for contamination or corrosion; • Chemical analysis of materials entering the reactor; • Inspection of non-return valves that prevent catalyst entering the EO system.	Ref. HS/9 Prevention of contaminants

6 RECOMMENDATIONS FOR FUTURE INVESTIGATION

To date, the investigation has not yet been able to reach firm conclusions on the causes of the accident. This has been due to a number of limitations as outlined in Section 2. As the investigation has proceeded, several outstanding questions remain unanswered. A number of additional tests have been identified. The following future actions are recommended:

1. Where possible, person to person interviews with key witnesses should be held, recognizing the time that has elapsed since the accident;
2. Alongside the interviews, information should be made available by IQOXE to fully answer the outstanding questions;
3. Further assessment of the final stage of the process before the explosion happened, i.e. assessment of the electrical power reduction by 430kW between 18:15 and 18:30 – in order to answer the question of whether the loop pumps were stopped and afterwards still heat induced by steam supply?
4. If possible, information, photographs and data collected by the police and judicial enquiry should be examined;
5. Several fragments of the damaged unit have been identified to GenCat for analysis of surface effects to determine to what extent they have been exposed to heat or have smoke deposits. This analysis should be carried out and the results assessed;
6. Subsequent to the initial thermal stability findings presented by IQS, further tests on the MPEG 500 reaction medium and product should be continued to understand its thermal stability as a function of time and temperature.

7 APPENDICES

7.1 Appendix: Terms of reference for Investigation Team

The purpose of DNV GL's investigation:

- What has happened?
- Why could it happen?
- What changes are required, to avoid such an incident from happening again?

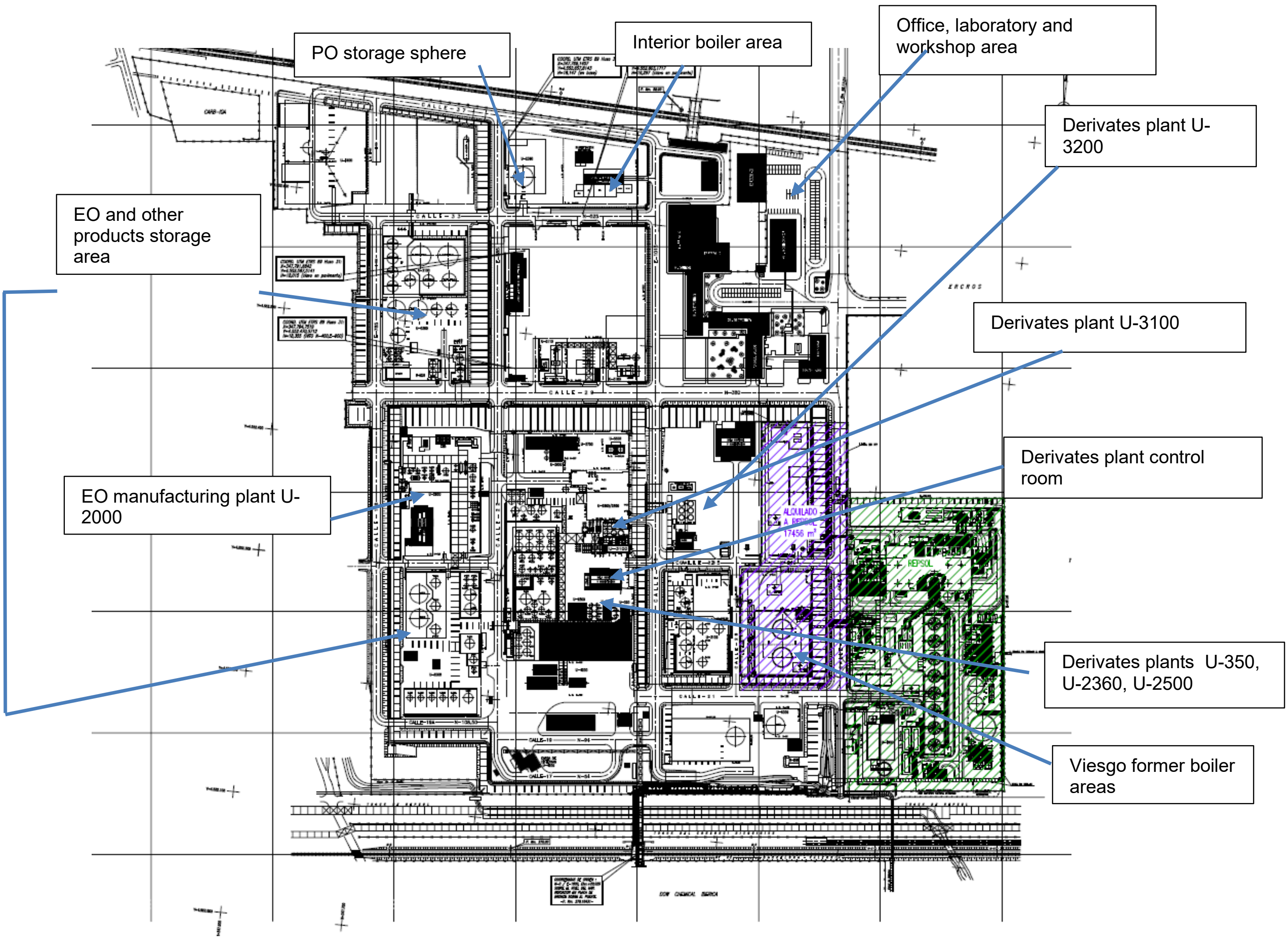
Scope of Work:

- Investigate and analyse the course of events of the incident and determine the causes incl. the weakness of the Affected Units management system.
- Develop improvement measures to avoid similar incidents in the future (ideally in cooperation with the Affected Unit).
- Provide input on wider application of the incident findings for the communication of learnings.
- Present results to Catalonian government.
- Share the findings with the affected unit, and other directly involved parties to assist with their internal investigation and improvement as agreed with the Catalonian government.

Investigation Team

Lead Investigator	Mark Hopwood; Masters of Science Chemistry, Fellow of Royal Soc. Of Chem. FRSC C.Chem, Chartered Chemical Engineer, MIChemE, CEng	Senior Principal Consultant DNV GL, Risk Management, UK
Deputy Lead Investigator and Project Manager	Hendrik Ebel, Master of Science Industrial Engineer	Senior Consultant DNV GL, Risk Management, Germany
General Support	Eduardo Pallarés, Master of Science Energy Technology	Consultant DNV GL, Spain
Process Safety Specialist	Benjamin Barbette, Master of Engineering Applied Chemistry	Senior Consultant DNV GL, Risk Management, Belgium
Explosions Expert	Clara Huéscar Medina, PhD CEng MIMechE	Senior Engineer DNV GL, Spadeadam Testing and Research, UK
Forensic Examination Expert	Jeff Jones, MIMMM C.Eng	Principal Engineer DNV GL, Materials & Corrosion, UK
Explosions Expert	Douglas Michael Johnson	VP Senior Principal Consultant DNV GL, Spadeadam Testing and Research, UK

7.2 Appendix: Plot plan of the IQOXE plant



7.3 Appendix: Operational aspects / process design

Unit U-3100 is a batch or batch production plant for ethoxylation or propoxylation of alcohols,acids, glycols and other raw materials, with the help of a catalyst. Some of the raw materials are solid at room temperature, so the pipes are heated. The process takes place in several stages:

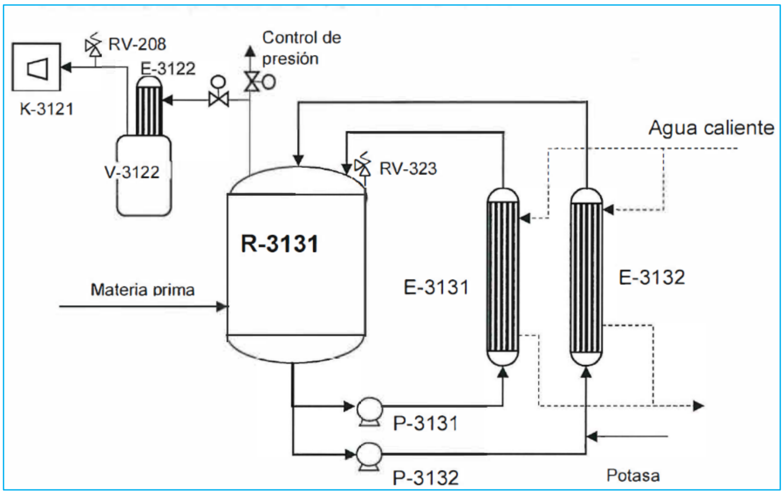
1. Raw material loading and dehydration

Please note, the below description is related to the initial process design, in a second step the pre-treatment process was conducted not in the reactor R3131 anymore, but in the vessel V3141 and related equipment. Please check the process flow diagram in Appendix 3 for the actual process design.

The raw material and the catalyst (usually 50% potash solution, but in the case of MPEG 500, sodium methylate is used)) are charged by means of mass counters in the R-3131 reactor. The mixture is circulated by the P-3131 and P-3132 pumps through external tubular exchangers (E-3131 and E-3132) to raise the temperature to around 100 ° C. The heating in said exchangers is carried out by means of a secondary hot water circuit.

If required, when potash solution is used, dehydration is carried out by applying vacuum to the raw material contained in the R-3131 reactor up to about 20 mbar by means of the vacuum pump K-3121. The water is condensed in the exchanger E-3122 with cooling water and is collected in the V-3122 tank, equipped with an external coil to prevent freezing of possible entrainment of raw material. The simplified scheme shows the described process.

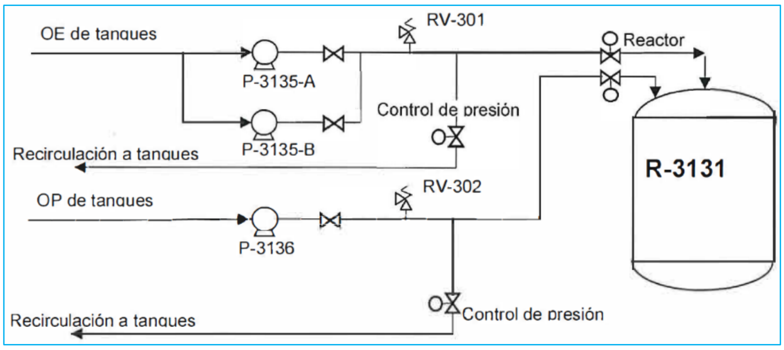
The R-3131, E-3122 and V-3122 equipment are designed to work in absolute vacuum. The V-3122-E-3122 assembly that works normally under vacuum is protected by the 31-RV-208 valve set at 3.5 barg, in the event of failure of the pressure control valve that communicates with R-3131 (during the reaction stage).



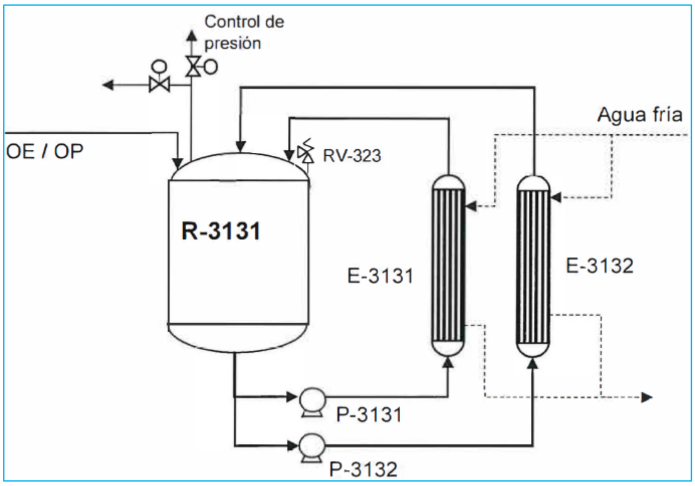
2. Feeding of ethylene oxide to the reactor

The ethoxylation reaction is carried out by adding ethylene oxide to the raw material charged to the reactor.

Ethylene oxide is pumped by centrifugal pumps P-3135A and P-3135B. After the reaction is complete, automatic stop valves are closed. To avoid the increase in pressure caused by the thermal expansion of ethylene oxide trapped between valves, the safety valve 31-RV-301 tared at 25 barg has been installed, which protects the 2 "-P-313007 A-3306Z line to the reactor.



3. Reaction

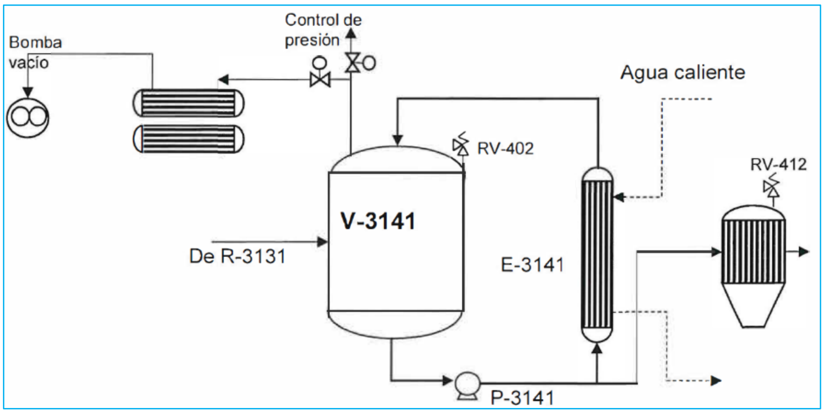


The ethylene oxide that is added to the reactor reacts with the raw material loaded in it. The reaction is exothermic so that the heat generated is extracted from the system by the exchangers E-3131 and E-3132, which on this occasion work by cooling the product with cold water from the secondary circuit. In case of failure of the cooling water the reaction can run away and cause an increase in pressure. Safety instrument trips are used to monitor the temperature in the reactor and stop the ethylene oxide feed if the temperature is out of the normal range.

4. Postreaction and Filtration

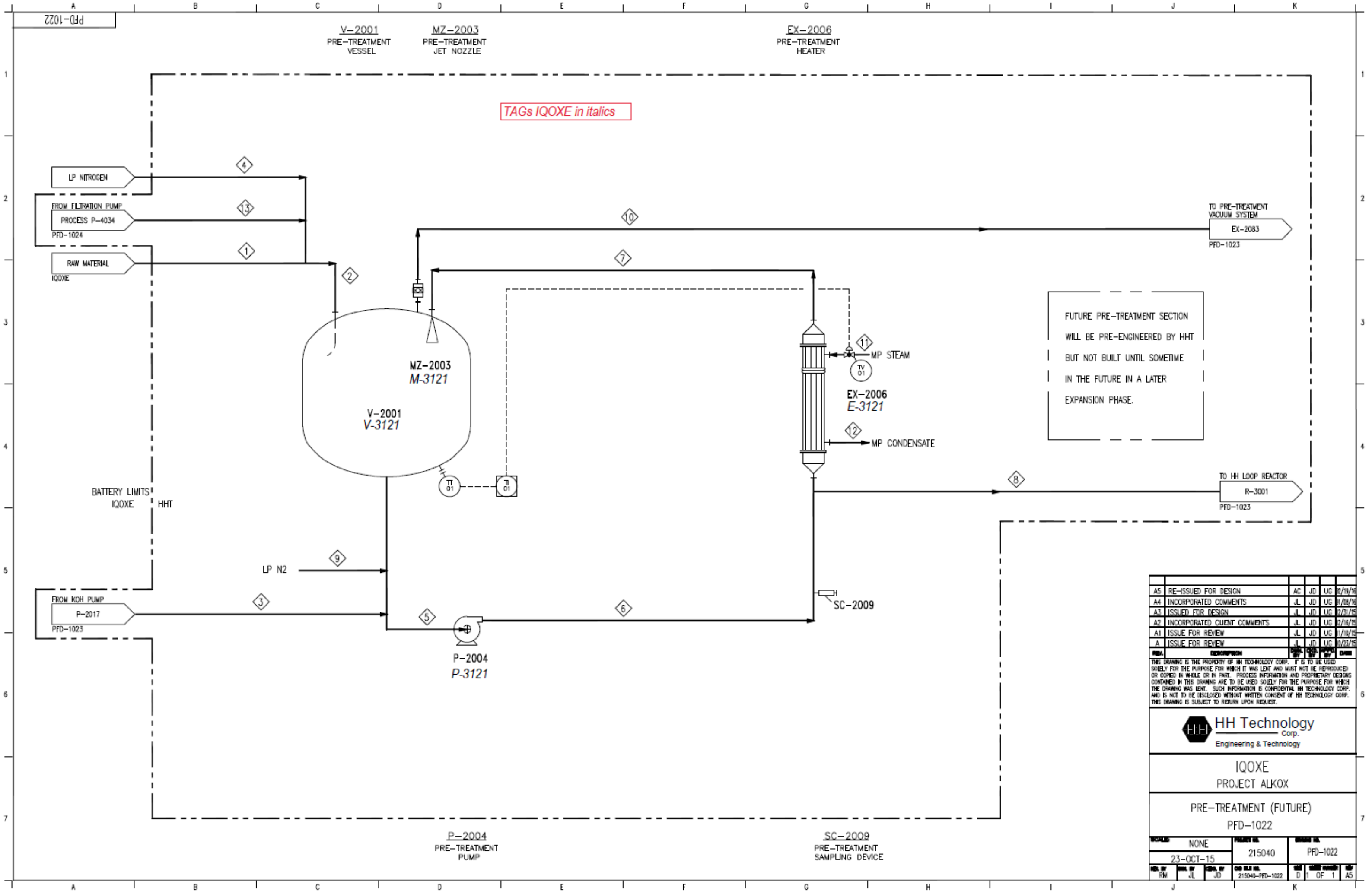
Once the ethoxylation reaction is complete, the product of R-3131 is sent to the postreactor V-3141 for neutralization and elimination of volatiles. Neutralization is carried out by addition of phosphoric acid in aqueous medium, crystallization of sodium phosphate salts and dehydration.
Usually it works under vacuum and temperature around 120 ° C. Heating is effected by circulation through an external exchanger, heated with a secondary hot water circuit.

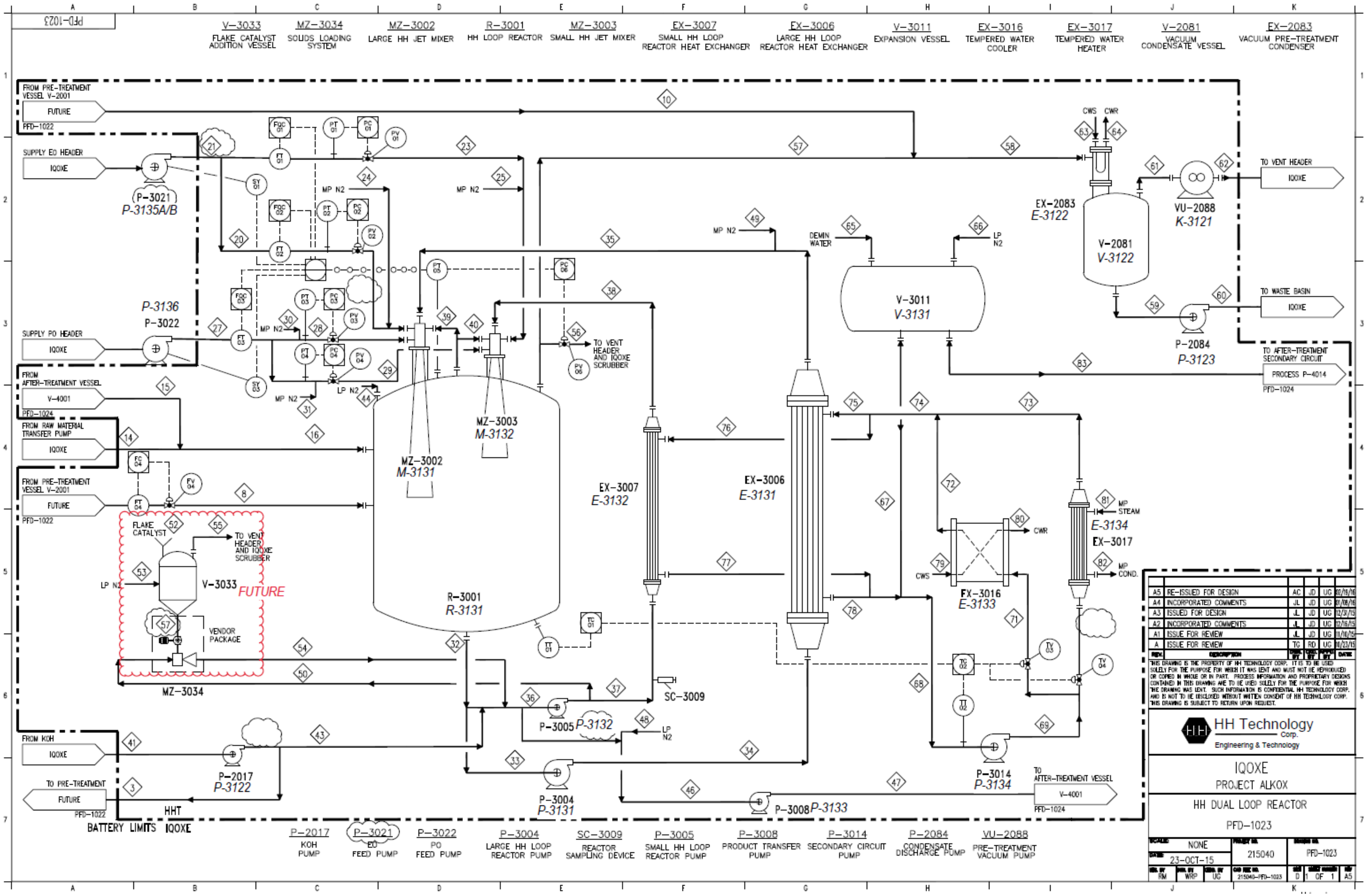
The evaporated water from the V-3141 postreactor is condensed in the E-A-3141-1 and E-A-3141-2 equipment by exchange with cooling water.
The product, once neutralized and the crystals formed, is passed through the S-3141 filter before sending it to final tanks. The filter is protected by the RV-412 safety valve rated at 10 barg.

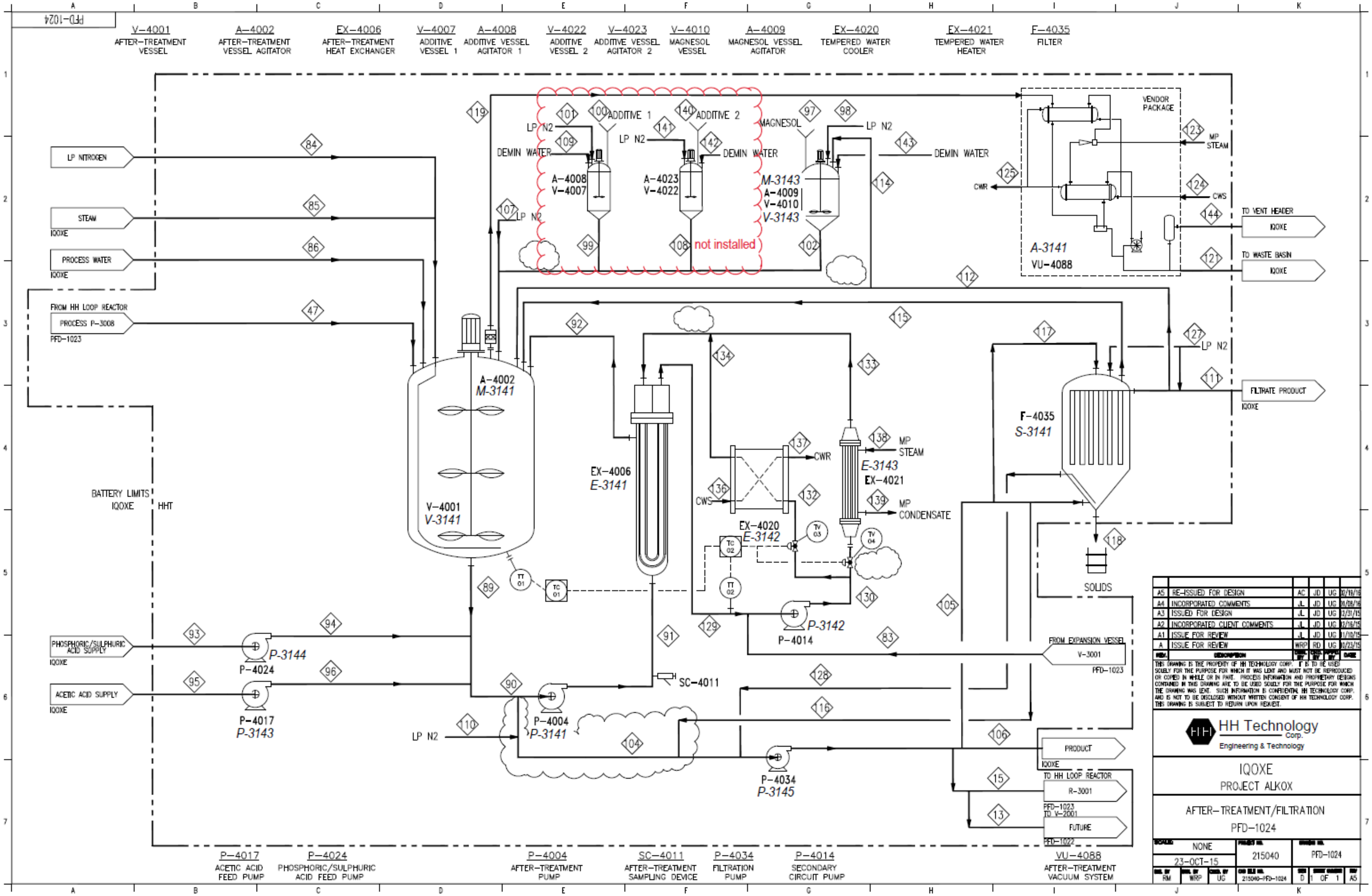


7.4 Appendix: Process Flow Diagrams

The three process flow diagrams below show the process and related main equipment.






PFD-1024
V-4001 AFTER-TREATMENT VESSEL
A-4002 AFTER-TREATMENT VESSEL AGITATOR
EX-4006 AFTER-TREATMENT HEAT EXCHANGER
V-4007 ADDITIVE VESSEL 1
A-4008 ADDITIVE VESSEL AGITATOR 1
V-4022 ADDITIVE VESSEL 2
A-4023 ADDITIVE VESSEL AGITATOR 2
V-4010 MAGNESOL VESSEL
A-4009 MAGNESOL VESSEL AGITATOR
EX-4020 TEMPERED WATER COOLER
EX-4021 TEMPERED WATER HEATER
F-4035 FILTER
LP NITROGEN
STEAM
IQOXE
PROCESS WATER
IQOXE
FROM HH LOOP REACTOR
PROCESS P-3008
PFD-1023
BATTERY LIMITS
IQOXE
HHT
PHOSPHORIC/SULPHURIC ACID SUPPLY
IQOXE
ACETIC ACID SUPPLY
IQOXE
ADDITIVE 1
ADDITIVE 2
MAGNESOL
LP N2
DEMIN WATER
A-4008
V-4007
A-4023
V-4022
M-3143
A-4009
V-4010
V-3143
not installed
VENDOR PACKAGE
MP STEAM
CWR
CWS
A-3141
VU-4088
TO VENT HEADER
IQOXE
TO WASTE BASIN
IQOXE
FILTRATE PRODUCT
IQOXE
A-4002
M-3141
V-4001
V-3141
EX-4006
E-3141
EX-4020
E-3142
E-3143
EX-4021
MP STEAM
MP CONDENSATE
F-4035
S-3141
SOLIDS
P-4014
P-3142
P-4024
P-3144
P-4017
P-3143
P-4004
P-3141
SC-4011
P-4034
P-3145
FROM EXPANSION VESSEL
V-3001
PFD-1023
PRODUCT
IQOXE
TO HH LOOP REACTOR
R-3001
PFD-1023
TO V-2001
FUTURE
PFD-1022
P-4017 ACETIC ACID FEED PUMP
P-4024 PHOSPHORIC/SULPHURIC ACID FEED PUMP
P-4004 AFTER-TREATMENT PUMP
SC-4011 AFTER-TREATMENT SAMPLING DEVICE
P-4034 FILTRATION PUMP
P-4014 SECONDARY CIRCUIT PUMP
VU-4088 AFTER-TREATMENT VACUUM SYSTEM
A5 RE-ISSUED FOR DESIGN
A4 INCORPORATED COMMENTS
A3 ISSUED FOR DESIGN
A2 INCORPORATED CLIENT COMMENTS
A1 ISSUE FOR REVIEW
A ISSUE FOR REVIEW
HH Technology Corp.
Engineering & Technology
IQOXE
PROJECT ALKOX
AFTER-TREATMENT/FILTRATION
PFD-1024
NONE
215040
23-OCT-15
PFD-1024

7.5 Appendix: Process and system data

Data for materials handled in the reactor:

	Sodium methylate 30% in methanol	Methanol	Ethylene oxide	MPEG 500
Boiling point at normal pressure	92°C	64.7°C	10°C	Not Available
Melting point	Cryst. 6.8°C	-97.8 °C	Not Available	27 to 32°C
Flash point	33°C	9.7°C	< -18°C	>225°C
Autoignition Temperature	455°C	455°C	445°C	Not Available
Heat of polymerisation			Exo 2324 kJ/kg	
Heat of decomposiition			Exo 3040 kJ/Kg	Not Available
Temperature of decomposition of gas phase			500°C (but as low as 450°C)	Not Available
Heat of ethoxylation reaction			Typically, EXO 100 kJ/mol EO	
Minimum ignition energy	Not Available	Not Available	0.06 mJ (very easily ignited by static discharge)	Not Available

7.6 Appendix: Consequences of a decomposition

In this section we describe how the thermal decomposition leads to explosion of the reactor and estimate the release of energy.

Ethylene Oxide vapour decomposes explosively at approximately 560°C. The temperature may be affected by impurities and the geometry of the vessel. Onset temperatures as low as 450°C have been reported. Burgoyne and Braithwaite carried out laboratory measurements to estimate the heat of decomposition as 133760 kJ/Kg.mol or 3040 KJ/kg or 3MJ/kg. The energy of detonation of TNT, for comparison, is 4.184 MJ/kg (NIST). Ethylene Oxide decomposition is therefore very energetic. (It is, however, not in the condensed phase like TNT and does not decompose as rapidly as TNT)

7.6.1 Pressure increase

Experiments in a 20L sphere, reported by Braithwaite and Pekalski[1], show that the gases released by the decomposition plus the rise in temperature cause a rapid rise in pressure. The final pressure depends on:

- The starting pressure
- The starting temperature
- The amount of dilution by nitrogen

The figures below are taken from this source as well.

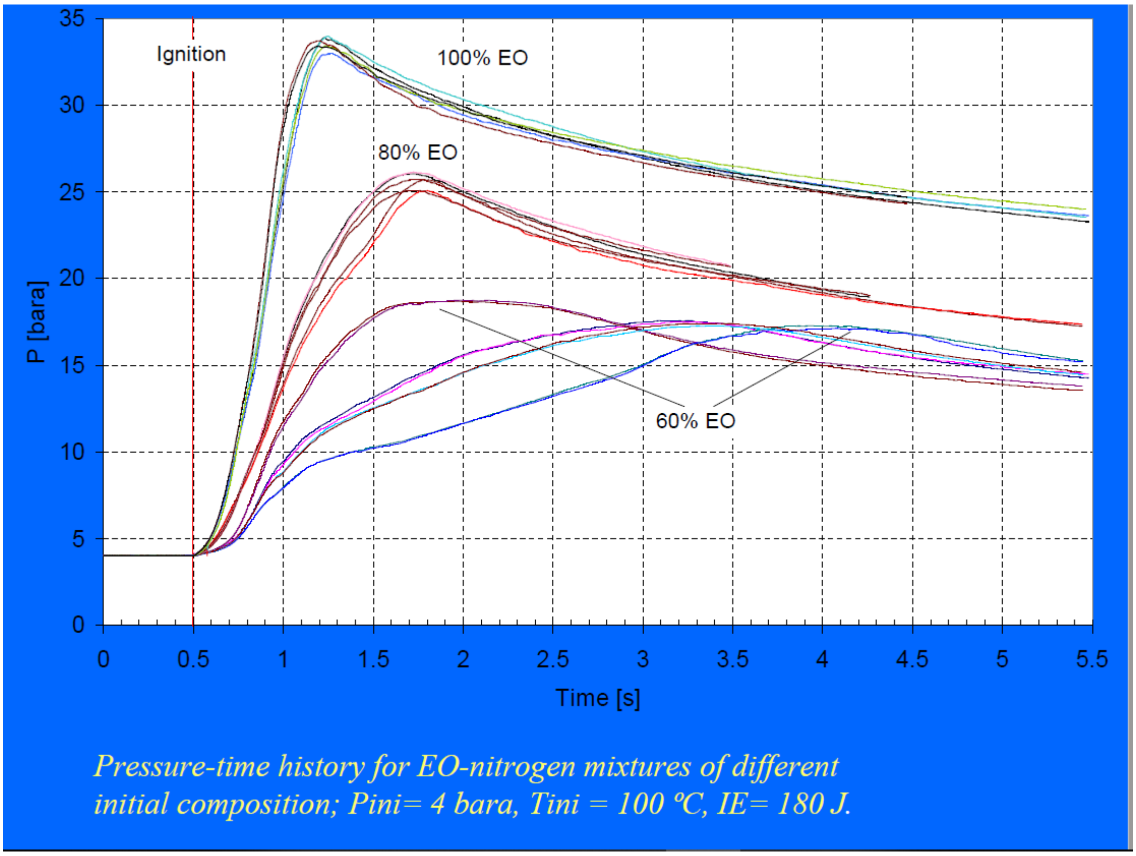


Figure 7-1: Pressure increase for EO-nitrogen mixtures of different initial composition

[1] Explosion Safety in Ethoxylation Reactors, M Braithwaite & A Pekalski, SAFEKINEX wokshop https://www.morechemistry.com/SAFEKINEX/workshop/3-ProblemAnalysis-MartinBraithwaite.pdf

Ethylene Oxide: Maximum rate of pressure rise &
maximum pressures - from 373 K and 4 bara

Composition EO/N2 [EO%]	Ignition Energy [J]	(dP/dt)max [bar/s]	Pmax [bara]
60	180	25.01	17.46
80	180	36.80	25.65
100	0.72	41.98	31.83
100	180	77.80	33.65
100	540	169.6	36.38

Figure 7-2: Ethylene Oxide - maximum rate of pressure rise & maximum pressure

They show that in a worst case, where the EO concentration has deviated to 100% EO, with no nitrogen present, the pressure increases from 4 bara to a maximum of 36 bara. This is a 9-fold increase in pressure. The selection of the reactor R-3131 design pressure at 45 barg = 46 bara seems consistent with this finding, with the intention the reactor should contain the overpressure of a decomposition.

The final pressure at the end of a normal reaction in the reactor is expected to be about 11barg= 12bara. In a deviation where the gas mixture had become 100% EO, the maximum decomposition pressure might be expected to reach 12 x 9 = 108bara which largely exceeds the design pressure of 46bara and also the test pressure of 68.5bara. If not relieved, this pressure would very likely rupture the reactor system.

With nitrogen present, the rate of propagation of the decomposition is reduced. The reduced quantity of EO within a given volume means that the pressure rise due to decomposition is reduced. If the EO content is less than 50%, there will be no propagation. Above 50% EO, the maximum pressure and the rate of pressure rise depends on the concentration. At 60% EO, the ratio of Pmax to the starting pressure is 4.4. If the pressure at the start of the decomposition were 12 bara, the final pressure might be expected to reach 52.8 bara.

7.6.2 Chemical energy released

The quantity of energy that could be potentially released in the decomposition is proportional to the mass of EO that decomposes. No data is available on the actual EO concentration prior to the explosion, nor the temperature in the reactor headspace. To estimate the energy, the following assumptions have been used:

Assumption		Notes
Volume of reactor	37100 L	
Volume of gas in the reactor at the time of the explosion	35050 L	This is the space at the **start** of a normal batch size of MPEG500.
Pressure in the reactor at the time of the explosion	12 bara	This is the pressure at the **end** of the reaction.
Temperature of gases in the headspace	25°C or 298K	This is probably lower than the temperature at the end of the reaction. Using this number will **overestimate** the quantity of EO.
Concentration of Ethylene Oxide in the gas mixture	50% by volume	This is likely to be an **underestimate** since 50% EO is not expected to propagate a decomposition.
Calculated mass of Ethylene Oxide gas present	385.6 kg	
Decomposition Energy per kg	3040 kJ/kg	
Decomposition Energy Potentially release by explosion	**1172 MJ**	

7.7 Appendix: Calculation of explosion energy

The most likely immediate cause of the explosion at IQOXE has been postulated as a thermal decomposition leading to overpressurisation of the reactor. In the following sections the energy available to cause overpressure and flying fragments is assessed and an estimation of overpressure and fragment distance travelled is compared to the evidence collected during the investigation.

The energy stored in the vessel was calculated in two ways:

1. Isothermal energy that would result from expansion of an ideal gas at constant temperature from the initial volume and burst pressure;
2. Energy available due to thermal decomposition of EO as described in Section 7.6.2.

Table 7-1

	Stored Energy (MJ)	**Kinetic Energy (MJ)**	**Fragment Velocity (ms^{-1})**	**Maximum Range (m)**
Isothermal	743	260	161	2640
Thermal Decomposition EO	1170	410	202	4160

The calculated stored energies were 743 MJ and 1170 MJ for the isothermal and thermal decomposition cases respectively. The mass of the reactor alone was 20,100 kg. Assuming 35% of the stored energy goes into kinetic energy of the vessel fragments the resulting velocities were calculated and are shown in Table 7-1. It is considered that the velocity calculated from the thermal decomposition reaction would be the 'worst case' velocity and range. The investigation confirmed one large fragment landed 2.5 km away from the location of the accident causing a fatality. This fragment was confirmed to be part of the affected reactor (R3131). Another large fragment was reported approximately 800 m in the South East direction near a Shell garage. This fragment was possibly a piece of stainless steel of considerable thickness, but its origin has not been confirmed. Numerous medium size fragments where photographed and/or collected approximately 100-120 m radius both towards the South West and East directions. Smaller fragments were found in neighbouring sites towards the South 300-500 m. The size and shape of fragments and other factors such as the reactor shape, fluid forces or initial trajectory angle influence the distance fragments can travel, however the estimated distances are consistent with the observed evidence.

The peak side-on overpressure at a given distance can be estimated using the stored energy and the Baker-Tang blast curves (CCPS, 2010). The investigation has determined that the control room which was sited approximately 25 m away from the affected unit was destroyed due to the event. A witness that was present on site on the day of the event suffered cuts from broken window glass at approximately 200 m (Security Manager, at office building).

Table 7-2 shows the estimated overpressure level ranges at 25 m and 200 m distance from the presumed accident location. At 25 m the estimated overpressure level would be expected to cause severe damage to buildings and distortion to steel frames (see Table 7-3). At 200 m distance windows would have been expected to shatter and cause injury from flying glass (see Table 7-3) which is not inconsistent with the evidence collected. The scenarios considered as most likely to have occurred at IQOXE appear to be consistent with the level of damage caused and the evidence provided by the investigation.

Table 7-2

	Stored Energy (MJ)	Overpressure (mbar) at 25 m	Overpressure (mbar) at 200m
Isothermal	743	400	30
Thermal Decomposition EO	1170	500	40

Table 7-3

Overpressure (mbar)	Expected Damage
30	**Minor structural damage.**
30-70	**Windows shattered, window frame damage.**
70-550	**Slight to serious laceration injuries from flying glass and other missiles.**
70	**Partial demolition of houses, made uninhabitable.**
165-840	**Range for 1-90% eardrum rupture among exposed population**
200	**Steel frame buildings distorted and pulled away from foundation**
700	**Probable building destruction**
1000-2000	**Range for 1%-99% fatalities among exposed populations due to direct blast effects**

*Lees, Frank P. 1980. *Loss Prevention in the Process Industries*, Vol. 1. London and Boston: Butterworths.

7.8 Appendix: Selected photographs

This appendix provides a selection of further photographs.

Several fragments that appear to be associated with the reactor do not show fire damage. Examples are the fragment of reactor wall that struck Pza Garcia Lorca, 20 and what appears to be the large jet head assembly. These are shown in Figure 7-3 and Figure 7-4. The large jet assembly does not appear to have any signs of combustion products (black soot) on its interior surfaces.

Figure 7-3 IMG-20200115-WA0018

Figure 7-4 IMG-20200115-WA0009

One of the fragments has been identified as the wall of the reactor. See Figure 7-5. There are two drilled supports visible in the photograph. Their shapes are consistent with the design of the support bases of the reactor normally positioned on the exterior of the cylindrical wall, 500mm above the tan line. The photo shows the inside wall in the area of these supports to be shiny and clean.

Figure 7-5: FOTOGRAFIA 262

Figure 7-6 shows a piece of distorted welded metal plate. At the time of writing it has not been identified. It appears to have been fire damaged prior to ejection by the blast. This fragment could be significant if it is part of the reactor R-3131, since it would imply at least partial exposure of the reactor to fire.

Figure 7-6: FOTOGRAFIA 182

Figure 7-7 shows a piece of pipe that has been exposed to heat.	 **Figure 7-7: FOTOGRAFIA 399**

7.9 Appendix: List of information

	Incident Investigation - Information Log							Print Date
	Type: Paper	Case:						
Running Number	Title	Actor	File Reference	Owner	Delivery Status (Dates)			relevant information
					requested	promised	received	
PAP_001	Incident notification to Authorities		20. Informe 72h	IQOXE			x	Accident happened in U-3100 during reaction to produce MPEG500. Loud deprssurisation noise (15 s) followed by strong explosion. Causes of accident not known. Control room destroyed as well as U-3100. Large number of projectiles impacted in other parts of installation. Later was found out that projectiles where found outside IQOXE. OP storage tank suffered damage in the form of crack and external fire when material ignited.
PAP_002	General operating manual (excerpt)		9 .Organización personal.doc (same doc as number 12)	IQOXE			x	Inforation about responsibilities: Level 1: Plant Manager Level 2: Supervisor Level 3: Unit manager A to F, Unit manager Packing Level 4: Operators (organised in teams) The following units are operated by the unit managers and their operator teams: - U-350 - U-2360 - U-2500 - U-3100 - U-3200 - U-4500 / U-4900
PAP_003	Brief description of the derivatives production process		1. Breve descripción proceso DRV.docx	IQOXE			x	
PAP_004	Operation Manual		P2. Manual de operación.docx	IQOXE			x	Description of analog control for the different sequence blocks of operation. During exhausting stage (block 6) the small and the big loop pump are working. The EO feed pumps are recirculating.

PAP_005	U3100 installation project		4. a Projecte de instal·lació de la Unitat U3100 and P15 PRUEBAS DE PUESTA EN MARCHA Y PROYECTOyecto de instalación U-3100.pdf	IQOXE			x	Presented memo to the authorities for the plant building Includes pressure of design of the equipment and pipes Detailed characteristics of the equipment Security valve RV323 that releases in case of failure of the cooling system After reaction: neutralization and volatile removal and dehydratation Safety elements description Maps of the plant, front view Equipment verification certificates incl. reactor system. The gas detector 31-AT-103 had been tested and calibrated in Nov 2019 The pump P3132 is used for circulation of the mixture of raw material and catalyst through external tubular exchangers (E-3131 and E-3132) to raise the temperature to around 100 ° C. It is located next to R3131
PAP_006	MPEG process description in U3100		2. Breve descripción proceso MPEG.docx	IQOXE			x	
PAP_008	Design process parameters		04. Receta MPEG500 estándar (003).pdf	IQOXE			x	MPEG 500 min and max values of process parameters
PAP_009	PFD for MPEG process		P21 diagramas de Proceso.pdf	IQOXE; HH Technology Corp.			x	This new flow sheet is still from 2015, but it contains the actual tagging.

PAP_013	Overview of Work Orders for U3100	P3132, P3152	200114_OTs_U3100_Comentarios.xlsx	IQOXE			x	In Unit3100 there are 3 WO for 13th of Jan and 2 WO for 14th of Jan: - 67.924-Remove the pump insulation to locate the leak. Change burnt fiber glass of the pump, 13th Jan, finish same day - 67.947-Add memory to the backup server to work remotely, 13th Jan, finish within 72h; - 67.957-Repair 31_X_320 Y 31_X_329 - ACCESORIOS, 13th Jan, immediately; - 67.993-Calibrate 31-L511, 521, 541 AND 551 FOR MPEG-1000, 14th Jan, finish within 72h; - 67.994-Check drainage line of the feeding pipe to the scrubber by technology order. Equipment 4701 does not show in CMMS, 14th Jan, finish within 72h
PAP_014	Work Orders from System for U3100	P3132, P3152	P15 ORDENES DE TRABAJO.pdf	IQOXE			x	The work orders are very brief and no document is signed
PAP_015	Analysis of WO 67924	P3132, P3152	Análisis de la Orden de Trabajo 67924_1.docx	IQOXE			x	On 14th of Jan. a vebal work order was given to reconnect the washing system of the pump seal of P3132 (it was out of service after the seal model was changed by the manufacturer on 28th Nov 2019 as it was not need anymore in this new model). During this work a probable leak was identified in the seal housing. Repair works were postponed by the responsible person.

PAP_018	HHT Safety Concept - Answer to P32 Process		HHT Safety Concept-RevA.pdf	IQOXE/HHT			x	6.14 Gas and fire detection in the neighbourhood of sources of possible leakage shall be installed. Dilution of leakage and control of fire will result if automatic operation of a water spray system is triggered by the gas detection system.
PAP_020	OPERATION OF THE SECURITY SYSTEM (ESD): INITIATORS and ACTIONS		P2. Funcionamiento del sistema de seguridad.docx	IQOXE			x	CONTENT: "The actions that the Triconex security system will carry out and the conditions that initiate these actions are described below. Two types of initiators can be distinguished to the actions of the security system: • Manual shooting from the field or control room. • Triggers generated by the Triconex programming based on the configured parameters."
PAP_021	Layout calculation Safety Valve 31-RV-323		P24 calculo valvula de seguridad.pdf	IQOXE			x	Pressure relief valve RV sized for fire case assuming methanol in reactor. Not sized for decomposition.
PAP_022	Safety Valve test certificate		14c. 31-RV-323.pdf (same doc as 13)	IQOXE; Valvulas Nacional S.A.			x	

PAP_027	Design of Fire Fighting "CHANGE OF THE U-350 UNIT PER UNIT U-3100 FOR THE MANUFACTURE OF PRODUCTS ETHYLENE OXIDE DERIVATIVES"		HSEQ - 41 - Proyecto PCI U 3100.pdf	IQOXE				The fire detection and firefighting systems have been designed and installed in line with Spanish regulations for industrial buildings. The process area is classified for intrinsic risk with Ci=1.6 (high risk) and Type D according to Annex I of the Fire safety Regulations for Industrial Establishments (Real Decreto 2267/2004, de 3 de diciembre, por el que se aprueba el Reglamento de seguridad contra incendios en los establecimientos industriales.). Accordingly, a manual fire alarm system and fire extinguishers have been selected as protection measures. Automatic fire detection systems as well as automatic water sprinkler systems were not selected, as they are not required for type D and E installations by the stated regulation. Smoke detectors have been installed in the technical room and control room buildings.
PAP_029	HAZOP for U3100 (Excel Sheet)		Còpia de 16 HAZOP U3100.xlsx	IQOXE; IDOM			x	The HAZOP covers the following systems: - Ethylene oxide feeding - Raw material and catalyst charge - Dehydration - Loop reactor - Postreatment + neutralization - Filtration + dehydration - Tempered water system The HAZOP Date shows: 16.04.2028, correct data is 16.04.2016 (PEO_01) The overall quality of the HAZOP is regarded as low (poor consequence description - e.g. stopping at pressure increase, safeguards not entirely listed)
PAP_030	HAZOP for U3100 (Report)			IQOXE; IDOM	x			There is no formal HAZOP report for U3100, only an completed HAZOP Excel sheet for U3100

PAP_037	Information on projects U3100 replacing U350		23. U 3100 Expediente T1CNS160011	IQOXE			x	construction of a new reactor at the Derivatives plant (U-3100 unit), which will be used instead of the current smaller one (U-350) in the production of Polyethylene Glycols (PEG's) and Ethoxylates.
PAP_038	Information on projects U3000, 3300, 5200		24. Cambio substancial Expediente T1CS190019	IQOXE			x	QRA in 2019 for the major projects: - U3000 project - extension of OE production capacity - U3300 project - sixth reactor for derivates plant - U5200 several small projects The results show only very little impact to citisens living nearby. - R3131 (prior name R-3001) was assessed for leakage, but not for other credible scenarios, such as runaway reactions or a thermal decomposition, which are known to happen from past incidents in EO plants of other EO operators.
PAP_043	OE User Guide - Answer to P33 Process		EthyleneOxid users guide 3r edition.pdf	IQOXE/HHT			x	The EO User Guide suggests applying NFPA 58 and API 2510 and 2510A to the design of fire protection systems for EO storage and processing areas. Moreover, it informs about different types of leak detection systems. The EO User Guide suggests using process hazards analysis methods that examine the severity of the consequences of a fire scenario for identification areas appropriate for deluge protection.
PAP_057	FiFi system layout		PREGUNTA 25 ISOS PROTECCION CONTRA INCENDIOS					unit U-3100 was provided with a sprinkler system located around the reactor R-3131 designed to cool the reactor surface in the event of fire impingement. The sprinkler system extends also to the post-treatment vessel. Further information on locations of pushbuttons and fire extinguisher.

	Incident Investigation - Information Log								Print Date
	Type: Position		Case:						
Running Number	Title	Actor	File Reference	Owner	Delivery Status (Dates) requested	promised	received	relevant information
POS_002	Layout plan derivatives		18 Plànol implantació detallat.pdf	IQOXE			x	Location of R3131 and propylene oxide tank (V2361) that was damaged and burning during and after the incident; Control room is located in approx. 15m distance to U3100
POS_003	Arrangement plan - U3100 view from sout		U3100 view from south_ATEX classification.pdf	IQOXE			x	Pump 3132 is located next to the reactor R3131 at the bottom level.
POS_004	Mechanical drawing Reactor R3131		14a. Plano reactor R3131 (003).pdf	IQOXE			x	
POS_007	Layout of the Control room		2501211210.pdf	IQOXE			x	Control room design from 1989 with update in 2016 due to U3100 construction.
POS_009	Position of pump 3152		P3- POSICIÓN P-3152 RESPECTO A R-3131	IQOXE			x	Pump P3152 is approx. 13m distance from reactor R3131

	Incident Investigation - Information Log							Print Date
	Type: IT / Electr.	Case:						
Running Number	Title	Actor	File Reference	Owner	Delivery Status (Dates) requested	promised	received	relevant information
IT_01	Process data for Unit MPEG 500 at incident time	EO flow	Envio OE.pdf	IQOXE			x	The differential pressure measurement shows a stop of EO flow on 14th Jan. at 17:58. The start of the EO flow cannot be retrieved from this graph
IT_02	Calculated OE feed to derivates unit 3100 for incident batch	EO flow	OEG EXC-2002 Consumo OE DRV dia 140120.xlsx	IQOXE			x	Calculated OE feed (by IQOXE) to derivates unit 3100: till 15:00: not included between 15-16:00: 1,014tn, between 16-17:00: 6,323tn, between 17-18:00: 9,876tn, between 18-18:38: 0,0tn
IT_03	Power consumption U3100	Electrical power U3100	Consumo eléctrico U3100.docx	IQOXE			x	The measurement shows power consumption from approx. 00:00 till 18:00 on 14th of Jan. The increase of power consumption at approx. 12:40 is related to the MPEG500 production (Startup of the small circulation pump).
IT_04	Power consumption U3100	Electrical power U3100	CONSUMOS ELECTRICOS.pdf	IQOXE			x	The power consumption indicates a complete shut down and restart of P3132 in the second half of its operating time, which was not done in the comparison batch from 10th of Dec 2019. Further and compared to the batch from 10th of December, it shows 1,5 times the duration for P3131 start-up (1,5h compared to 1h) and only less than half time for maintaining power (1,25h compared to 2,75h) Considering a maximum flow rate for OE (flow controler 301 and 302) 10.5t/h, it can be assumed, that the OE feed was stoped earliest at 17:53. The cooling duration after OE feed stop was then approx. 20min, which is less than the duration of prior batches. Indication for switch-off of approx. 430 kW

IT_06	Overview of electrical consumers	Electrical power U3100	VISITA 9 JUNIO.pdf	IQOXE			x	Together the big and the small circulation pumps account for 197kW. Further clarification required for electrical consumers in operation during different steps of the normal process to analyse the power decline before the incident and thus receive indications on the actual process stage
IT_07	steam consumption U3100	Steam	Consumo de vapor.docx	IQOXE			x	The steam graph is the general consumption of the facility and shows that the instants before the explosion there is a steam consumption greater than usual which is due to the derivative plant and reaching the exhausting phase It is a flow measurement and the increment represents aroun 5-10Tn/h The total consumption represents the overall facility consumption
IT_08	Info on steam supply	Steam	Documentació visita empresa 2020-06-09					Steam supply is provided at 18barg
IT_10	Video showing oxplosion from distance (supermarket)		VID-20200114-WA0085.mp4	?, GenCat			x	The video contains time information. It showes 18:40:53 for explosion.
IT_11	Video showing destroyed U3100		VID-20200115-WA0002.mp4	?, GenCat			x	Destroyed U3100 and surrounding facilities after the incident showing cooling activities for an equipment
IT_13	Video showing the origin of the explosion in slow motion		VID-20200114-WA0074.mp4 (and WA0076)	?, GenCat			x	When the video starts, there is already a fire (may have just started, or even longer before). There are two fireballs within a timeframe of 1-2 seconds, no time stamp. Aprox. 20ms after the video starts and already showing a fire from the beginning, the first explosion occures. A second and several times bigger explosion is visible from 2sec after video started. The video is on You-tube and uploaded the first time here: https://www.youtube.com/watch?v=kjWjU0QPn3M
IT_22	Unit MPEG 500 process data (previous batch fabricate)		20.a Dades anterior batch fabricat mpeg500_10_12_19.pn	IQOXE			x	10th of Dec. at 2:29

7.10 Appendix: Electrical consumption and steam graphs

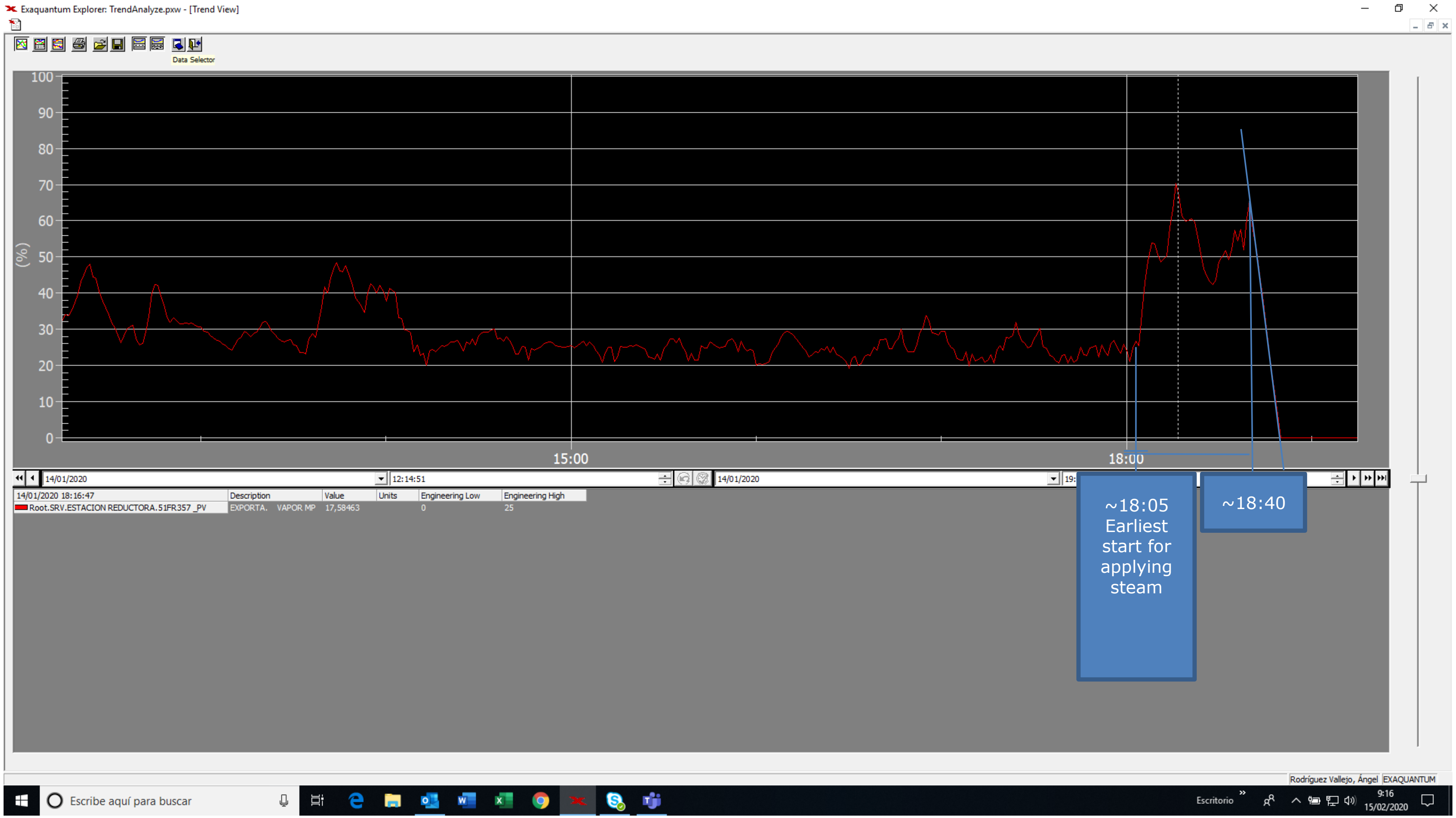


Figure 8: Steam for entire IQOXE plant

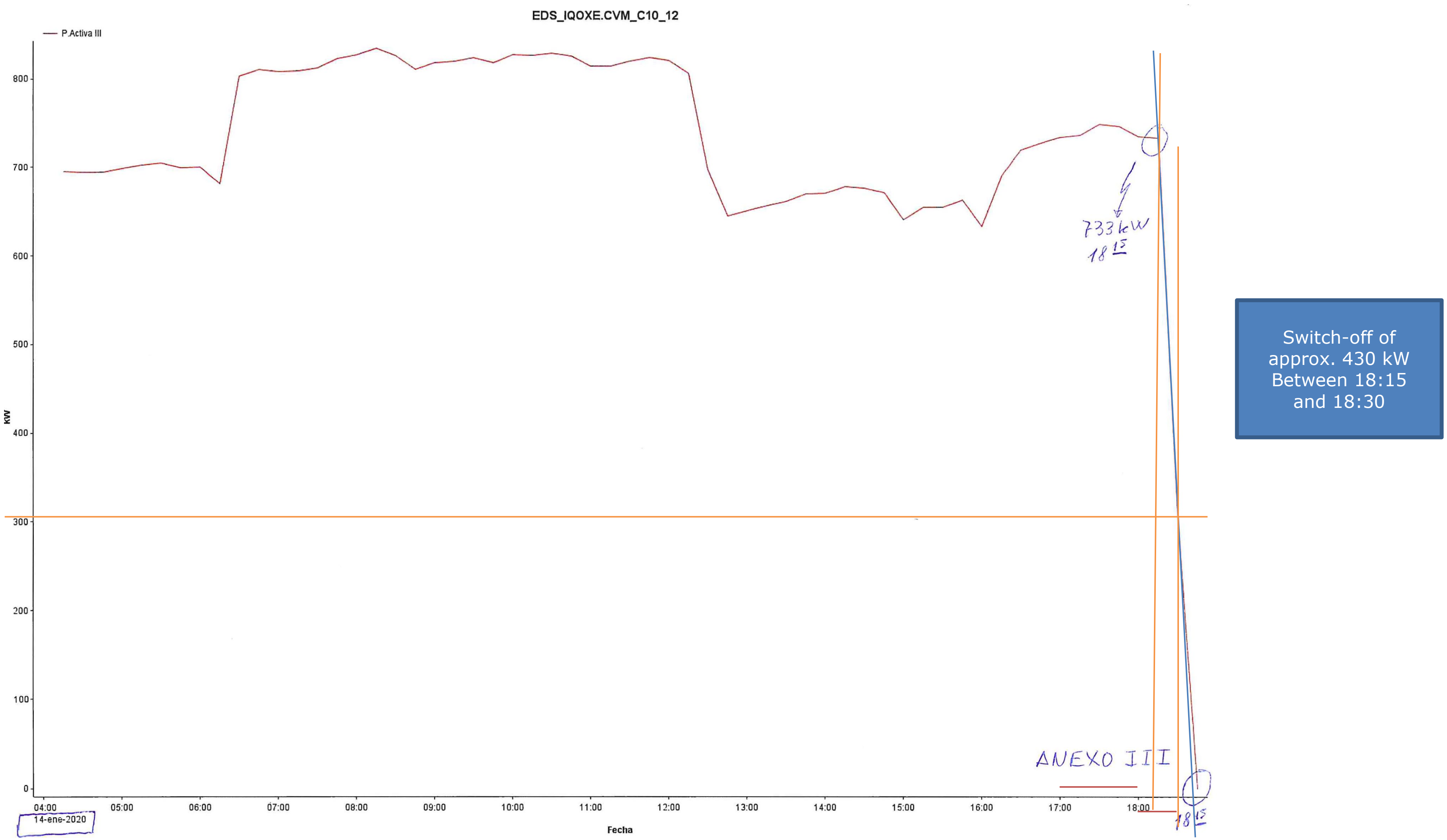


Figure 9: Electrical consumption of U3100 on 14th of January 2020

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