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Human Reliability Analysis for Dynamic Risk Assessment: a case of ammonia production plant

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Reliability, Availability, Maintainability and Safety (RAMS)
Submission date: February 2018
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February 2018

PROJECT / MASTER THESIS
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Executive Summary

Human and organizational factors play a key role for the prevention and mitigation of major accidents. Risk assessment techniques, as the classical Quantitative Risk Analysis (QRA), are only focused on the analysis of technical factors. Integration with Human Reliability Analysis methodologies can cope this problem, but their application is still limited to the nuclear and, more recently, to the petroleum sector. Moreover, the inability of the QRA to represent the evolution of system conditions affecting risk is another limitation that built up the basis for the Dynamic Risk Assessment. The present work shows how these models can be applied also for the chemical process industry, emphasizing the influence on risk of the human and organizational factors and how they can be accounted into the risk assessment. As a representative sector of the chemical process industry, the ammonia production plant is considered. To better understand the nature of incidents and the main problems related to the ammonia plant, a description of the process with a discussion about the most common problems in the apparatuses involved is performed. A creation of a database about past incident, accident and near misses occurred in the ammonia plant accounting nine different sources was created. The analysis of the database showed that the most frequent general cause of incident is a mechanical failure (over 60%). Nevertheless, the work will focus on the human factors, representing the second cause of incidents (38%). While assessment of technical failures is consolidated, human aspects may be relatively disregarded and represent a critical aspect. A catastrophic rupture occurred in Lithuania in 1989 is taken as a representative case study to demonstrate how human and organizational factors can be considered into the risk assessment. A preliminary bow tie diagram to identify causes of the rupture and safety barriers is performed. Then, an overview of different methods for the analysis of human and organizational factors is performed. In particular, the three following methods were applied to a representative real case study. The Resilience-based Early Warning Indicator (REWI) methods, establishing a set of indicators, whose periodic monitoring can contribute to manage risk in a proactive way. It addresses organizational aspects related to the entire installation and to all its risks. The Petro-HRA method. which is a novel technique for the Human Reliability Analysis suited for the petroleum industry. It provides a systematic way to assess human and organizational factors through a detailed step procedure. In this way, factors and systems that can be improved to reduce the HEP and the overall system are pointed out. Moreover, the quantification of the Human Error Probability of a specific operation allows the application of this method within a QRA framework, giving a more detailed overall risk assessment. Eventually, the TECnical Operational and organizational factors (TEC2O) method for Dynamic Risk Assessment is also evaluated. It allows risk variation to be accounted through the frequency modification factor Ω (t) which updates the frequency of a selected dangerous phenomenon during the lifetime of the plant. It takes into account technical, human and organizational factors, combining the strength of the HRA methods to the dynamic and resilience characteristic of the REWI methodology. The result show a more complete and realistic risk assessment and allow identifying weak and strong points of each method.

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Chapter 1

Introduction

Human and organizational factors have been demonstrated to play an important role in causes and mitigation of incidents and accidents in many industries (Massaiu and Paltrinieri, 2016). According to HSE (access date: january, 2018), human factors are intended as ”environmental, organizational and job factors, and human and individual characteristics, which influence behavior at work in a way which can affect health and safety". Also, HSE (access date: january, 2018) defines three aspects of this definition of human factor which are dependent on each other: the job, e.g. tasks, workload and working environment; the individual, e.g. skills, attitude and risk perception; the organization, e.g. work pattern, communications and leadership. All of these aspects are usually not considered in the classical Quantitative Risk Analysis (QRA), where the focus of the analysis is more on technical factors (Laumann et al., 2015). Human and organizational factors can be estimated through Human Reliability Analysis (HRA). According to Paltrinieri and Øien (2014), human reliability is the probability of successful performance of the human activities necessary for either a reliable or an available system. This discipline was developed for the nuclear power plant industry, where up to 90% of incidents are caused by human error (French et al., 2011). Recently, HRA is growing in popularity within the petroleum industry (especially to the offshore sector) (Massaiu and Paltrinieri, 2016). The integration of these techniques within QRA allow a more complete and realistic risk assessment.

According to Villa et al. (2016), another QRA limitation is its intrinsic static nature, being not capable to capture risk variation as deviation or changes in the process and plant. Because of that, the development of a dynamic assessment which accounts the evolution of conditions affecting risk was the focus of many researchers in the past decade. Several methodologies for the Dynamic Risk Assessment (DRA) were recently developed (Landucci and Paltrinieri, 2016a), which aim to support precise, risk-informed and robust decision-making or, e.g., to support safety operations.

In this work, methodologies for the risk assessment thought for the petroleum industry are applied to the chemical process industry, focusing on human and organizational factors. The ammonia production was adopted as a representative example to show how human and organizational factors can lead to major accidents in the chemical process industry. After this introductive chapter, the ammonia production unit is presented in Chapter 2 from the process point of view. In Chapter 3, the most common problems in the apparatuses involved from literature review are identified. Then, a database containing accidents, incidents or near misses about ammonia plant is presented and a discussion of the main results is performed. In Chapter 4, an overview of different methods for the analysis of human and organizational factors is done. In Chapter 5, a selected representative real case study to show the application of the discussed methods is described. Also, the application of the ARAMIS project to build the bow-tie diagram is outlined. In Chapter 6, three different methods, i.e., the Resilience based Early Warning Indicators (REWI), Petro-HRA and the TECnical Operational and Organizational factors (TEC2O) to assess human and organizational factors are considered. The outcomes and the assumption made for the applications of these methods are presented. In Chapter 7, the results are analyzed and connections between methods are profiled. Eventually, the main conclusion of this work are summarized in Chapter 8.

Chapter 2

Ammonia production

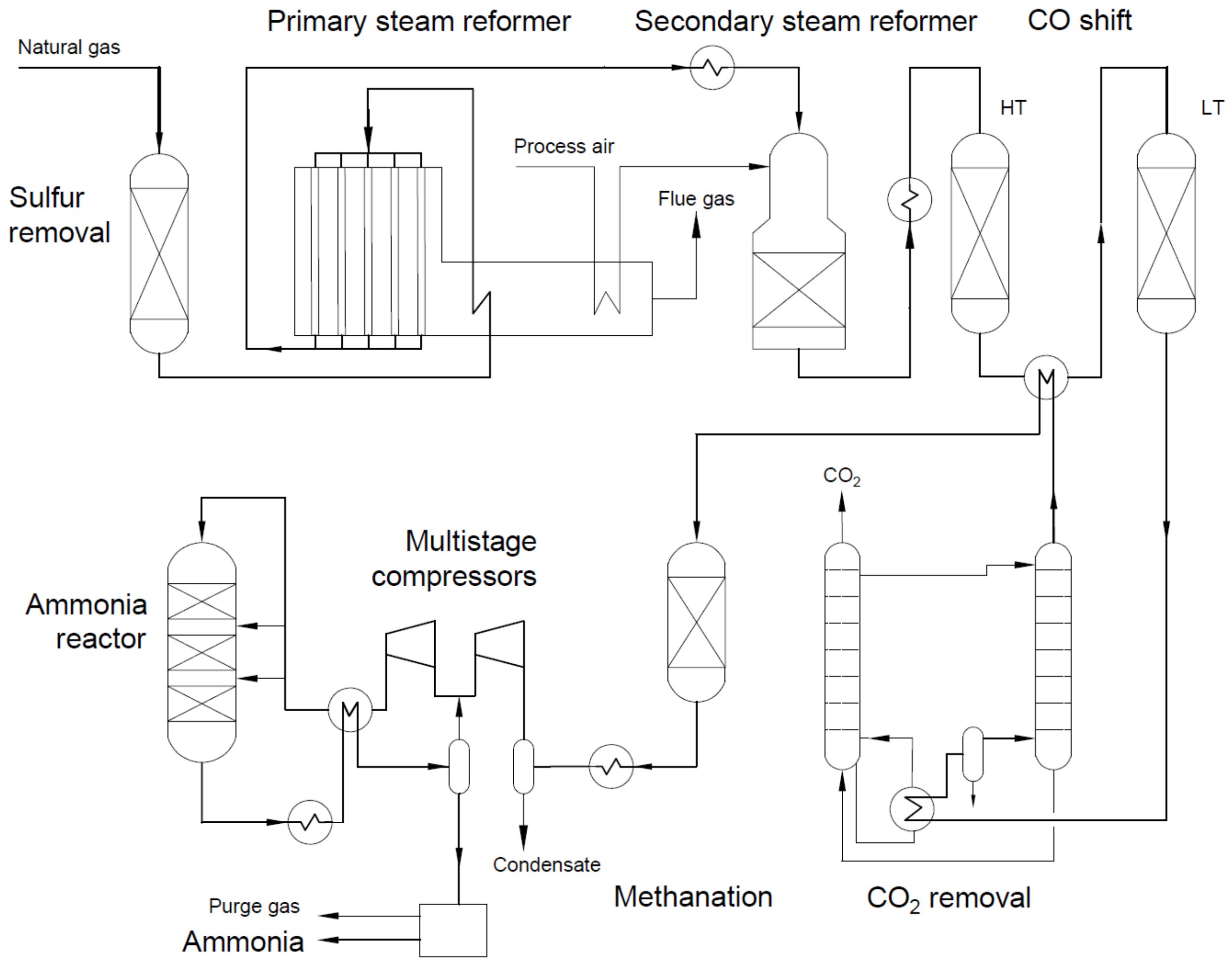


Figure 2.1: Typical ammonia process flow diagram.

2.1 Background

Ammonia is one of the most important products of the whole chemical industry. It plays a key role in the production of many compounds: today it is mainly used for fertilizers (up to 85% of ammonia production), but it represents a building block, for example, for plastic, pharmaceutical and explosives industry (Moulijn et al., 2001). World ammonia production started to increase exponentially in the first half of the last century, due to the improvement of catalysts technology that allows realizing feasible processes in terms of operating temperature and pressure (Moulijn et al., 2001). In fact, in 2010 it can count more than 160 million of tons per year of ammonia and a single plant can reach 4000 tons per day. Ammonia production is based on Haber-Bosh process, carrying out the following reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta_\mathrm{r} H_{298\mathrm{K}} = -91.44 kJ/mol$$

that is an exothermic reaction (Moulijn et al., 2001). From the stoichiometry of the reaction, it is more convenient operate with high pressure (100-275 bar). From the thermodynamics, the temperature should be as low as possible to maximize the conversion. However, the reaction is conducted typically between 675 K and 770 K, because at a lower temperature the kinetic would be too slow and the catalyst would not be activated (Moulijn et al., 2001).

Nitrogen and hydrogen are necessary for the reaction: the former is usually derived from air and it can be provided through a separate process step (cryogenic air separation) or by integrating processes (oxygen from air is consumed in other steps for the gas preparation); the latter typically derives from synthesis gas from natural gas or light hydrocarbons because of their high H/C ratio. Therefore, the ammonia process is generally preceded by synthesis gas production, described in the following section.

2.2 Synthesis gas section

Synthesis gas (or syngas) is a mixture mainly formed by hydrogen and carbon monoxide in a composition depending on the raw material employed. A mixture of hydrogen and nitrogen is used to be called syngas only within ammonia production. In syngas production, the choice of the raw material is based on an economical evaluation, its availability and syngas usage in downstream processes. In Figure 2.2 different processes are represented, based on the choice of the raw material. Syngas produced from natural gas is typically used because of the higher H/C ratio than coal and the higher purity of the raw syngas obtained.

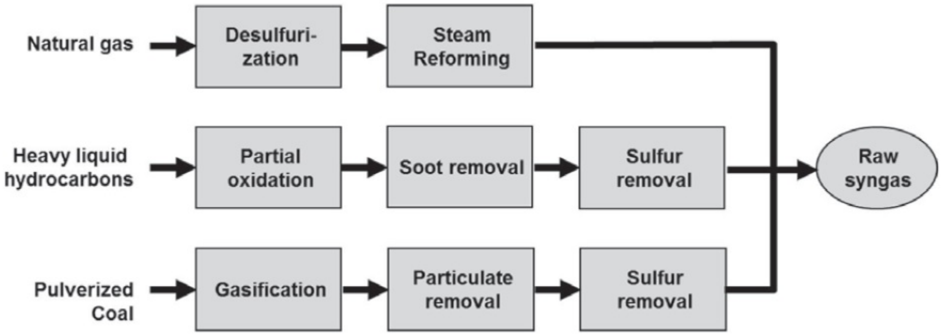


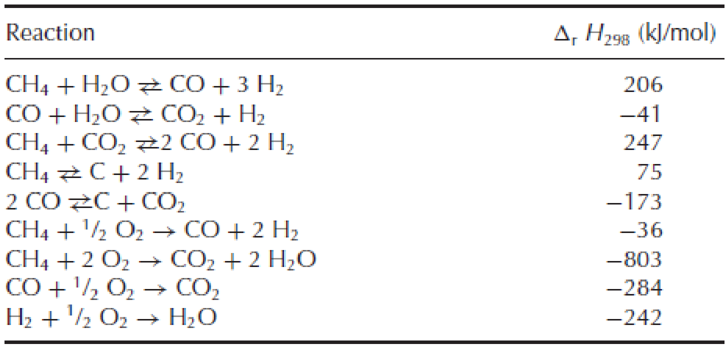
Figure 2.2: Different processes depending on the raw material selected (Moulijn et al., 2001).

2.2.1 Syngas production from natural gas in a typical ammonia facility

Natural gas is mainly formed by methane and some impurities, whose ratio depends on the provenience. Therefore, natural gas is treated before the steam reformer: in particular, a desulfurization process is applied (as shown in Figure 2.2. Sulfur represents a poison for metal catalysts of the downstream processes because it forms stable sulfides on the catalyst's surface hindering its activity (Ojha and Dhiman, 2010). This process is typically performed in two steps: the hydrodesulfurization, producing H_2S; the hydrogen sulfide adsorption (operating with zinc oxide at 570 K) where all the H_2S produced is removed (Moulijn et al., 2001).

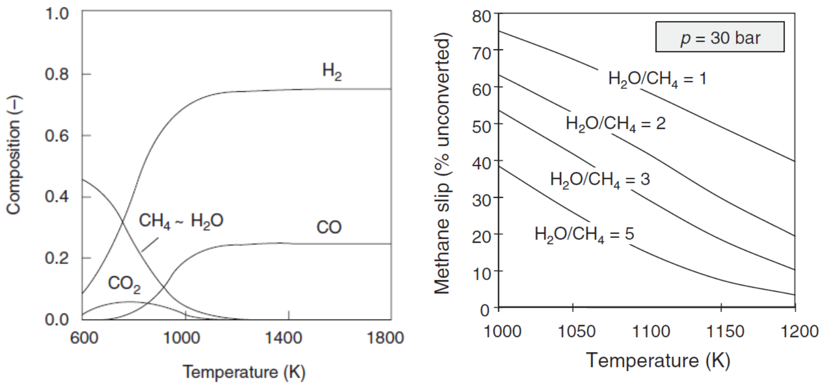
2.2.2 Steam reformer

The stream without sulfur is mixed with steam and preheated recovering heat form hot flue gases of the reformer. The temperature can reach 750-800 K and then the stream is sent to the reactor. Here the reactions reported in Table 2.1 take place (Moulijn et al., 2001). The steam cracking reaction (first one of the Table 2.1) is endothermic, so it is suggested to operate at high temperature and, from the stoichiometry of this reaction, it would be more convenient to operate at low pressure. Nevertheless, typical operating conditions are up to 30 bar and 1050-1200 K. High pressure is applied for economic reasons, it allows to save energy in downstream compressors and reducing the volume of the reactors. High temperature facilitates the H_2 and CO conversion (Figure 2.3(a)) and it is limited by a minimum temperature for activating the catalyst and a maximum due to the material mechanical properties (1200-1400 K). High temperature is not enough to succeed the steam cracking reaction because of the high stability of methane, so a catalyst is applied. The typical catalysts for this reaction are metal based, in particular they are Nickel based ($Ni/MgAl_2O_4$) due to its good catalytic activity and its relatively low cost. The



Reaction	$\Delta_r H_{298}$ (kJ/mol)
$CH_4 + H_2O \rightleftarrows CO + 3\,H_2$	206
$CO + H_2O \rightleftarrows CO_2 + H_2$	−41
$CH_4 + CO_2 \rightleftarrows 2\,CO + 2\,H_2$	247
$CH_4 \rightleftarrows C + 2\,H_2$	75
$2\,CO \rightleftarrows C + CO_2$	−173
$CH_4 + {}^1/_2\,O_2 \rightarrow CO + 2\,H_2$	−36
$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$	−803
$CO + {}^1/_2\,O_2 \rightarrow CO_2$	−284
$H_2 + {}^1/_2\,O_2 \rightarrow H_2O$	−242

Table 2.1: Reactions in the reformer (Moulijn et al., 2001).



(a) **(b)**

Figure 2.3: (a) Equilibrium gas compoisition at 1 bar for steam reforming of methane (H_2O/CH_4=1 mol/mol); (b) Methane slip as a function of temperature and H_2O/CH_4 ratio.(Moulijn et al., 2001)

catalyst is placed inside the tubes of the tubular reactor, where the reaction occurs. Heating is provided from the other side of the tubes by external burners. In this step, coke could be formed by methane decomposition ($CH_4 \rightleftharpoons C + 2\,H_2$) and by the Boudouard reaction ($2\,CO \rightleftharpoons C + CO_2$), supported by high temperature. The coke hinders the catalyst activity and could obstruct the tubes creating hot spots, but its formation can be limited by an excess of steam in the feed, respect to the stoichiometric quantity. In addition, steam excess reduces the methane slip (Figure 2.3(b)) produced by the process, that it usually has a great impact on the economy of the process.

Syngas for ammonia production needs a high percentage of H_2, but the outlet of steam reformer contains approximately only 50% of hydrogen. Methane, water, carbon dioxide and carbon monoxide are still present. This is because the conversion of natural gas is approximately 70%. In the next sections, the main steps to upgrade the syngas for ammonia process are rapidly summarized.

2.2.3 Conditioning of the syngas for ammonia production

After the steam reforming, other downstream processes are typically provided to achieve the desired composition of the syngas: a secondary reforming is provided to convert the methane slip from the reformer, a carbon monoxide shift step, a carbon dioxide removal and a methanation step (Moulijn et al., 2001).

In the second reforming step, after a slight cooling to 1000 K, an autothermal catalytic reactor, fed with steam reformer outlet and air, concludes the conversion of methane with an oxidation. The heating for steam reforming reaction is provided by the exothermic reaction of combustion between oxygen and methane unconverted. The oxygen of the air is consumed by the reaction and only the nitrogen remains in the stream process as an inert, supplying the quantity of N_2 to obtain the desired H_2/N_2 ratio at the end of the syngas synthesys. In this way, the quantity of nitrogen necessary for the ammonia synthesis is carried inside the process by air, more convenient instead of a cryogenic process.

The next step is removing CO and CO_2 from the stream process, also called syngas upgrading. Carbon monoxide is typically converted to carbon dioxide by the water-gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta_r H_{298\mathrm{K}} = -41 kJ/mol$$

The water-gas shift reaction increase the H_2/CO ratio. This reaction is quite exothermic and a high conversion of CO is achieved only at low temperature. However, the kinetic of the reaction is relatively slow, so this reaction is typically performed in two steps: high-temperature reactor (HT) with fast kinetic followed by a low-temperature reactor (LT) for high conversion of CO. The former operates between 640K and 710 K with an iron-oxide-based catalyst, the latter operates between 470 K and 510 K with a copper-based catalyst. In the LT reactor, a higher amount of catalyst than the quantity needed is placed in order to reduce shutdowns for substitution of the catalyst. After the water-gas shift reaction, the stream is cooled for removing unreacted water by condensation.

The carbon dioxide is mainly removed by Pressure Swing Adsorption (PSA). This step is provided by several parallel reactors divided into units. They interchange high and low pressure steps to adsorb impurities on the catalyst (high-pressure step) and regenerate it (low-pressure step). One unit could be formed by 4 or 5 reactors working in different phases at the same time. The phases of the single reactor are: adsorption CO_2 on the catalyst with high pressure (40 bar), depressurization (atmospheric pressure, carrying out the purified gas), counter-current depressurization (filling with some of the purified gas in order to desorb impurities), purge with purified gas, repressurization with feed gas from water-gas shift reaction.

Alternatively, it is common to remove carbon dioxide through an absorption process with alkanolammine, for example monoethanolamine (MEA) or diethanolamine (DEA). This operation is performed in two columns where one of them absorb CO_2 and the other one regenerates the solvent stripping CO_2. Then the solvent is recirculated to the absorption column and the CO_2 could be stored or used in other downstream processes (like urea production).

The last step of syngas conditioning is methanation: the carbon monoxide and carbon dioxide still present are converted into methane. This reaction is performed in an adiabatic reactor adding hydrogen . This step is necessary because both compounds represent a poison for ammonia catalyst. Moreover, the methane produced in this step could be used for the others upstream processes. The main reactions, carried out at approximately 600 K, are the reverse of the steam reforming process:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta_r H_{298K} = -206 kJ/mol$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \Delta_r H_{298K} = -206 kJ/mol$$

These reactions are highly exothermical, but the quantity of carbon dioxide and monoxide is relatively small. The heat generated from this process is usually recovered for the production of steam and hot water. The water produced from the reaction is condensed at 300 K and removed while the hydrogen-nitrogen mixture is sent the to the ammonia synthesis reactor.

2.3 Ammonia synthesis

Syngas for the ammonia synthesis already has the right composition of N_2 and H_2. This stream is sent to a multistage centrifugal compressor (where some interstages cooling are provided), that raises the pressure up to 300 bar, and then to the ammonia reactor. Here an exothermal reaction occurs and low temperature is preferred for high conversion. Because of the slow reaction kinetic, temperature up to 770 K and a catalyst (iron-based catalyst) are applied (Moulijn et al., 2001). Despite the hard operation conditions, the conversion of the reagents is not complete anyway (Figure 2.4). The conversion of hydrogen in the reactor is up to 30%. Also, from Figure 2.4 the effect of rising pressure into the reactor over the conversion is clear : the higher is the pressure, the more is the conversion, due to the decreasing number of moles during the reaction. Nowadays, new catalyst are applied instead of iron-based catalyst, in order to reduce the operative pressure and increase the efficiency of the reaction. These catalysts are based on iron-titanium metals, ruthenium alkali metals (Ojha and Dhiman, 2010).

The unconverted gas from the outlet is easily separated from the ammonia through refrigeration and expansion. One part of it is recirculated to the reactor and another part is purged, while the pure ammonia condensed (more than 99%) is ready for stocking or for other downstream processes. In fact, it is very common to find in the same plant other production processes like urea, nitric acid, ammonium nitrate and other processes that use ammonia as a raw material.

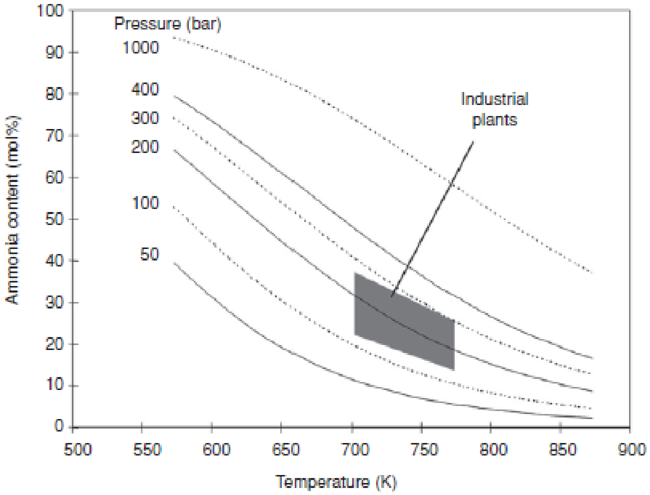
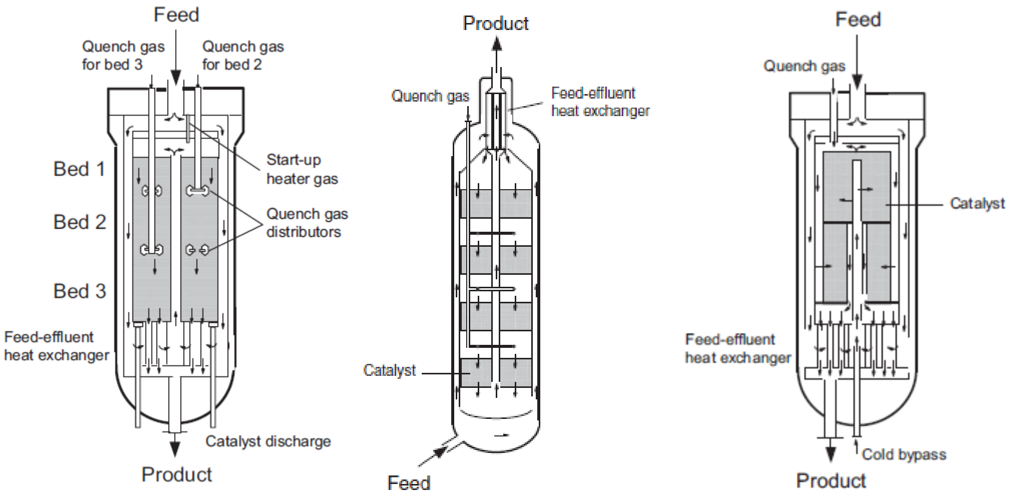


Figure 2.4: Operability region of ammonia processes: ammonia content in equilibrium gas (H_2/N_2=3 mol/mol) (Moulijn et al., 2001).

2.3.1 Ammonia reactors

To maximize the rate of reaction, it is possible to carry out the reaction along the maximum rate curve (Moulijn et al., 2001). For this aim, reactors with several cooling stages are applied. In particular, two different ways for cooling are applied to the reactors: direct cooling (quench reactors) and indirect cooling (with heat exchangers). In the former (for example: ICI reactor, Figure 2.5(a) and the Kellog reactor, Figure 2.5(b)), cooling is provided feeding with cold feed or high-pressure steam between the different catalytic beds. For the latter (for example, Haldor Topsøe reactor, Figure 2.5(c)) cooling is performed with one heat exchanger at the bottom of the reactor and/or heat exchangers between the catalytic beds (Moulijn et al., 2001). For all the three type of reactors, the feed introduced is preheated flowing along the reactor between the shell and the catalyst container. Then, the feed is preheated with hot product stream and finally is sent to the catalytic section. In particular, ICI and Kellogg reactors have three and four catalytic beds respectively and quench gas distributors are placed in the gap between beds.
The Haldor Topsøe reactor has two annular catalytic bed: the feed gas exits from a central pipe and flows radially through the catalyst, then it crosses the second catalytic bed. This stream goes to a heat exchanger where it is cooled down and the heat is recovered for preheating the feed gas. Then, one part is recycled to the inner pipe and the other part leaves the reactor (Moulijn et al.,



(a) **(b)** **(c)**

Figure 2.5: (a). ICI quench reactor; (b). Kellogg quench reactor, axial flow; (c). Haldor Topsøe reactor, radial flow. (Moulijn et al., 2001)

2001).

Nowadays, the indirect cooling reactors are preferred to quench reactors because the heat recovery takes place where the temperature is higher inside the reactor, that is the outlet. A drawback of the indirect cooling system is the cost, that is higher than quench reactor because of the heat exchangers (Moulijn et al., 2001).

Other important ammonia reactor parameters are the flow type and the catalyst particle size: the former can be axial, radial or counter flow (Moulijn et al., 2001). For example, Kellogg reactor represented in Figure 2.5 (b) is an axial flow reactor, while Halder Topsøe reactor (Figure 2.5 (c)) is a radial flow reactor. The latter should be as small as possible for increasing active surface for the reaction. Flow type and dimension of the catalyst particles are parameters that influence the pressure drop inside the reactor. In order to reduce the size of the catalyst particles and have feasible pressure drops, a radial flow reactor is suggested or an axial flow reactor with a larger cross sectional area.

2.3.2 Hydrogen recovery

Hydrogen recovery in an ammonia plant is an important step for the economy of the process: for example, because of the low conversion during the synthesis loop, a consistent quantity of hydrogen is still present in the purge gas. Three different approaches are typically used (Moulijn et al., 2001) (Ojha and Dhiman, 2010): adsorption and desorption of acid compounds on a catalytic bed, made by pressure swing adsorption (PSA) or a temperature swing adsorption (TSA) and membrane gas separation; cryogenic separation.

Membrane separation is performed by a pressure difference, that is the driving force of the process. This process is also easy to carry out and it does not require an additional phase for the separation, but its performances are strongly influenced by fouling and aging of the membrane.

The cryogenic process separates hydrogen condensing all the other compounds, as nitrogen, methane and argon.

Pure hydrogen stream recovered is sent to the synthesis gas compressor if the membrane process is applied, because of the pressure drop due to the membrane. Otherwise, if the cryogenic technology is applied, the purified stream is fed directly to the ammonia synthesis reactor. Other different approaches can be used, but actually, these three processes are the most suitable for the ammonia process to obtain a high purity of hydrogen. After an economic evaluation, it is possible to establish which one is the most convenient.

Chapter 3

Safety issues on the ammonia plant

3.1 Concerns about ammonia plant

The ammonia production is the first large-scale process in history performed with high pressure and temperature: since 1910, a feasible and reliable process was realized (Moulijn et al., 2001). Despite ammonia technology is a consolidated process, typical and atypical accidents are registered. Nowadays, a great part of ammonia plants is single-trained plants. It means lower investment cost because all the apparatuses are single units, but a failure in a unit can lead to the plant shutdown (Moulijn et al., 2001). Starting from the synthesis gas to ammonia synthesis, some of the most common problems in the apparatuses involved are presented. Typically, steam reformer and ammonia synthesis reactor are most affected in failures, due to their operational conditions and the substances treated (Ojha and Dhiman, 2010).

3.1.1 Steam reformer

This reactor operates at high temperature (wall temperature 1200-1400 K) to carry out the main endothermic reactions. Many accidents are related to unwanted overheating condition and the most affected parts are the reformer tubes. Overheating leads to degradation of mechanical properties of the steel and it can change its micro-structure, causing the tubes collapse (Ojha and Dhiman, 2010). It also accelerates aging process reducing design life of the material.

Partial blockage of burner tips can lead to a direct contact between flame and tubes and then their failure. The unwanted increase of temperature can be also developed by the chocking of the tube: damaged catalyst can accumulates and chocks the tube, where temperature and pressure increase. In this case, creep rupture of the tubes can occur and it usually causes a longitudinal crack along the tube. The worst final scenario could be the explosion of the reformer.

The same final scenario could be obtained by stress corrosion cracking. It occurs especially on the inside part of the tube, where hydrogen and acid gas flows. It could be aggravated by improper welding procedures applied, for instance, in the proximity of inlet or outlet flanges (Bhaumik et al., 2002). After weldings, the steel of the tube involved is more sensitive and the stress corrosion cracking can occur easier. Improper weldings can also produce defects (like pinholes) in the steel, those are starting points for cracks leading to the tube collapse.

Also, pigtails are critical parts: they are short and flexible pipes that allow the expansion of tubes and this movement increases stress in the tube material.

3.1.2 Secondary reformer

Here, the unconverted methane is burned with air oxygen and the other steam reforming reactions are carried out. Inside the reactor, carbonaceous gases are present, so the metal dust phenomena can occur (Gunawardana et al., 2012). This is a degradation of the metal surface where it forms metastable species with carbon composts that leave the surface as a dust. So, the surface becomes rapidly pitted. This phenomenon is typically observed in the range temperature 450°C to 900°C. It is detected by presence of metal carbides and magnetic corrosion product of graphite and other oxides on the pitted surface. To avoid metal dusting, a proper protective surface is provided: it was observed that a film of Cr_2O_3 applied on Alloy 800 can reduce this phenomenon (Holland and Bruyn, 1996).

The overheating leads to failure due to creep in this reactor too. Increasing temperature is mostly determined by deposits due to corrosion (as Fe_2O_3) that forms a thick deposit layer.

3.1.3 CO_2 removal

Sour gas removal can cause corrosion problems for examples in the condenser, cooler and reboiler. In fact, in some processes (like Benfield process) some corrosion inhibitors are added to the process stream (Ojha and Dhiman, 2010). There are some causes that enhance corrosion phenomenon, like a wrong concentration of anodic inhibitor, the presence of hydrocarbon, the formation of sulphide layer, galvanic interactions and, in case of absorption with alkanolamine, malfunctioning of the column (like loading, frothing and foaming).

3.1.4 Methanation

In this process, all the CO_2 and CO of the process stream are removed feeding with hydrogen. Two main highly exothermic reactions are carried out:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$
$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

Because of that, this reactor could be considered as the most critical in term of safety. It could happen that a disturbance in the water-gas shift reaction can lead to an increasing of CO, leading to a temperature runaway and collapse of the reactor (Alhabdan and Elnashaie, 1995). For example, the water-gas shift catalyst can be hindered due to aging and it can not convert all the CO in CO_2. But carbon monoxide is not well carried away by CO_2 removal, so it goes to the methanator increasing its temperature.

Another critical aspect is the presence of hydrogen that, due to the high temperature, can cause an High Temperature Hydrogen Attack (HTHA): hydrogen forms methane reacting with unstable carbides in the steel (Ojha and Dhiman, 2010). This phenomenon can cause a loss of mechanical properties that can lead to a crack on the reactor. To reduce the risk of failure due to HTHA, additional protection layer are provided inside the vessel.

3.1.5 Compression stage

Compressors working with lubrificant oil at relatively high temperature and high pressure are typically used. The oil drawbacks are the needs of frequent maintenance (and so more frequent shut down), it can lead to a fire and it can contaminate the process stream. Safety of compressor stage is significantly improved by using Dry Gas Seal (DGS) (Krivshich et al., 2003). This is a seal where there is a gap between the rotating part and the stationary part when the compressor is operating. The rotation generates a fluid-dynamic lifting force that brings on the separation of the two surfaces. This seal allows the compressor to work without lubrication oil. Because of that, energy saving is improved because of the low friction between rotor and stator and it simplify the servicing system.

3.1.6 Synthesis loop

During ammonia synthesis, high pressure and temperature are applied. Moreover, the presence of hydrogen can cause an embrittlement of the vessel and all the other apparatuses connected (Ojha and Dhiman, 2010). This phenomenon is strongly promoted by high temperature. This is why the cold feed flows first between vessel and catalytic container of the ammonia reactor.

Wrong welding procedure can also produce defects like pinholes that, due to high pressure, can be the starting point for more severe cracks. In fact, areas near nozzles and flanges are the most affected by this two effects (Ojha and Dhiman, 2010). So, the consequences can be prevented by a correct welding procedure, inspections and an hydraulic test before the installation.

3.1.7 Ammonia storage

Ammonia is typically liquefied and stocked at ambient pressure at -33°C in a double wall vessel with capacity of tons. In some facilities, a small quantity of ammonia is stocked in spherical pressure vessel at ambient temperature. Those vessels can be affected by brittle fracture, especially for aged vessels (Ojha and Dhiman, 2010). This fact can cause the catastrophic rupture of the vessel, so many inspections are required and they should be more frequently for old vessels. For examples, acoustic emission test or a magnetic particles inspection can be performed. Both methods are non destructive. In particular, the latter is applied to detect Stress Corrosion Cracking (SCC). SCC derives from a long duration of stress condition for the material: for examples, an uneven settlement can be affected by SCC after a long period. Moreover, this phenomenon can be supported by welding defects. So, a risk based inspection becomes important to define the probability of failure and the maximum filling level of the vessel.

3.2 Creation of a database

The goal of this section is to show all the steps followed to obtain a unique database about incident, accident and near misses occurred in the ammonia plant. So, a data mining process was performed. The first step is data collection. 9 different sources were consulted and the results obtained are discussed. Then, data preprocessing was applied. All the information collected are uniformed using a common list of keywords to identify, for example, in which section of the plant the accident occurred, the substances involved, which are the consequences, etc. All these information were collected under a general database and a discussion of the results is performed.
To better understand the nature of the general database, it is necessary to define the keywords employed, to explain how each source consulted works and the approximations applied to unify all of these different information.

3.2.1 Data mining: definition

Data mining is a process where the data are extracted, elaborated and analyzed. The results are discussed in order to achieve different goals. For instance, it is possible to apply this procedure to transform raw data in useful information in order to find relationship between variables, useful patterns, models and trends (Talia et al., 2016). Two different ways of data mining can be performed: descriptive and predictive data mining. The former task, according to He (2015), is to organize and present data in a concise, informative and discriminate form. In this work, this kind of analysis is performed. The latter focuses on the developing models to make predictions or taking decisions. These models are typically based on data input (Talia et al., 2016).
In any case, data mining is performed following different steps: it starts with the data collection, data preprocessing and concludes with data analysis.

3.2.2 Data collection

This is the first step of data mining. It consists of a collection of as many data as possible. However, good evaluation of the quality and coherence of data with the goals has to be performed. As shown by He (2015), selection of the ”relevant data” is a key point of data analysis. In this work, all the incidents occurred in an ammonia plant or the incidents occurred in plants employing the same technology were accounted.
In the following sections, nine data sources have been consulted and a data selection according to the goals of the work has been performed. All of these sources are presented and a brief discussion of the accounted cases is carried out.

3.2.2.1 Ammonia plant safety and related facility, articles by AIChE

This collection of technical articles was made by American Institute of Chemical Engineers (AIChE, 2001). It consist of 42 volumes collecting a series of papers about new process development, maintenance and troubleshooting, revamping and upgrading of older ammonia facilities. Also, works reporting past accidents can be found. The goal of the collection is to study all the circumstances that led to a scenario or, for a great part of the cases represented, to a near miss. Then, the authors propose solutions as improving the design of some apparatuses, suggesting a different material or redefining organizational factors.

The most representative and significant cases on the ammonia plant were found in eight volumes. In particular, 31 cases contained from the volume 35 to the volume 42 were analyzed. All of these cases are described through detailed technical reports made by researchers and/or companies. So, the keywords listed in the Table 3.2(a) were assigned for describing each case and then they were added to the general database.

Most of the incidents accounted in this collection are caused by mechanical failure (almost 60%). This is because these books are technical manuals. In fact, there are several studies on the mechanical properties of the materials and how they change due to the interactions with the process stream. For example, High Temperature Hydrogen Attack (HTHA) and Stress Corrosion Cracking (SCC) failures are largely discussed.

Another characteristic of this collection is the higher percentage of accidents in the ammonia reactor (up to 45%) respect to the other sources (for example, ARIA: 27%; MHIDAS: 17%). This is probably because the collection is completely focused on the ammonia plant and it is quite difficult to find incidents about ammonia reactors in literature. Moreover, the ammonia reactor is very sensitive to mechanical failure due to substances contained in the process stream (as hydrogen). So, all of these incidents are very interesting for technical manuals like these ones.

3.2.2.2 ARIA Database

The ARIA (Analysis, Research and information on Accidents) database is managed and administrated by the BARPI (Bureau for Analysis of Industrial Risk and Pollution), in collaboration with the French Minister of the Environment and the General Directorate for Risk Prevention. This database is free and it is possible to consult it on its web page. It collects a series of industrial and technological accidents from all over the world, containing over 46.000 reports about accidents and incidents. An average of 1.200 new events per year are added (ARIA Database (access date: october, 2017)).

The Database is updated by engineers and technicians. In fact, it is possible to find detailed reports describing the main circumstances, outcomes, accident causes, how they managed the incident and the actions taken to avoid it. Nevertheless, they underline that the cases repre-

sented are not exhaustive, but the only aim is to make risk prevention and mitigation.
Looking for incidents occurred in an ammonia plant, 16 inherent cases were found. Some of these cases were integrated with information from other databases. All these cases were accounted as reports. So, an interpretative work during the data preprocessing phase was done.

3.2.2.3 eMARS

The eMARS database is an accident and near miss database, open to the public, established by the EU's Seveso Directive 82/501/EEC in 1982. The name is an acronym and it stands for "Major Accident Reporting System": as a matter of facts it was previously called "MARS", then was later renamed "eMARS" after going online (MAHB, 2017).
EU, EEA, OECD and UNECE countries (under the TEIA Convention) provide reports to the Major Accident Hazards Bureau (MAHB) of the European Commission's Joint Research Center (JRC), about chemical accidents and near misses. These data are included into the eMARS database directly from the recognized authority reporting the event. The reports are compulsory for EU Member States when a major accident - as defined by Annex VI of the Seveso III Directive (201218/EU) - occurs in a Seveso establishment. For all the other countries previous listed, reporting the event is voluntary (MAHB, 2017).
The goal of the database is to collect all possible information about accidents, near misses and so on, and sharing them with everyone, in order to learn from these information and to use them as an instrument to prevent future dangerous events. To do so, it has been decided not to show company names and location. This way, reporting the event in an accurate and detailed way is supported (the company will not be judged from anyone) and the focus of the reader goes completely on the accident information and not on the company or on the country associated with it.

3.2.2.4 Japanese Failure Knowledge Database

The Japanese Failure Knowledge Database (JFKD) is an accident and failure database, whose aim is to make companies learn from past events in order to prevent future accidents and to improve reliability and safety of technology in society. The database started to be provided on the 23rd of March 2005 by the Japan Science and Technology Agency (JST) and it is managed by the Hatamura Institute for the Advancement of Technology (JFS, 2017).
Accidents and failures are divided in sixteen categories: selecting one of these categories it is possible to consult the corresponding accidents (JST, 2017).

3.2.2.5 Major accidents from *Lees' Loss Prevention in the Process Industries*

Another source of relevant accidents, from which some events have been considered and added to the final database, is the "Lees' Loss Prevention in the Process Industries" book (Lees, 2005). Loss prevention approach is a wide field and it is rapidly developing. The author of the book felt the need to integrate the basic elements of the subject in a textbook, in order to give assistance to the direct interested, especially engineers. That is how and why "Lees' Loss Prevention in the Process Industries" has been written, as an attempt to meet this need. The book is divided in three different volumes. Volume 3 contains a series of appendices reporting reports or information about past accidents. In Appendix 1, table 1.2, some major accidents in process industries are listed in chronological order: from 1911 to 27.04.1995.

3.2.2.6 MHIDAS (Major Hazard Incident Data Service)

In 1986, the Major Hazard Assessment Unit of the United Kingdom Health and Safety Executive (HSE) launched the Major Hazard Incident Data Service (MHIDAS). The database was maintained by AEA Technology. It is based on public domain information sources. In fact, a drawback of this source is the variability of quality and accuracy of reports (A.B.Harding, 1997). This database had been updated until mid 1990's (Hare et al., 2009).

All the cases presented in the database are accounted through keywords (mostly presented in Table 3.2(a)) and a very short description of the accident could be reported. The search was firstly based on looking for accidents occurred in an ammonia plant and then on the main sections of the process. Here are listed only the keywords used for the search that they have produced acceptable results:

- Ammonia plant;
- Ammonia synthesis;
- H_2S;
- Syngas production.

15 cases are identified as relevant. Three of these cases were integrated with information from other databases. For other three incidents, it is unknown if they occurred in an ammonia plant, but the same technology was employed. For instance, in October 1981 in Czechoslovakia, a case of a catastrophic failure in a synthesis gas reactor that led to a severe flash fire was accounted, even if it is not specified that the accident occurred in an ammonia plant.

It is worth mentioning that 6 over 15 cases found are incomplete for general and specific causes, confirming that the data quality of this database is not always guaranteed.

3.2.2.7 National Response Center (NRC) database

The National Response Center (NRC) is one of the first "layers" of the National Response System (NRS). NRS is a multi-layered system: every layer has a function in order to respond effectively to hazardous substance releases. When a release occurs, the organization responsible for the release or spill is required by law to notify the NRC. Its function is to collect data in a national database and to notify the On-Scene Coordinator, which is responsible to evaluate and coordinate the response needed (EPA, 2017).
NRC is managed by United States Coast Guard (USCG). Its database is composed by annual reports available on-line, from 1990, and it is currently updated to 2017 (USCG, 2017).

3.2.2.8 Fatality and Catastrophe Investigation Summaries - OSHA

"Fatality and Catastrophe investigation Summaries" is an accident database managed by "Occupational Safety and Health Administration" (OSHA). OSHA is one of the agencies of the United States Department of Labor (DOL). Its role is to guarantee safety and health to wokers in the workplace, through training, outreach, education, assistance and by setting and enforcing standards (OSHA, 2017).
OSHA's database is a collection of accident summaries developed after an inspection, performed by an OSHA's ispector, in response to a fatality or a catastrophe. It is possible to find summaries about accidents from 1984 to one year earlier than today's date. As a matter of facts, one year is necessary to compute all the steps needed to post online the summary.

3.2.2.9 ZEMA

ZEMA stands for "Zentralen Melde-und Auswertestelle für Störfälle und Störungen in verfahrenstechnischen Anlagen" (Infosis, 2017) which means "Central Reporting and Evaluation Station for Accidents and Faults in Process Plants". It is the german accident database, containing, mostly, events occurred in the german territory. It is managed by "Umweltbundesamt" (UBA), the main environmental protection agency in Germany (UBA, 2017). It has been instituted in 1993 to collect, evaluate and post all the events reportable to the "Störfall-Verordnung (12. BImSchV)" - the 12th Federal Immission Control Ordinance. ZEMA aims for being an important strating point for the development of technology and safety, making companies learn from past mistakes, in order to do not repeat them again. Since 1999, with the arrival of internet, all the infomation included in the database had been open to the public. Nowadays, it is possible to count more than 570 national reports (Infosis, 2017).
Data are reported in "Jahresberichte", which are annual reports. On ZEMA website, reports from 1995 to 2014 are currently recorded. The last one is a biennal report: 2012-2014 (UBA, 2017). In "Anhang 1" - Appendix 1 - of these reports, a list of accidents of the corrisponding year is in-

cluded, followed by detailed reports for each accident, in chronological order.

3.2.3 Data preprocessing

The aim of this step is to prepare data for the data mining analysis. As presented in the previous sections, the accidents found in literature or in databases were reported in different ways and some of them are incomplete. So, all the accidents were accounted following a defined common structure, that is described in the keywords section. Then, according to He (2015), a data cleaning and integration was applied. All the incomplete incidents were filled integrating information from other databases or applying some approximations listed in Section 3.2.3.2.

3.2.3.1 Keywords

All the sources contain information reported in different ways. For example, some database describes information through reports, brief summary or using their own keywords. So, to create a unique database, a list of common words to use for describing each incident is defined. All the cases found have to be based on this list.
First of all, it has to be establish which aspects of a case have to be presented. It was defined that the general database has to report the following fields: date, location,substances involved and their quantity, type of event (release, fire, explosion), origin, general causes, specific causes, injured, killed, damage (material) and the section of the plant involved. In Table 3.2(a), an explanation of these main fields and all the keywords applied in databases can be found. The keywords employed are taken from MHIDAS (Major Hazard Incident Data Service) database, that it has already a proper organization of keywords with a brief description. Moreover, new keywords are added to represent some aspects that MHIDAS did not account. They are listed and defined in Table 3.2(a). For instance, sections of the process where the incident occurred are reported to identify the most critical section.

MAIN FIELD	KEYWORDS	DESCRIPTION
Date		Date of the accident.
Location		The country where the accident took place.
Substance	AMMONIA ARSENIC OXIDE CATALYST FUEL HOT AIR	Substance involved.

MAIN FIELD	KEYWORDS	DESCRIPTION
	HYDROGEN	
	HYDROGEN SULFIDE	
	MDEA	
	MEA	
	NAPHTA	
	NATURAL GAS	
	NITROGEN	
	OIL	
	OXYGEN	
	STEAM	
	SULFUR DIOXIDE	
	SYNGAS	
	WATER	
Quantity		Quantity of substances involved. (kg)
Event	RELEASE	A liquid or gas leakage.
	FIRE	Including pool fire, jet fire and flash fire.
	EXPLOSION	Including VCE.
Origin - General		General origin of the incident.
	PROCESS	The incident is originated in items of process plant or in an area of process plant.
	STORAGE	The incident originated in items/area of storage plant.
Origin - Specific		Specific origin of the incident.
	FIREDEQUIP	Fired process equipment, including furnaces, incinerators, stacks, chimneys.
	HEATXCHANG	Heat exchangers, including shell and tube, plate exchangers, evaporators, condensers, boilers, reboilers.
	HOSE	Hoses and other similar loading/unloading connections.

MAIN FIELD	KEYWORDS	DESCRIPTION
	MACDRIVE	Process machinery drives, including electric motors, engines, turbines.
	PIPEWORK	On-plant pipes and associated valves, joints.
	PVESSEL	Pressurised storage vessels.
	PUMP	Any type of pump, compressor, ejector, fan.
	PSVESSEL	Process vessels, including items such as centrifuges, towers, columns, dryers, distillation, absorption, filtration, cyclones, ion-exchange, crystallizer equipment, etc.
General causes		General cause of the incident.
	EXTERNAL	External events.
	HUMAN	Human factor.
	INSTRUMENT	Instrument failure.
	MECHANICAL	Mechanical failure.
	PROCOND	Upset process conditions.
Specific causes		Specific cause of the incident.
	BRITTLE	Brittle failure.
	COMPAIR	Compressed air or nitrogen.
	CONSTRUCT	Construction error.
	CONTROL	Controller error/failure.
	CORRODE	Corrosion failure.
	DESIGN	Design error.
	ELECTRIC	Electricity (for example, an outage).
	EXTNLFIRE	External fire.
	FLANGCOUPL	Leaking coupling or flange.
	GENERAL	General management error.
	GENERALOP	General operational error .
	GLANDSEAL	Leaking gland or seal.
	INCOMPAT	Use of incompatible material.
	INTNLFIRE	Internal fire.
	MAINTAIN	General maintenance.

MAIN FIELD	KEYWORDS	DESCRIPTION
	METALLURG	Other metallurgical failure.
	OVERHEAT	Overheating.
	OVERPRES	Overpressure.
	VALVE	Leaking or passing valve.
	WELDFAIL	Weld failure.
Injured, Killed, Damage		People injured, people dead and amount of material damage.
Section*	ALL*	If the incident involves all the plant (for example, an outage).
	AMMONIA SYNTHESIS*	One or more incidents occurred in the ammonia synthesis loop, including the reactors (as ammonia reactor), all the separator vessels or all the mechanical devices operating in this section.
	CO2 REMOVAL*	One or more incident occurred in one or more vessels for the CO2 and CO separation or in mechanical devices operating in these sections.
	DESULFURIZATION	One or more incidents occurred in the hydrogen sulfide removal section.
	REFORMING*	One or more incidents occurred in the primary reforming or secondary reforming or in mechanical devices operating in these sections.
	STORAGE*	One or more incidents occurred in the reservoir for stoking products or raw material or during the transfer.

Table 3.1: fields employed in MHIDAS database to describe events (MHIDAS (2000)). (*) These fields are not from MHIDAS and they have been added in the databases.

3.2.3.2 Approximations and interpretative work

In the previous section, a way to report information in the same format was discussed. But sometimes, the insufficient availability of the information leads to make approximation reporting what happened. Some databases are updated by operators and personnel that sometimes don't have sufficient knowledge to fill a detailed report. At least, sometimes, they don't know which information is more relevant and in which way they have to report it. Because of that, companies are trying to focus on a better formation of the personnel involved in writing reports, in order to have more detailed ones. For instance, during a workshop, Yara International ASA said that they are teaching it through a sort of "reverse engineering approach". In other words, they are teaching to personnel to report what they would need to know in the future if they will have to read it.

Another problem faced reading reports is the subjectivity of the information. There are two different ways where the subjectivity plays: information accounted by the operators, that they have already assigned keywords; to assign keywords reading reports. About the latter, many detailed reports have been found and an interpretative work has been done. For examples, a lot of causes contribute to the development of an accident. Sometimes, address the cause of an incident to only one factor was not possible. Because of that, more keywords were assigned for each main fields. Moreover, a general rule was applied to classify the general causes of the incident: the main cause declared in the report has to correspond to the general cause; if other obvious general causes were detected, more fields can be assigned. For examples, there are some cases where a mechanical failure could be generated by other factors, as maintenance or operational errors. The incident was classified as a technical failure (so, General cause: Mechanical), and, only if the organizational factor is clearly involved, the "Human" keyword was added as a generic cause (e.g., the explosion of a pressure vessel in Chicago, USA in 1981) .

In some sources analyzed, the number of injured and dead was not always specified. In these cases, three options were distinguished:

1. the number of injured is known and the number of dead is unknown;
2. the number of injured is unknown and the number of dead is known.
3. the number of injured is unknown and the number of dead is unknown;

In the first option, it is possible to suppose that if the number of dead is not reported, this is because they did not occur. This is because the dead is more severe than an injury. In the second case, the number of injured has been considered as zero. This is an approximation because the number of injured is obviously considered of minor severity than death and the reporters could had been omitted. The last case was classified as no dead and no injured. This is because it is reasonable to suppose that an injury or a death can be considered significant for every reporter and if nothing is written is because they did not occur.

3.2.4 General database and results

In the previous sections, how to report accidents following a single format and the limits faced are presented. All the results are collected in a unique database containing 140 reported accidents covering a time period from 1959 to 2016. In Appendix B, the outcome of this operation is reported. This information comes from nine sources and their weight contribution on the general database is shown in Figure 3.1. Here it is possible to figure out that the National Response Center (NRC) and the ”Ammonia plant safety and related facilities” (APSRF) collection are the most influencing sources. Both sources account a lot of cases without injured and dead (100% of known cases in NRC and up to 94% in the APSRF, instead of 33% found in known cases in MHIDAS). Another common characteristic is the high percentage of mechanical failure as a general cause (78% for known cases in NRC and 60% for APSRF, e.g., comparing to 25% of known cases found in ARIA database). The drawback of the NRC database is the lack of information: a high percentage of cases with unknown main fields were found. For examples, a general cause for the 65% of NRC accidents is not assigned, increasing up to 87% for the specific causes.
Analyzing the results of the general database, it is possible to find again the main aspects of these two databases. For examples, 60% of the all the incidents are caused by mechanical failure and the percentage of no injured and dead is up to 73%.

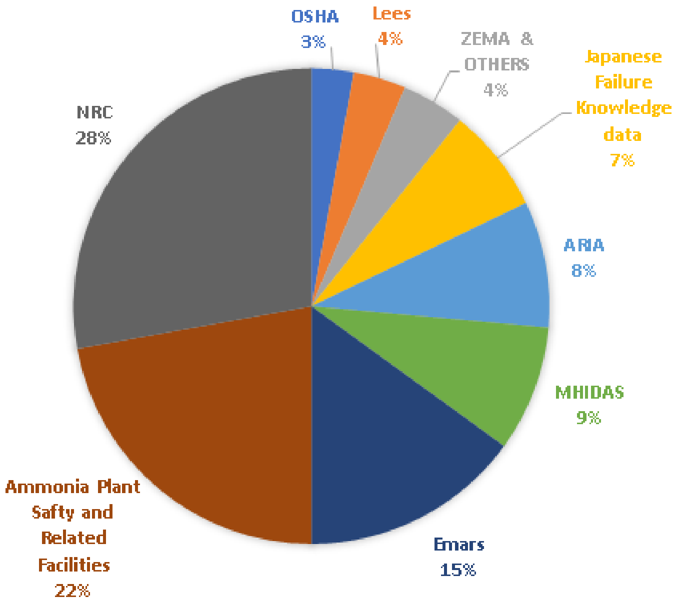


Figure 3.1: Contribution of the 9 sources analyzed: percentage of cases found per database over all cases found

In general, the main conclusions from an analysis of the unique database are:

- The substances mostly involved in incidents is ammonia (48% of known cases). Its hazard properties are related to its toxicity: it is very corrosive and irritating for humans. In fact it could be fatal if inhaled (CAMEO chemicals (access date: october, 2017)). Despite its low molecular weight, ammonia vapors can form a heavy cloud, especially if the cloud is formed by flashing of cold ammonia. It leads to a higher concentration to the ground (Ojha and Dhiman, 2010). As shown in the previous section, under certain conditions, ammonia can corrode few specific steels leading to an embrittlement (Ojha and Dhiman, 2010).

  The other two most involved substances in accidents are syngas (32% of known cases) and hydrogen (11% of known cases). The syngas hazards are mainly related to the hydrogen hazards, that is extremely flammable and explosive if mixed with air (CAMEO chemicals (access date: october, 2017)). As shown in section 3.1.6, also hydrogen can interact with materials leading to the embrittlement. For example, where a high hydrogen concentration and hot zones are present, the HTHA can occur (Ojha and Dhiman, 2010).

- As shown in Figure 3.2(a), the most frequent general cause of incident is a mechanical error (over 60% of incidents with known general cause) and the second is human error (up to 38% of incidents with known general cause). All the substances involved in the process interact with materials reducing their mechanical properties (for example, hydrogen and sour gas). But also problems as a lack/totally missing maintenance led to incidents (Specific cause: Maintenance, up to 25%). As shown in Figure 3.2(b) most common problems linked to human error are wrong operating procedure applied (up to 17%) and wrong welding procedure (up to 9%).

- The most common top event registered is the release: 77% of known cases were found, with only the 11% of unknown cases. In fact, for the 11% of cases with a known specific cause (more than 60%) the ”flangecouple” keyword is registered. While fires and explosions are respectively 36% and 28% of known cases.

- Only for the 61% of the incidents was possible to establish the section involved. As shown in section 3.1, the most involved sections of the ammonia plant are the reforming (40% of the known section incidents) and the ammonia synthesis (up to 30% of the known section incidents). The former includes primary and secondary reformers, all the mechanical devices and pipes between these apparatuses. The latter includes all the vessels, pipes and drivers of the ammonia synthesis loop. These are the most critical section because of the substances that they threat. Hydrogen, methane, ammonia, carbon monoxide and fuel gas are the most dangerous substances involved in the process and, in these two sections,

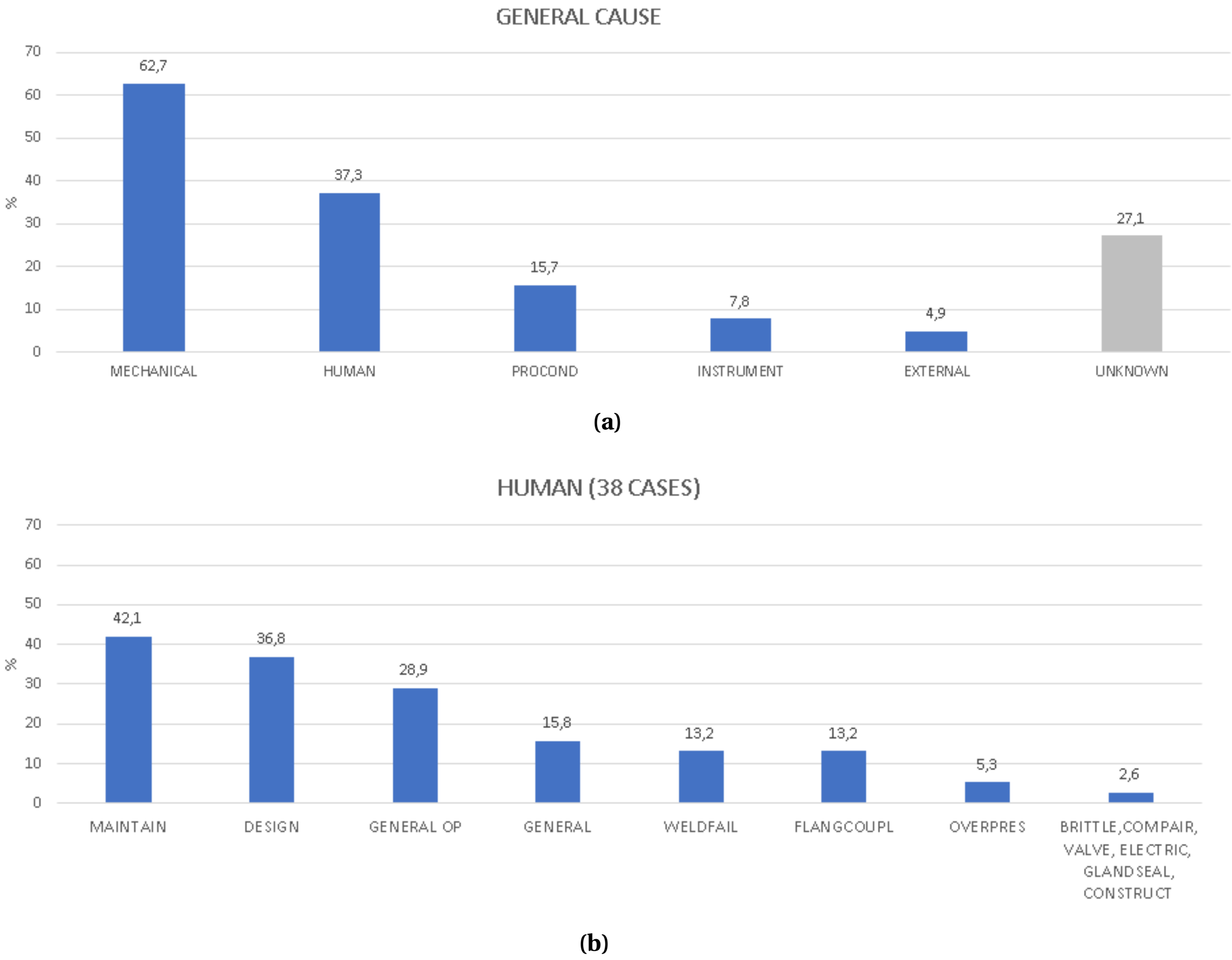


Figure 3.2: (a). Keywords about general cause field. The percentages are referred to the known cases (i.e., 102 incidents), while the percentage of unknown is referred to the overall cases considered (i.e., 140); (b). Specific cause keywords found in incident caused/influenced by human factor.

they are present in a high concentration.

Other involved sections are the ammonia storage (12% of known accidents) and the syngas purification section, including desulfurization (up to 10%) and CO_2 removal (up to 10%). It can be underlined how storage accidents caused more frequently severe consequences because of their bigger hazard potential.

3.2.5 Conclusion

The main results of the database analysis confirm what expected from the literature review performed in Section 3.1. From the general causes analysis, the technical factors are the principal causes of incidents in the ammonia plant. Nevertheless, the work will focus on the human factors as cause of incidents. According to the database results, they represent the second cause of incidents. These incidents have different critical levels: almost 30% of them cause at least one death, up to 30% cause at least one injured and the rest of the incidents cause any dead or injured. In addition, while technical failures are inspected, determined and predicted with physical models, for the human factors is not the same. They can be studied through appropriate methods presented in the next chapter.

Chapter 4

Methodology

In this chapter, an overview of different methods for the analysis of human and organizational factors is presented. The methods presented have different objectives with different level of details, but all of them can be used together to achieve the same goal: Dynamics Risk Assessment (DRA). DRA approaches can be particularly useful in managing risk. Industrial accidents can be the cause of loss of containment, which can be followed by events, such as fires, explosions and toxic dispersions. More generally, approaches for dynamic risk assessment are based on the use of models integrating parameters that change over the time. Dynamic factors impact on both frequencies and consequences of incidents and, thus, on final risk results. Moreover, it is well-known that the integration of real-time monitoring data offers the opportunity to achieve a more effective control of activities, carried out in the workplace in view of worker safety, by allowing the prevention of accidents and the timely implementation of protective actions. Currently the use of DRA is becoming more widespread, some examples from the literature are given by Paltrinieri and Khan (2016). As pointed by Paltrinieri and Reniers (2017), DRA allows improving decision-making and supporting critical risk operations; it can also be used to describe the impact of innovative technologies on the overall safety.

The first method presented is the Resilience Based Early Warning Indicator (REWI) (Øien et al., 2010) method, that is applied for the identification and monitoring of resilience based indicators. It can be applied to define a set of indicators. Then, a novel HRA method to evaluate the human error contribution to the risk is presented, that is the Petro-Human Reliability Analysis (Petro-HRA) (Bye et al., 2017). Eventually, the TECnical Operational and Organizational factors (TEC2O) (Landucci and Paltrinieri, 2016c) method for the dynamic risk assessment is described. It takes into account both technical and management factors, giving a more complete risk picture. To provide a full spectrum of methods for the analysis of human and organization factors, other different methods are evaluated. For instance, MANAGER (Pitblado et al., 1990) and the Model of Accident Causation using Hierarchical Influence NEtwork (MACHINE) (Embrey, 1992) inspired many further models. The former point to the tailorization of the frequency of hazardous events (Yang et al., 2017), while the latter proposes the influencing factor as a modeling technique. Then, the Barrier and Operational Risk Analysis of hydrocarbon releases (BORA-Release) (Aven et al., 2006), RISK_OMT (risk modelling e integration of organisational, human and technical factors) (Vinnem et al., 2012) and the Hybrid Causal Logic (HCL) (Røed et al., 2009) are analyzed as models based on the influencing diagrams.

4.1 The Resilience Based Early Warning Indicator (REWI) Method

In the chemical process industry, risk arises from complex systems and their management requires a large number of control measures (Rademaeker et al., 2014). In this context, a common practise is to track performance of activities by using indicators, in order to continuously improve the safety and the operability. As defined by Øien (2001), an indicator is a measurable/operational variable that can be used to concisely describe a phenomenon occurring when a plant is operating. A small number of key indicators can monitor the status of whole systems. In the chemical industry, the most relevant indicators are those used to assess safety or risk performance of systems. The terms safety indicator and risk indicator are distinguished by Øien et al. (2011). A risk indicator is a risk influencing factor, i.e. an event/condition that affects the risk level of a system/activity; whereas a safety indicator is a factor that as an effect on safety as it is related to some measures, different than risk metrics (as number of accidents or incidents or other). Thus, risk indicators are derived from a risk-based approach (Øien K., 2001), whereas safety indicators may be developed from a safety performance-based approach. Indicators are also distinguished as leading and lagging indicators (Health and Safety Executive, 2006): leading indicators represent a form of proactive monitoring of the effectiveness of a Risk Control System (RCS), by providing feedback about safety outcomes before an incident occurs; whereas, lagging indicators represent a form of a reactive monitoring of the effectiveness of a RCS, given that they provide feedback after the occurrence of a negative event.

Approaches to develop safety and risk indicators are grouped in two perspective typologies by Øien et al. (2011), i.e. technical-human-organisational perspective and predictive-versus-retrospective perspective. The first perspective allows developing safety indicators as it searches for causes of accidents occurred in the past, starting from technical to human and further to organisational causes (Leveson, 2004). The second one gives risk indicators and aims predicting potential accidents by including all possible causes or by trying to establish the causes after the event (according to a retrospective point of view); this approach requires the use of quantitative risk models.

Prevention of major accidents can benefit from the synergy of dynamic risk analysis techniques and safety/risk indicators. The application of dynamics risk assessment techniques based on proactive indicators is suggested by Paltrinieri et al. (2016), it brings additional benefits, since the risk analysis is supplemented by information related to the early warning, which supports to manage in advance unwanted events. The integration of a set of collected indicators provided the risk assessment with dynamic and proactive features. Data collection and processing, for the purpose of DRA, take advantage of information technology supporting real-time data collection, sharing, processing, visualization, etc. According to Paltrinieri et al. (2016), dynamics risk assessment techniques based on proactive indicators can be classified in four levels by referring to the basic theory and provided results. The first level concerns to the use of safety indicators, it takes into account the effect of technical, human and organization factors; the second one is related to the use of risk indicators, thus the application of risk models is needed; the third level refers to the application of techniques for frequency updating; finally, the forth level refers to the use of techniques for the aggregation of information, which are provided by indicators. This aggregation allows an accurate assessment of the variation of overall risk, also based on real-time data.

The REWI method is for the development of early warnings indicators. It is inspired by a developed method for the nuclear power industry, i.e., the Leading Indicators of Organizational Health (LIOH) method. The REWI is based on the concept of resilience and resilience engineering. Resilience concept can be defined as the capability of recognizing, adapting to, and coping with the unexpected (Woods, 2006). While resilience engineering approach provides methods, tools and management approaches to manage the risk in a proactive way (Paltrinieri

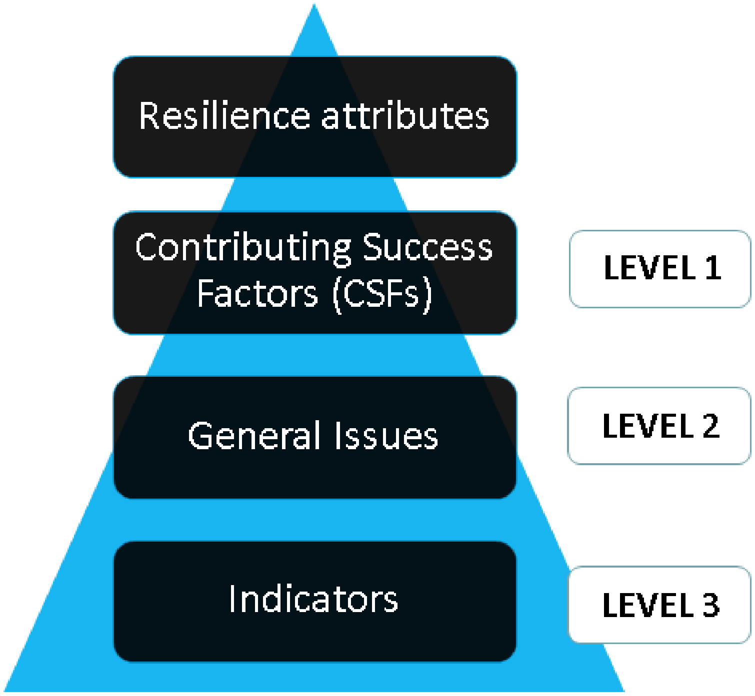


Figure 4.1: Hierarchy structure of the REWI method.

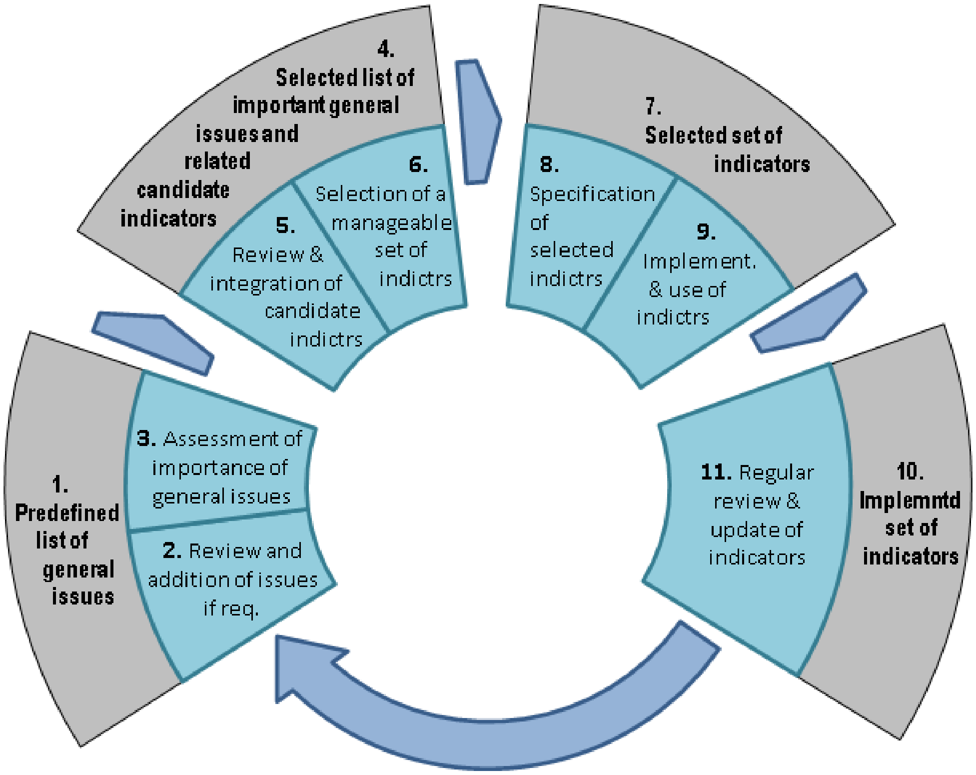


Figure 4.2: Steps for the REWI method (Paltrinieri et al., 2012).

et al., 2012).

According to Øien et al. (2010), the method consists of three main parts, that also represent the different levels of the approach (Figure4.1). The first consist of a set of eight Contributing Success Factors CSF (i.e., risk understanding, attention, anticipation, response, resourcefullness/rapidity, robusteness, decision support and redundancy) which are attributes of resilience. They are developed from a literature review and empirical study about successful recovery of high risk incidents. The second part, a list of general issues contributing to the CSF goals is presented. In the last part, a set of early warnings indicators for each general issue is proposed.

According to Paltrinieri et al. (2012), a representation of the steps to carry out for the REWI method is shown in Figure 4.2. In particular, from the step 1 to 3, a review/selection of important general issue is performed and a list of suggested indicators can be obtained. From the step 4 to 6, a second review is carried out. Then, from step 7 to 9, the indicators are specified and applied to the system. Eventually, from step 10 to 11, a review and updating of the set of indicators can be done.

4.2 Petro-HRA

This method by Bye et al. (2017) is thought for the oil and gas industry. It has been developed by the Institute for Energy Technology (IFE, project owner), the Norwegian University of Science and Technology (NTNU), DNV-GL, SINTEF Technology and Society, the Idaho National Laboratory and Statoil (Institute for Energy Technology, IFE). The sponsors were the Research Council of Norway, Statoil Petroleum AS and DNV-GL. The Petro-HRA method focuses on the estimation of the likelihood of human failure events (HFE) in post-initiating event scenario. It is a qualitative and quantitative method and it can be applied within a QRA framework (as shown in Figure 4.3) or as a stand-alone analysis (Bye et al., 2017). Moreover, it can be applied to analyze effects of early design choice, e.g.the decision on design options.

The basis of this method is inspired by the SPAR-H method: Statoil compared some HRA methods and evaluated SPAR-H as the most applicable method (Laumann et al., 2015). In the guideline presented by Bye et al. (2017), a step procedure for the qualitative data collection and anal-

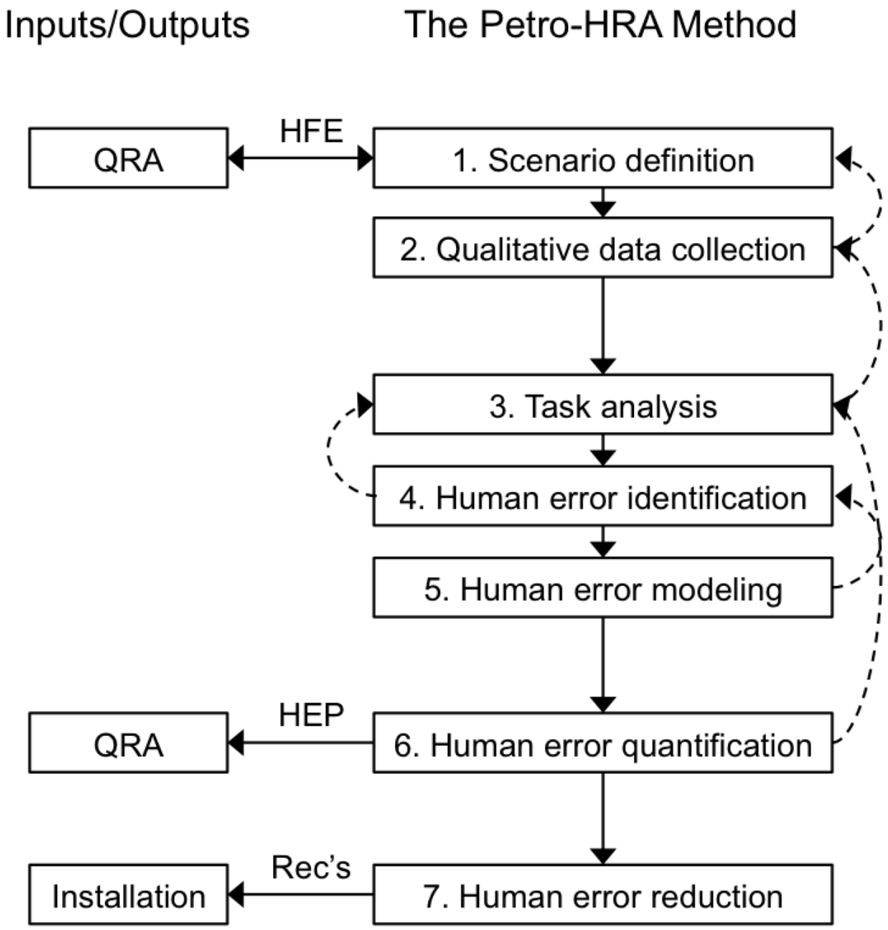


Figure 4.3: Relationship between the Petro-HRA method and QRA (Bye et al., 2017).

ysis, quantitative analysis and integration in QRA is provided. In particular, as shown in Figure 4.3, it consists of seven steps:

1. Scenario definition: it defines scope and boundaries of the analysis. It is one of the most important steps in the procedure because the qualitative and quantitative results are strongly related to it. The individuation of the major accident scenario depends on the quality of the QRA performed, where the Human Failure Event (HFE) is defined. In fact, a good knowledge about relevant HFEs and critical operator tasks (that are already identified in the QRA) is needed for a better choice of the scenario. In the procedure, how to perform initial meetings, the document review and the scenario description is presented.

2. Qualitative data collection: gathering more specific data about factors that can affect human performance (positively or negatively) and the outcome of the scenario. It is typically performed through a scenario walk and talk-through, observations and interviews with operators. In the guideline, a list of questions and advice helping the analyst to complete this task is reported. So, the analyst should get an in-depth understanding of the tasks or task steps performed by operators. Moreover, the analyst should be able to carry on an initial Timeline Analysis, to figure out the relationship between the operator actions, how much time these actions require and if the operators have enough time.

3. Task Analysis: describing the steps carried out by the operators during an activity. The goal is to determine deviation paths resulting in different analysis outcomes (Laumann et al., 2015). In this way, this step should help to define HFEs and possible human errors related to a specific activity. Moreover, the Task Analysis helps to understand the impact of the PSFs on the human tasks, providing the basis for the quantification.
   To perform a task analysis, all the information gathered in the previous steps should be organized into a Hierarchical task analysis (HTA). It breaks down the main task (that is the successful outcome of the HFE) into goals, task and task steps. Drawing a graphical clear visualization of the main task decomposition, an evaluation of opportunities of error can be done easier. To include more information, the HTA should be extended in a tabular form through a Tabular Task Analysis (TTA). It helps to figure out where the data collection activities should be focus on. Moreover, a column for the Human Error Identification (HEI) and for the Performance Shaping Factors (PSF) can be added. Then, the TTA can be updated afterwards when more information are available. So, it will become a focal point for the steps following (i.e. for the HEI and Human Error Modeling (HEM)).

4. Human Error Identification (HEI): identification of potential errors associated to task steps in the scenario. Other goals of this step are describing the likely of consequences of each error, identifying recovery opportunities and describe the PSFs that could have influenced

the error probability. A list of error taxonomy from the Systematic Human Error Reduction and Prediction Approach (SHERPA) for considering error in the task analysis is proposed (Bye et al., 2017). Moreover, the analyst can use/add different error taxonomy if it fits well with the tasks analyzed.

5. Human Error Modeling (HEM): the aim is modeling and make a graphical representation of the task steps (i.e., actions) in order to clarify the links between errors, PSFs, task steps and HFE. In this way, during the next step, a quantification of the HEP of a specific HFE should be easier.
   HEM is performed in four steps: to build an operator action event tree (OAET) starting from the Task Analysis and afterwards an event tree; evaluate errors that may contribute to the HFE, if they are not already detected during the HEI; determine a set of most relevant PSFs that contribute to the HFE; after HEQ (next step of the procedure), apply the event tree to calculate the HEP (input for the QRA).

6. Human Error Quantification (HEQ): the HEP of each chosen event or task step is quantified through a nominal value and a defined set of PSFs. All the results from the previous steps are inputs for the HEQ. In the guideline, nine PSFs inspired from SPAR-H are described. Moreover, several levels with corresponding multipliers for the PSFs are provided by Bye et al. (2017). The levels range from ”very high negative effect on performance” to ”moderate positive effect on performance”, where the multipliers range from 50 to 0,1 respectively. In addition, the ”extremely high negative effect on performance” represent the worst level and a HEP=1 is assigned.
   When all the multipliers for each level are assigned, the following equation is applied (Bye et al., 2017):

$$\begin{aligned} HEP = 0.01 \times \text{Time multiplier} \times \text{Threat stress multiplier} \times \text{Task complexity multiplier} \times \\ \times \text{Experience/Training multiplier} \times \text{Procedures multiplier} \times \text{Human Machine} \\ \text{Interface multiplier} \times \text{Attitudes to Safety, Work and Management Support} \times \\ \text{multiplier} \times \text{Teamwork multiplier} \times \text{Physical working environment multiplier.} \end{aligned} \tag{4.1}$$

   But if all PSFs have the nominal value (i.e., 0,01), the HEP is equal to 0,01.
   So, at the end of the HEQ, a value of the HEP ranging from 0 to 1 can be obtained. Furthermore, an evaluation of the most influencing PSFs take into account can be done, that is useful for the last step: the human error reduction.

7. Human Error Reduction: developing recommendations to reduce the risk due to the HFEs. This task is performed firstly assessing if the HEP assigned to each HFE is acceptable (us-

ing the criteria reported by Bye et al. (2017)) respect to the overall risk determined after the QRA. Then, an Error Reduction Analysis (ERA) to understand which event has more influence on the HEP is carried out. So, a screening of the most influencing PSFs should be done and different measures and/or strategies can be proposed to compensate them.

4.3 TEC2O

The TECnical Operational and Organizational factors (TEC2O) is a method for the Dynamic Risk Assessment (DRA). As shown in Eq. 4.2, trough a frequency modification factor Ω(t), the baseline frequency of an accident scenario F_0 can be updated in time (Landucci and Paltrinieri, 2016c).

$$F(t) = F_0 \times \Omega(t) \tag{4.2}$$

$$\Omega(t) = TMF \times MMF \tag{4.3}$$

According to API 581 (American Petroleum Institute, API, 2000), such frequency modification factor is divided into two other factors (Eq. 4.3): the TMF represents the technical modification factor and the MMF is the management modification factor. The former is related to the equipment and process aspects. The latter focuses on the operational and organizational aspects. Further works are focusing on the integration of another factor (Human Modification Factor (HMF)) that it should modify the Eq. 4.3 into the following equation:

$$\Omega(t) = TMF \times (MMF + HMF) \tag{4.4}$$

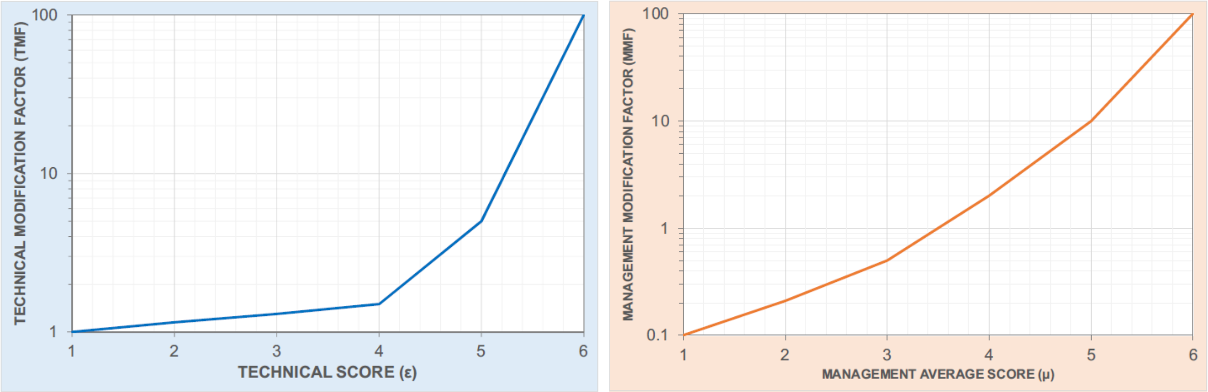
For the HMF, more specific PSFs from SPAR-H related to human error are taken into account (Tereziu, 2017).

The technical and management modification factor can assume values between 1 and 100. These values are assigned through the technical score ϵ for the TMF factor and the management average score μ for the MMF using Fig.4.4(a) and Fig. 4.4(b) respectively.

4.3.1 Technical score (ϵ)

The technical score takes into account technical issues that can influence the likelihood of failure. According to API 581 (American Petroleum Institute, API, 2000), four subfactors are considered in the evaluation of the ϵ:

- Ageing subfactor (TM): it accounts the ageing of the equipment and its erosion/corrosion;



(a) **(b)**

Figure 4.4: (a).TMF as a function of the technical score ϵ (Landucci and Paltrinieri, 2016c); (b). MMF as a function of the management average score ϵ (Landucci and Paltrinieri, 2016c).

- Environmental subfactor (U): it considers natural hazards, extreme weather conditions and features of the plant layout;
- Construction subfactor (M): it accounts mechanical aspects of the equipment analyzed and the design complexity;
- Process subfactor (P): it evaluates the stability of the process and the status of protection systems.

A set of indicators is assigned for each subfactor. A value on an arbitrary scale is assigned to each indicator. Then, all the indicators are combined through a mathematical relationship to give the subfactor value. A score ranging from 1 to 6 is assigned to each subfactor's value. Finally, as shown in Eq. 4.5, the four subfactor scores are combined to give the technical score through a weighted sum:

$$\epsilon = \omega_{\mathrm{TM}} \times STM + \omega_{\mathrm{U}} \times SU + \omega_{\mathrm{M}} \times SM + \omega_{\mathrm{P}} \times SP \tag{4.5}$$

where ω_{TM}, ω_{U}, ω_{M}, ω_{P} are weights associated to each subfactor mentioned. Each weight can be set to the default value of 0,25. Otherwise, after a company workshop, the weight of each subfactor can be changed to penalize one subfactor respect to the others (Landucci and Paltrinieri, 2016c).

4.3.2 Management average score (μ)

As the technical score, the management average score is divided into subfactors (Landucci and Paltrinieri, 2016c):

- Operational subfactor (OP): that is about skills, experience, penalizing poor training and communication between personnel;
- Organizational subfactor (ORG): it deals with safety culture and safety procedures.

As the technical score's subfactors, these two subfactors range from 1 to 6 and they are combined into the following equation:

$$\mu = \omega_{\mathrm{OP}} \times OP + \omega_{\mathrm{ORG}} \times ORG \tag{4.6}$$

The weights can be set to 0,5 each one, but they can change in agreement with a company workshop (Landucci and Paltrinieri, 2016c).
To obtain the subfactor scores, a set of indicators is associated with both operational and organizational factors. The REWI method (Øien et al., 2010) proposes a list of candidate indicators based on the resilience concept. After a company workshop, the final list of the most relevant indicators should be done. If the selected indicators are quantitative parameters, they are monitored and updated in time. While if they are qualitative, a qualitative score is assigned. According to Landucci and Paltrinieri (2016c), both indicator's values are converted into scores ranging from 1 to 6 (e.g., scores for qualitative indicators: GOOD=2, MEDIUM=4, BAD=6). Then, through a weighted sum, the OP and ORG subfactors can be obtained:

$$OP = \sum_{i=1}^{M} \omega_i S_{OP,i}; \qquad ORG = \sum_{j=1}^{N} \omega_j S_{ORG,j} \tag{4.7}$$

where M and N are the number of operational and organizational indicators respectively; ω_{i} and ω_{j} are weights associated to the scores $S_{\mathrm{OP,i}}$ and $S_{\mathrm{ORG,j}}$ respectively. In general, for each subfactor, indicator's weights are assigned as equal in the base-version (i.e, ω_{i}=1/M and ω_{j}= 1/N), but they can be changed to empathize importance difference between indicators.

4.4 Other methods

4.4.1 MANAGER

The management safety systems evaluation technique (called MANAGER) was developed by (Pitblado et al., 1990) for the Chemical Process QRA (CPQRA). As shown in Eq.4.8, MANAGER provides a value of the management factor (MF) that modifies the generic frequency of failure (called generic frequency, F_{Generic}) to get an estimate frequency (F_{Estimate}).

$$F_{\mathrm{Estimate}} = F_{\mathrm{Generic}} \times MF \tag{4.8}$$

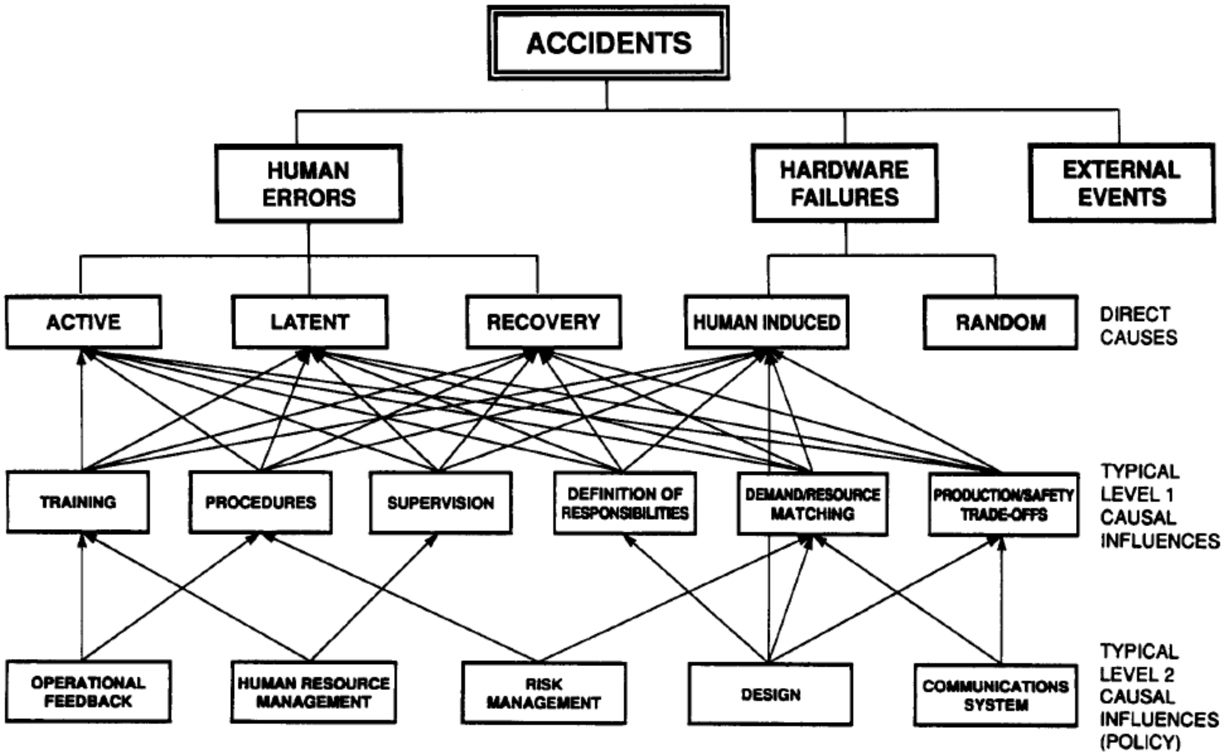


Figure 4.5: A typical model of accident causation for the MACHINE method (Embrey, 1992).

The MF takes into account both organizational and technical factors (Landucci and Paltrinieri, 2016b). For the quantification of the MF, a questionnaire containing 260 questions is proposed. A qualitative grade to the answers or a group of similar answers is assigned. In particular, they can be graded as being average for the industry, better or worst than average.

4.4.2 MACHINE

The Model of Accident Causation using Hierarchical Influence NEtwork (MACHINE) was developed to analyze railway accidents. It describes how the management influences, immediate causes and operational error interact each other (Embrey, 1992). This approach can assess qualitatively and/or quantitatively the human contribution to the risk. In this method, the error is divided into three categories: active error, having a direct and immediate impact on the safety; latent error, divided into operational errors (caused by wrong performed activity, e.g., maintenance) and organizational errors (e.g., design error); recovery errors, which leave the latent errors undetected. Moreover, it classifies the PSFs into error-inducing factors and organized them in different levels.

In the model for the accident causation (Figure 4.5), a many-to-many relationship between PSFs and the direct causes is proposed (Yang et al., 2017). Then, the conditional probabilities for all possible combination of states of the PSFs are assigned. But this evaluation can be difficult in practice. So the Success Likelihood Index Method (SLIM) is proposed (Yang et al., 2017). It evaluates the probabilities as a function of variations in PSFs.

4.4.3 BORA-Release

The Barrier and Operational Risk Analysis of hydrocarbon releases (BORA-Release) method by Aven et al. (2006) integrates human, technical and organizational factors into the performance of safety barriers. It focuses on the qualitative and quantitative risk assessment of a specific hydrocarbon release frequency for the offshore oil and gas production platform Yang et al. (2017). The main steps of this method are eight:

1. Development of a risk based model and all the representative hydrocarbon release scenarios;
2. Modeling of the performance safety barriers, typically through fault tree analysis;
3. Assign an industry average probabilities/frequencies to the initiating events and risk quantification based on these probabilities/frequencies;
4. Development of risk influence diagrams, in order to include the effects of the human, operational, organizational and technical RIFs on the barrier performance;
5. Scoring of RIFs;
6. Weighting of RIFs;
7. Adjustment of industry average probabilities/frequencies;
8. Recalculation of the risk, using the new calculated probabilities/frequencies.

Aven et al. (2006) classified the PSFs (called Risk Influencing Factor, RIF) in five categories: personal characteristic, task characteristic, characteristics of the technical system, administrative control and organizational factors/operational philosophy. In the guideline (Aven et al., 2006), a list of PSFs assigned for each category is presented. The score of each PSF can be assigned during a PSF audit (called in the guideline as Risk influencing factor (RIF) audit) or through methods found in the literature(e.g., Technical Condition Safety (TTS) or Risk Level on the Norwegian Continental Shelf (RNNS). The weights of each PSF are assigned through expert judgment.

4.4.4 HCL

The Hybrid Causal Logic (HCL) model is thought for the aviation industry. But Røed et al. (2009) have demonstrated its applicability for the Norwegian offshore oil & gas industry. It combines the traditional risk analysis tools with Bayesian Belief Networks (BBNs). While the event an fault trees allow to model the deterministic cause-effect relationship, the BBN for a better description of non deterministic relationship is utilized. As shown in Figure 4.6, the BBN is applied to provide inputs information to the fault and event trees. The main steps of the procedure are six (Røed et al., 2009):

1. RIFs and causal relationship are assigned for the relevant basic events of the fault tree;
2. Identify concurrent RIFs, to make sure that they are accounted only once in the BBN;
3. Build a BBN based on the RIFs and causal relationship selected in the previous steps;

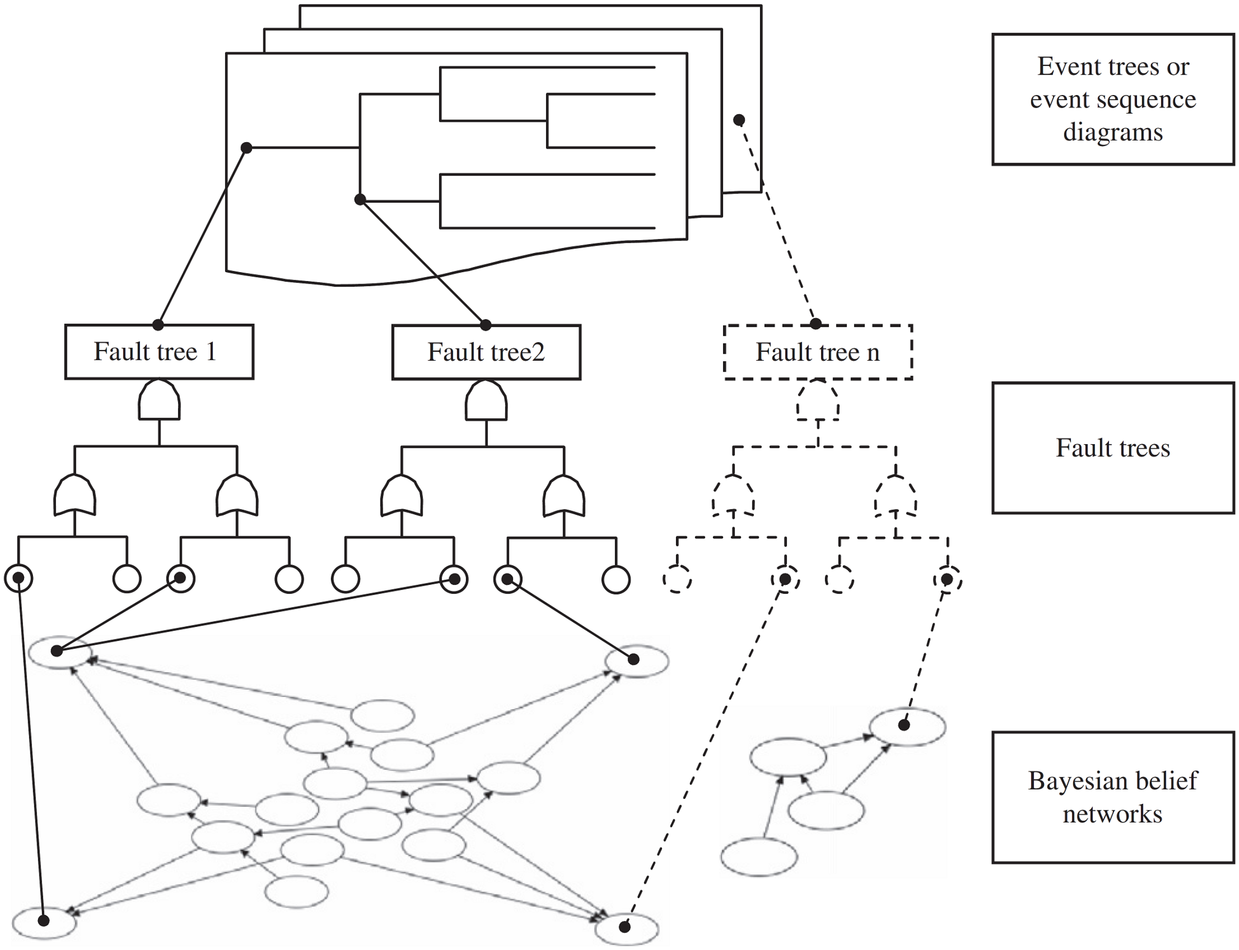


Figure 4.6: Structure of HCL model (Røed et al., 2009).

4. Assign conditional probability tables, so quantifying the causal relationships in the BBN;
5. Evaluate the performance of the RIFs in the BBN and assign one or more states (from ”a” for the best state to ”f” for the worst state respect to the average) to the RIFs;
6. Calculate the risk.

The assignment of RIF states is performed through expert judgment or technical conditions safety audit approach (TTS), that is an evaluation system mainly focused on technical aspects (Røed et al., 2009).

4.4.5 RISK_OMT

This is an extension of a previous method denominated BORA-Release Aven et al. (2006). It is developed for the offshore oil and gas industry to understand how the technical, organizational and human factors influence the risk. In particular, it focuses on the maintenance work on process equipment on offshore installation (Vinnem et al., 2012). Respect to BORA, it presents a more comprehensive model for the Risk Influencing factors (RIFs) and how they modify the performance of operational barriers (Gran et al., 2012). Because of that, a model based on Bayesian networks is applied. Here, all the RIFs are considered as stochastic variables and the weight of each RIF is assigned. But, before the implementation of the Bayesian network, a RIF modeling is performed. Two RIFs models are presented: for planning; for execution and control activities

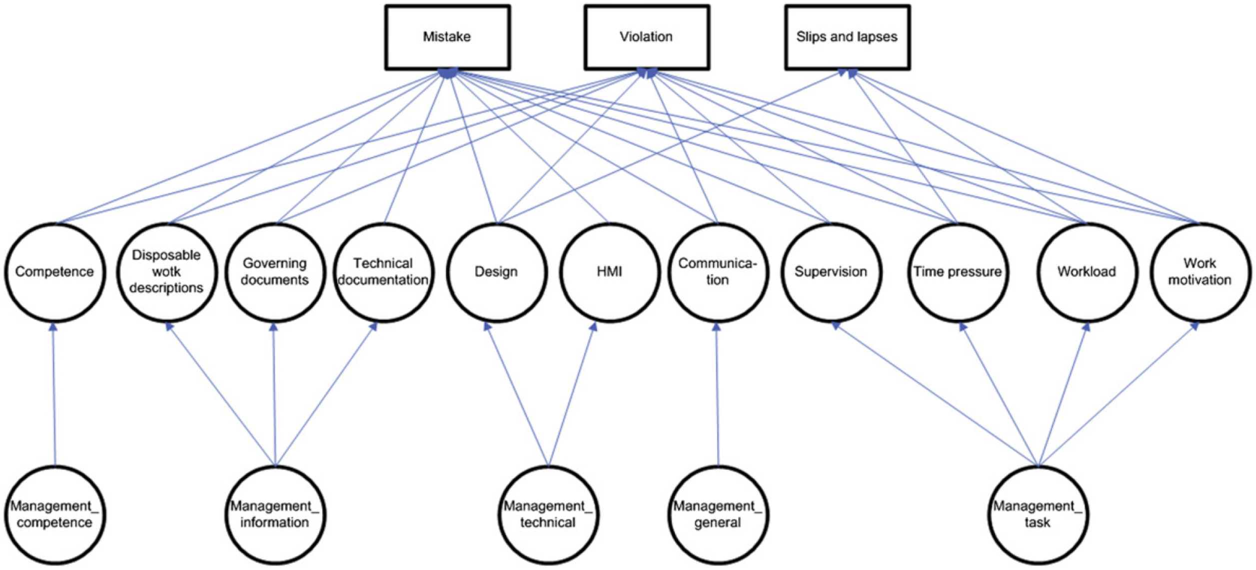


Figure 4.7: RIF model for execution and control activities for RISK_OMT model (Vinnem et al., 2012).

(Figure 4.7). For both models, two levels of RIFs are considered. The first level influences the human error, while the second level can only influence the first level. Eventually, the outcome of the model is a new failure probability of the basic event of the fault/event tree (Yang et al., 2017).

Chapter 5

Case study

5.1 March, 20th, 1989

The accident occurred in an ammonia cryogenic storage vessel of an NPK production plant located in Jonova, Lithuania. On 20 March 1989, the pressure into the storage vessel (capacity of 10000 t) climbed abruptly. The vessel burst at its base. Because of the wave of ammonia escaping from the breach, the vessel broke free from its stand and destroyed its reinforced concrete protecting wall. So, 7000 t of ammonia were spread over the ground, forming a pool 70 cm deep. With light wind condition (2 m/s), up to 12 hours for the evaporation of the pool were needed. Moreover, a jet fire towards the phosphonitrate production building occurred, leading to a fire in the fertilizer depots.

5.2 Consequences

A toxic cloud of ammonia vapors and products of thermal decomposition of the fertilizers contaminated a zone of 400 km^2, causing 7 deaths and 57 wounded. According to Andersson (1990), an emergency evacuation of the employees was accomplished. The municipal authorities were alerted 25 minutes after the incident, which decided to evacuate the population from the high-risk zone. So, 32000 people were evacuated. Water curtains to reduce the impact of the cloud were adopted.

5.3 The causes of the accident

According to ARIA Database (access date: october, 2017), several causes were identified. The day of the accident, the liquefying turbo-compressor for the transfer of the ammonia from the production unit to the cryogenic storage vessel was stopped because of long-term maintenance. Also, the second turbo compressor was unavailable because of short-term maintenance. Then, the safety piston pump was put into service, but some problems with the compressor of the cooling system delayed the transfer of the gaseous ammonia from the process to the storage. So, the ammonia from the process unit had to be sent to the flare stack but, for the first 15 min, 14 t of warm gaseous ammonia (+10 °C) were introduced from the bottom of the storage. Under the hydrostatic pressure, the gaseous ammonia bubble remained in the bottom of the vessel. After an hour, a phenomenon similar to rollover occurred: this bubble reached the surface causing a sudden increase in internal pressure. The two pressure relief valves were not designed to protect the reservoir for such over-pressure.

5.4 The rollover phenomenon in the ammonia storage tank

This phenomenon is caused by a stratification of the density in a cryogenic storage tank. The hazard derived from the rollover is linked to the large amount of vapor released in a very short time, leading to the over-pressurization of the vessel (Culkin et al., 2015).

The stratification can occur by filling of the vessel or by an ”autostratification”. The former can occur when the tank is filled with a fluid having different density. For instance, if the tank is filled from the top with a less dense fluid than the liquid already stored, a stable lighter layer on the top of the surface can be formed. If this stratification lasts for some considerable time, the top layer becomes colder (and denser) due to the evaporation of the substance (Figure 5.1). Under the hydrostatic pressure, the lower layer (denser) gets lighter due to the heat leak into the walls of the tank. When the densities of these two layers approach at the same value at the surface, they become to mix. For the LNG tanks, the superheated lower layer gives a boil-off rate up to ten times more than the normal one (Baker and Creed, 1995).

The latter (known as nitrogen stratification in case of the LNG storage tank) derives from some change of the composition of the upper layer due to the preferential boil off of the more volatile compound (Culkin et al., 2015). For instance, in the LNG storage, the nitrogen present in the LNG evaporates preferentially causing a decrease in density.

This phenomenon is well known for the LNG storage tanks. About the ammonia storage, different opinions about its occurrence can be found in literature. Rollover in the ammonia storage intended as a “spontaneous and sudden migration of a substantial mass of liquid ammonia

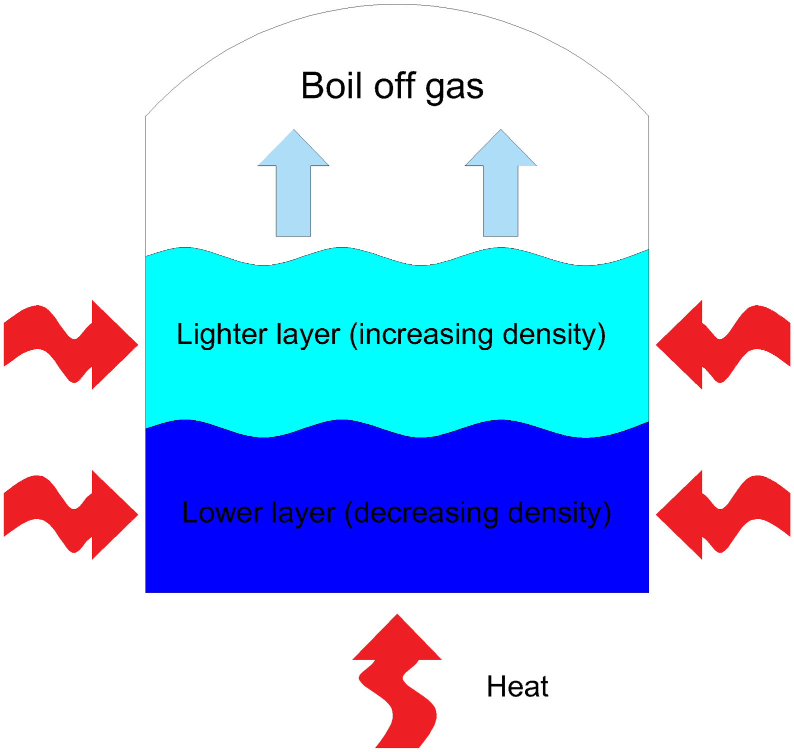


Figure 5.1: An example of stratification in a cryogenic storage tank.

from the bottom of the tank to the surface" is considered by some researchers unlikely (Squired, 1990). According to (McGowan, 2000), rollover in an ammonia storage tank cannot occur. His conclusion was that every adverse temperature gradients can dissipate themselves before leading to dangerous phenomena. At the same time, some ammonia storage tank accidents caused by rollover can be found in literature. For instance, the incident reported at Rostock, Germany in 2005, occurred during the filling of the ammonia storage tank was attributed to rollover (ARIA Database (access date: january, 2018), ARIA Database (access date: october, 2017)). Moreover, the rollover phenomenon for the accident occurred in Lithuania is not completely discarded (McGowan, 2000). It is considered as the cause of over-pressure by some reports (e.g., ARIA Database (access date: october, 2017), Pattabathula et al. (2014), Andersson (1990)).

A definition of rollover for the ammonia storage tanks is given by Squired (1990). He defines rollover a limit case of the "thermal overload". This is a situation, generated by some external action (e.g., unsatisfactory operation, recycling of warm ammonia), where a considerable mass of ammonia comes upwards from the bottom to the top of the tank. According to this definition, the rollover phenomenon can be explained in the Jonova accident. So, rollover is still considered one of the main cause of over-pressurization for the ammonia storage tank (Hossain, 2012).

5.5 Development of the bow-tie diagram for the case study

In this section, the method developed in the ARAMIS project to build a bow-tie diagram is introduced and used to outlined the Jonova accident. The choice of the selected branches and safety barriers is discussed.

5.5.1 The ARAMIS project

The identification of possible accident scenario is typically performed by the evaluation of the worst cases scenario, i.e., without considering safety devices or safety policy implemented. So, ARAMIS methodology was developed to identify major accidents (no safety barriers considered) and evaluate the safety system, causes of accidents and probabilities. In this way, the Reference Accident Scenarios (RAS), which consider safety systems, can be identified. The RAS represent the real hazardous potential of the equipment. In the RAS identification, the safety management system is also considered.
Two methods are applied in ARAMIS:

1. The Methodology for the Identification of Major Accident Hazards (MIMAH): it identifies the ”Major Accident Hazards”, i.e., the worst accidents that can occur without considering safety system. The MIMAH is typically performed developing a bow-tie diagram. This is a tool to display links between causes, critical event and consequences of an accident. It is made of three parts: the central part represents the critical event (i.e., loss of containment (LOC) or Loss of Physical Integrity (LPI)); on the left there is the Fault Tree, which identifies the causes of a critical event; in the right part there is the event tree, which represents the possible consequence of a critical event.

2. The Methodology for the Identification of Reference Accident Scenarios (MIRAS): it studies causes of accidents, probability levels and safety system. So, the RAS can be defined.

Then, the RAS is modeled to obtain the severity mapping, which is compared to the vulnerability mapping of the surroundings of the plant.

5.5.1.1 The Methodology for the Identification of Major Accident Hazards (MIMAH)

As shown in Figure 5.2, MIMAH methodology consists of seven steps. In particular:

1. Collect needed information: all the information necessary for the further steps has to be gathered. Only from the first to the third steps of the procedure, a data collection is

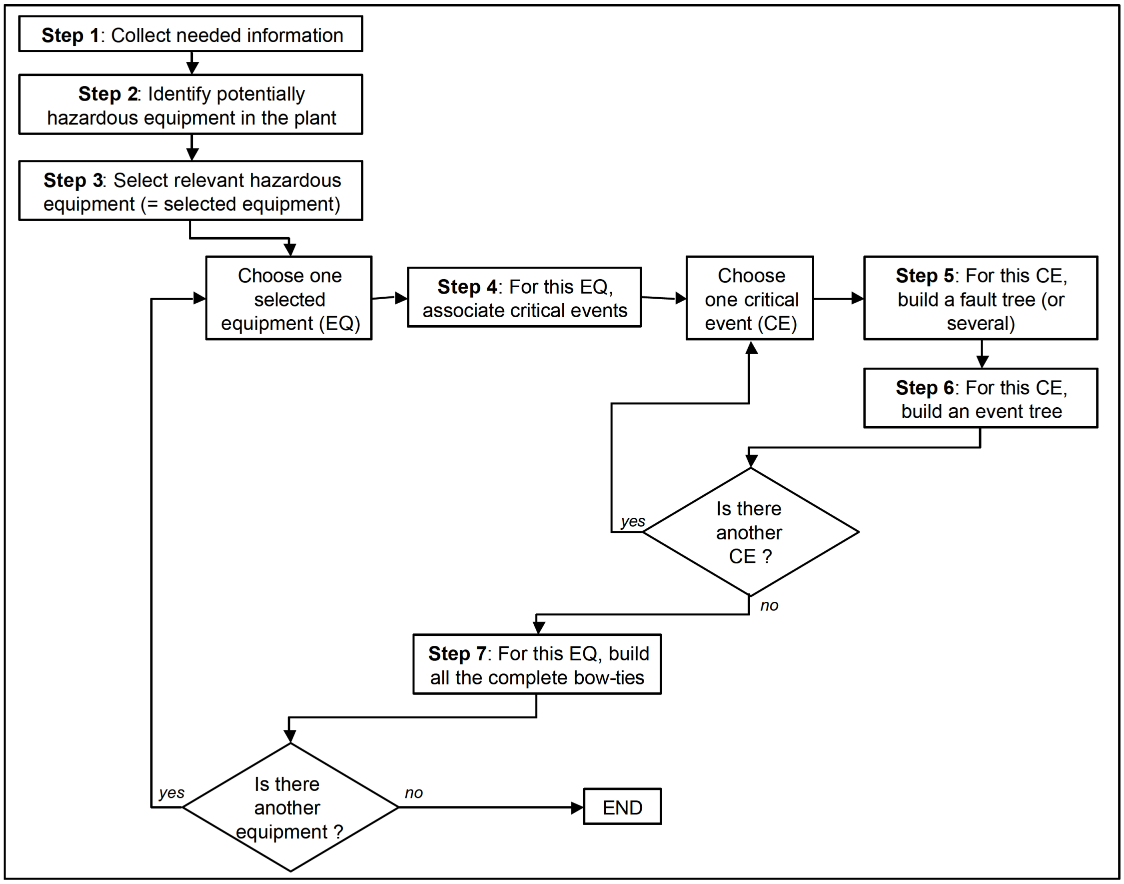


Figure 5.2: Rappresentation of the MIMAH steps (Delvosalle et al., 2004).

needed. To have a general overview of the process, a layout of the plant and a brief description of the process and equipment is needed. For the second step, a list of substances treated in the plant with a description of the hazardous properties is needed. Eventually, for the third step, the size, operating conditions and the properties of the substance involved in the hazardous equipment have to be provided.

2. Identify potential hazardous equipment: based on the information gathered in the step before, the identification is divided into two phases: identify the hazardous substances involved in the plant; make a classification of the equipment containing these substances in unit (i.e., storage, (un)loading, pipe networks and process unit) and define the state of the substances. All the equipment, which can be hazardous because they can cause domino effect but do not contain hazardous substances, are not considered.

3. Select relevant hazardous equipment: a threshold of the quantity of the hazardous substance is defined. If the equipment contains more quantity of the hazardous substance, it would be studied in the following steps. The threshold depends on the properties, physical state so the substance and its location respect to the other hazardous equipment.

4. For each hazardous equipment, associate one or more critical events. A Loss of containment is generally assigned if the substance involved is in the fluid state. While if it is in the solid state, the Loss of Physical Integrity is considered.

5. For each critical event, build a fault tree: a list of generic fault trees for each critical event is proposed. All the fault trees are limited to five levels, which are: undesirable events (UE, the deepest level of the FT), the Detailed direct cause (DDC), that can provoke the Direct Cause (DC), the Necessary and Sufficient Causes (NSC) which are the immediate causes that generate the Critical Event (CE). The fault tree is constructed starting from the CE and, through a deductive sequence, the UE can be derived. It is worth mentioning that the human error appears only at the last level while the other levels are caused by a technical failure. This is because the human error is never considered as a direct cause of a rupture but it can provoke its direct causes or the detailed direct causes.

6. For each critical event, build an event tree: that is the right part of the bow-tie diagram. It is typically formed by five levels. It is built starting from the critical event, then the Secondary critical event SCE (e.g., pool formation), the Tertiary Critical Event TCR (e.g., pool ignited) leading to a Dangerous Phenomena DP (e.g., fire, VCE, flash-fire) and eventually to the Major Event ME. ME identifies the effects (e.g., thermal radiation, over-pressure) of the DP on targets (e.g., human, environment). As shown in Figure 5.3, a procedure to build the event tree starting from three input (i.e., the critical event, the physical state and the hazardous properties of the substance involved) is described.

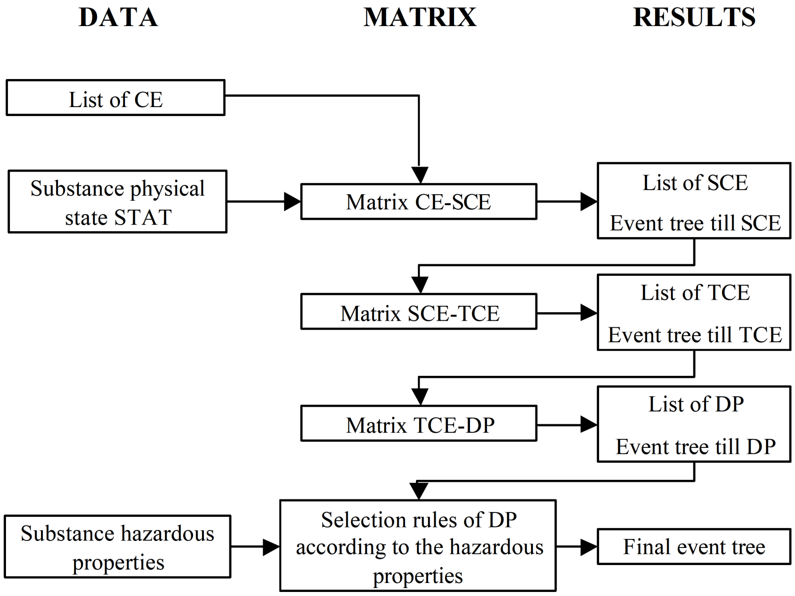


Figure 5.3: Graphical representation of the steps to build an event tree (Delvosalle et al., 2004).

5.5.1.2 The Methodology for the Identification of Reference Accident Scenarios (MIRAS)

Starting from the bow-tie diagram built with MIMAH, the influence of safety devices and policies on scenarios have to be defined and quantified. In fact, the Reference Accident Scenario (RAS) which considers safety systems can be defined. In this way, a more realistic description of the hazardous potential of the equipment can be represented.
As shown in Figure 5.4, the Methodology for the Identification of Reference Accident Scenarios (MIRAS) consists of eight steps:

1. Collect needed data: information regarding initiating events frequencies/probabilities, safety barriers for fault and event tree side with all the information to assess their performance(e.g., the probability of failure on demand, response time, etc) and ignition probability have to be collected. Moreover, for the calculation of the severity (the last step), information regarding the characteristic of the equipment (e.g., the dimension of the vessel, the quantity of substance, etc), meteorological conditions and a description of the surrounding of the plant are needed.

2. Make a choice between step 3 and step 4: both steps estimate the frequency per year of the critical event of the considered bow-tie diagram.

3. Calculate the frequency of the critical events analyzing the fault tree: the frequencies of the initiating events are assigned. In the appendix of the ARAMIS project, some of these values are proposed. Then, the safety barriers are identified and their performances are assessed. Four type of barriers (i.e., passive barriers, activated barriers, human actions and symbolic barriers) with four different safety function (i.e., to avoid, to prevent, to control, to mitigate) are defined. The performance of the barriers is defined according to three parameters: the level of confidence of a safety barrier (related to the probability of failure on demand), the effectiveness of the safety function (expressed in percentage) and the response time, defined as the time between when the barrier start working and the complete achievement of the safety function. Eventually, the frequency of the critical event can be calculated.

4. Estimate the frequency of the critical events from the generic critical events frequencies. This step is performed if it is not possible to analyze the fault tree. A bibliographic review of published data about these frequencies is proposed by Delvosalle et al. (2004).

5. Calculate the frequencies of the dangerous phenomena (e.g., fire, poolfire, jetfire, explosion, etc): an evaluation of the transmission probabilities in the event trees can be performed. Different situations can occur, i.e, rain out, immediate/delay ignition, Vapour Cloud Explosion (VCE). For the evaluation of the probability of dangerous phenomena, also the safety barriers can be considered.

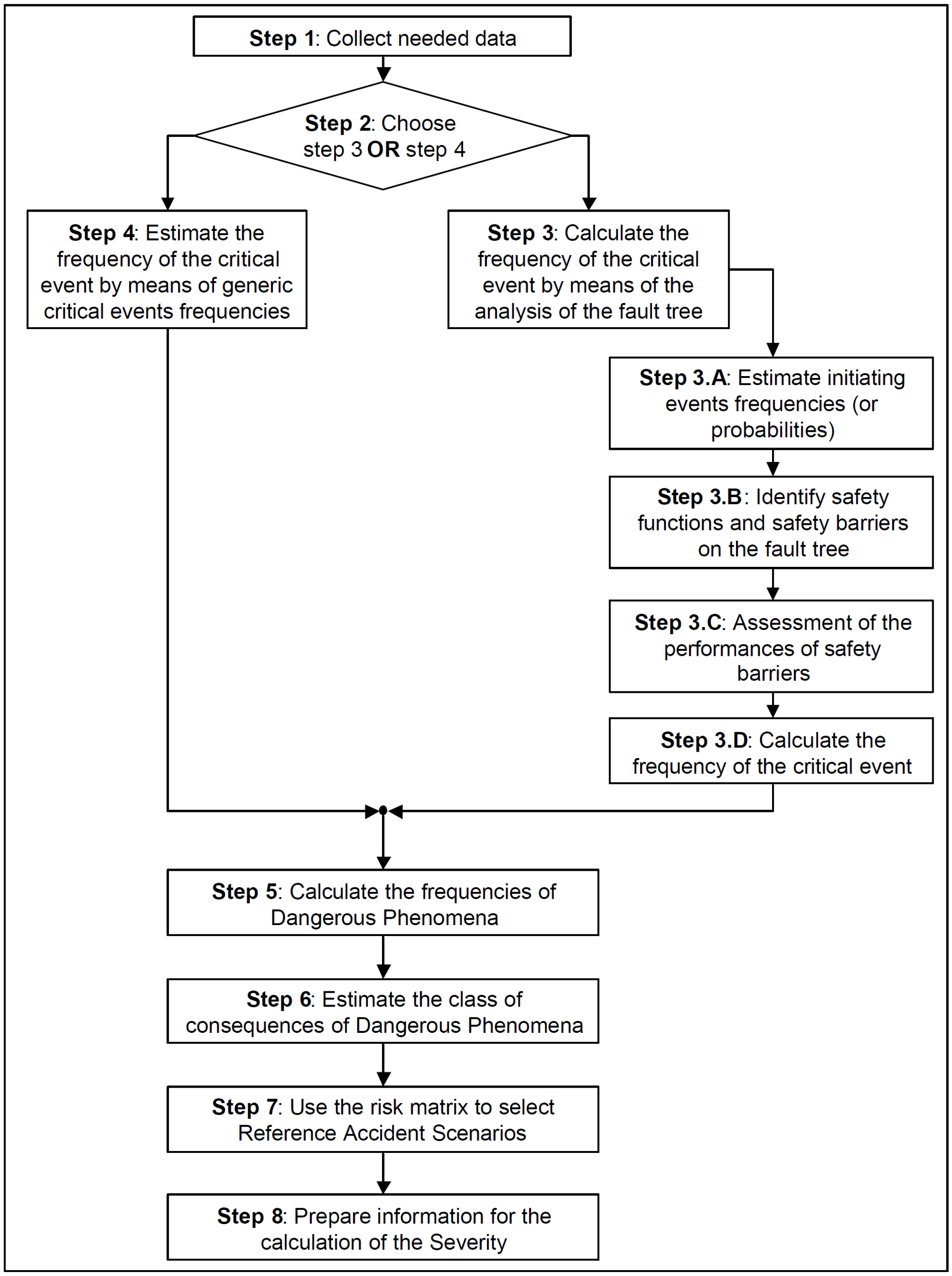


Figure 5.4: Rappresentation of the MIRAS steps (Delvosalle et al., 2004).

6. Estimate the class of the dangerous phenomena (DP): from this step to the end of the procedure, a qualitative methodology to select the dangerous phenomena for the calculation of the severity is proposed. In fact, a qualitative class of the dangerous phenomena can be assigned according to Table 5.1. These class for each dangerous phenomena can be modified by the user if the DP is ”fully developed” or ”limited” by safety barriers.

7. Use the risk matrix to select the RAS: from the frequency and the qualitative consequence

class for each DP, the risk matrix can be drawn. This matrix is not used to define the acceptability of the risk, but only to identify which RAS has to be considered for the calculation of severity. In Figure 5.5, three zones can be identified: the green zone, which it corresponds to a low frequency and low consequences of the DP; the yellow zone representing a DP that can have an effect on the severity, so it can be selected as a RAS; the red zone, where all the very DP are placed. For this last zone, additional safety barriers should be considered: if the DP still lay down in the red or yellow zone, it has to be considered for the severity calculations.

CONSEQUENCES		**CLASS**
Effect on human target	**Effect on environment**	**Ranking**
No injury or slight injury with no stoppage of work	No action necessary, just watching	C_1
Injury leading to an hospitalization > 24 hours	Serious effects on environment, requiring local means of intervention	C_2
Irreversible injuries or death inside the site. Reversible injuries outside the site	Effects on environment outside the site, requiring national means	C_3
Irreversible injuries or death outside the site	Irreversible effects on environment outside the site, requiring national means	C_4

Table 5.1: Class of consequence (Delvosalle et al., 2004).

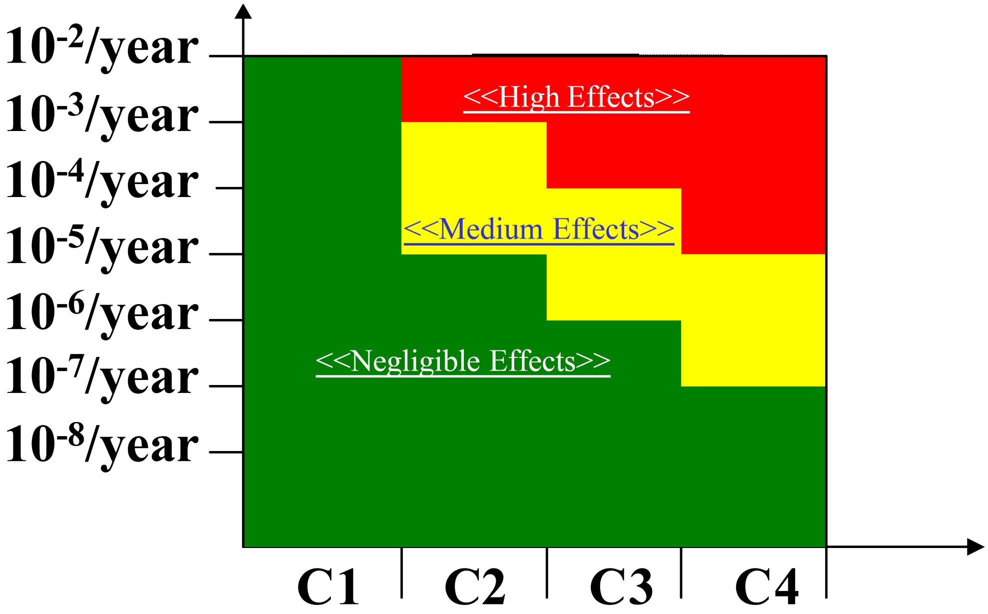


Figure 5.5: Risk matrix for the selection of the RAS (Delvosalle et al., 2004).

8. Organize the information for the calculation of the severity, providing: the equipment type and its design/rupture temperature and pressure, the properties of the hazardous substances and their quantities, the operating conditions, the bow-tie diagram for the RAS with the safety barriers, the frequency of the DP, the meteorological conditions, etc.

5.5.2 Representative bow-tie diagram for Jonova accident

In this section, the application of the ARAMIS project to the Jonova accident is carried out. The fault tree and event tree referred to the case study with the respective safety barriers are presented and quantified. Information gathered from OCI Nitrogen, Yara International ASA and literature to draw and quantify the bow-tie diagram were utilized.

5.5.2.1 Fault tree

Following the main steps presented in the previous section, the Methodology for the Identification of Major Accident Hazards (MIMAH) is applied. The fault tree presented in Figure 5.6 is based on the generic fault tree presented in the ARAMIS project. The selection of the representative branches considers the most common problems of the ammonia storage tanks based on information gathered from a collaboration with Yara International ASA and from the literature review. As a representative fault tree, it cannot be considered as exhaustive. More detailed fault trees developed with ARAMIS project are shown in Appendix C. Representative branches associated to the following unwanted events are selected:

- Over-pressure: according to Christou et al. (1999) and Hossain (2012), over-pressure is considered one of the most common causes of accident for the ammonia storage tank. Over-pressure can be generated from rollover phenomenon and overfilling (Hossain, 2012). Both are proposed as representative branches.

- Brittle rupture: as mentioned in Chapter 3 (concerns about ammonia plant), brittle fracture represents an issue for the ammonia storage tank. As shown by Ojha and Dhiman (2010), brittle fracture can lead to major accidents. For instance, in 1973 at Potchefstroom (South Africa), 38 ton of ammonia were released causing 18 deaths.

- Under-pressure (pressure below the containment limit of the vessel): according to Hossain (2012), a common cause for the ammonia release is the under-pressure. For instance, when the outflow is more than the inflow (e.g., during emptying), a catastrophic rupture due to vacuum conditions can occur.

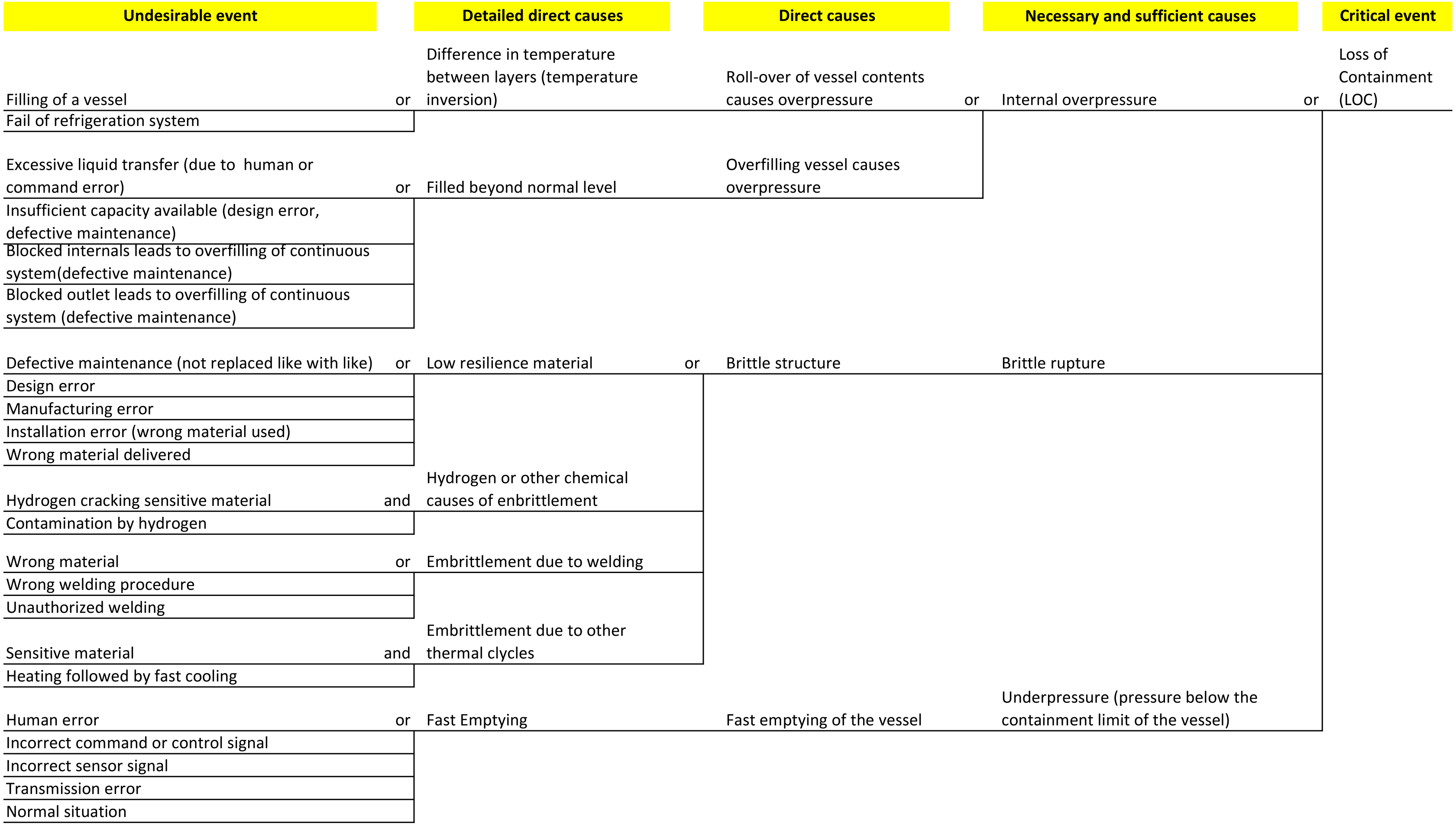


Figure 5.6: Representative fault tree for an ammonia storage tank built with the MIMAH method.

Human barriers	**PFD (from literature, industry)**	**Level of confidence**
Prevention	10^{-2} (PFD)	LC 2
Normal operation	10^{-2} (PFD)	LC 2
Intervention	10^{-1} (PFD)	LC 1

Table 5.2: Level of confidence of human actions (Delvosalle et al., 2004).

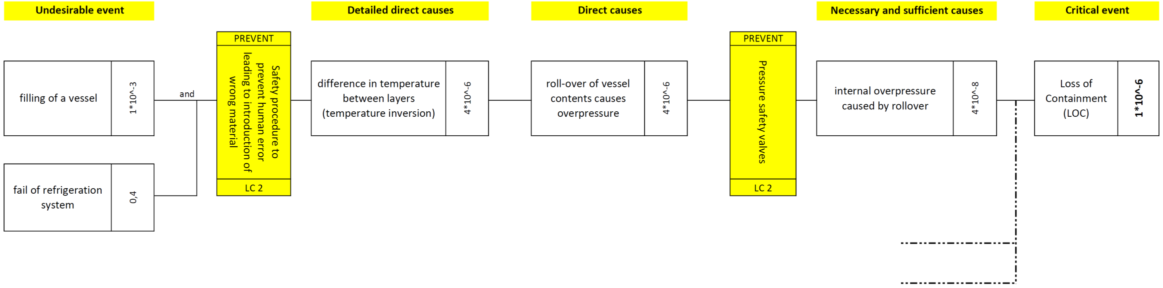


Figure 5.7: Branch representing the Jonova incident in 1989. Safety barriers are considered.

From the fault tree reported in Figure 5.6, the branch representing the Jonova accident that led to the catastrophic rupture was selected (Figure 5.7). Then, the MIRAS methodology was applied. According to Andersson (1990), all the refrigeration compressors were out of operation. Although the warm ammonia should be sent to the flare stack to prevent over-pressurization (Hossain, 2012), according to ARIA Database (access date: october, 2017), 14 ton were introduced from the bottom of the tank. Moreover, the safety valves were not designed for such overpressure. The quantification of the performance of the safety barriers presented in Figure 5.7 was performed according to Table 5.2 for the barrier regarding ”Safety procedure to prevent human error leading to the introduction of wrong material”. Regarding the ”pressure safety valves”, a Level of Confidence 2 is typically considered (Delvosalle et al., 2004).

5.5.2.2 Event tree

A generic event tree for the ammonia storage tank is presented in Figure 5.8. The red branch represents the Jonova accident. The construction and the quantification of the event tree is based on information collected from OCI Nitrogen. To support this phase, information gathered from the ARAMIS project and Uijt de Haag and Ale (1999) were employed.

Two barriers are considered in Figure 5.8: the internal evacuation of the personnel and the intervention of the fire crew. According to V. Ramabrahmam et al. (1996), the internal evacuation is carried out by two main responsible, i.e, the on-site works main controller (WMC) and the on-

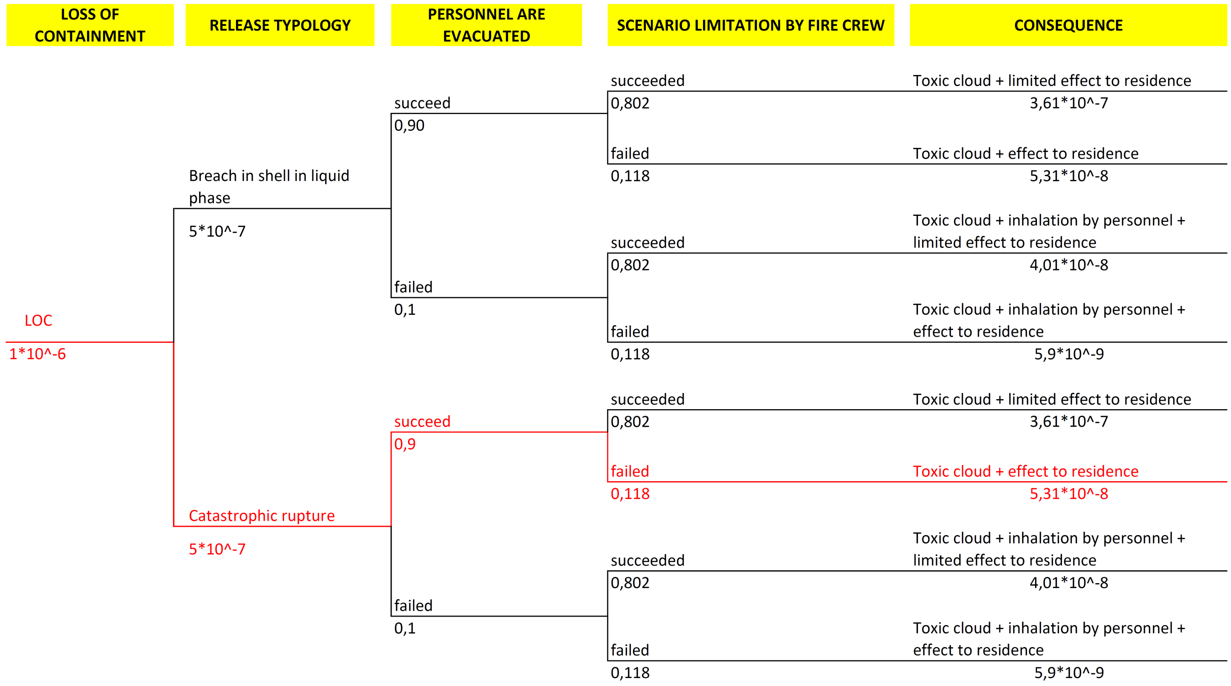


Figure 5.8: Generic event tree for an ammonia storage tank. The branch coloured in red represents the Jonova accident.

site works incident controller (WIC). Once alerted, the former takes charge of the situation and coordinates from the emergency control room all the Emergency Response Team (ERT), which includes different departments, i.e., the Fire, safety and environmental, Personnel, Security and Medical department. According to V. Ramabrahmam et al. (1996) and Center for Chemical Process Safety, CCPS (1995), the WMC has to perform the following main steps:

- Informs district/local emergency authorities/local fire, police and medical services;
- Communicates and arranges additional help for WIC from other plants, if required (under a mutual aid scheme);
- Checks the wind direction and looks for secondary effects;

According to V. Ramabrahmam et al. (1996) and CCPS (1995), the WIC has to direct his team to control the LOC and operates to ensure the safety of the rest of the plant. In particular, once the WIC receives the call from the incident identifier, he has to:

- Alerts works main controller (WMC) through telephone/radio;
- Concentrates only on containing the source of emissions directing his team to: stop loading and unloading operations; stop all transfer operations in the plant and to relieve the tank pressure through the flare stack;

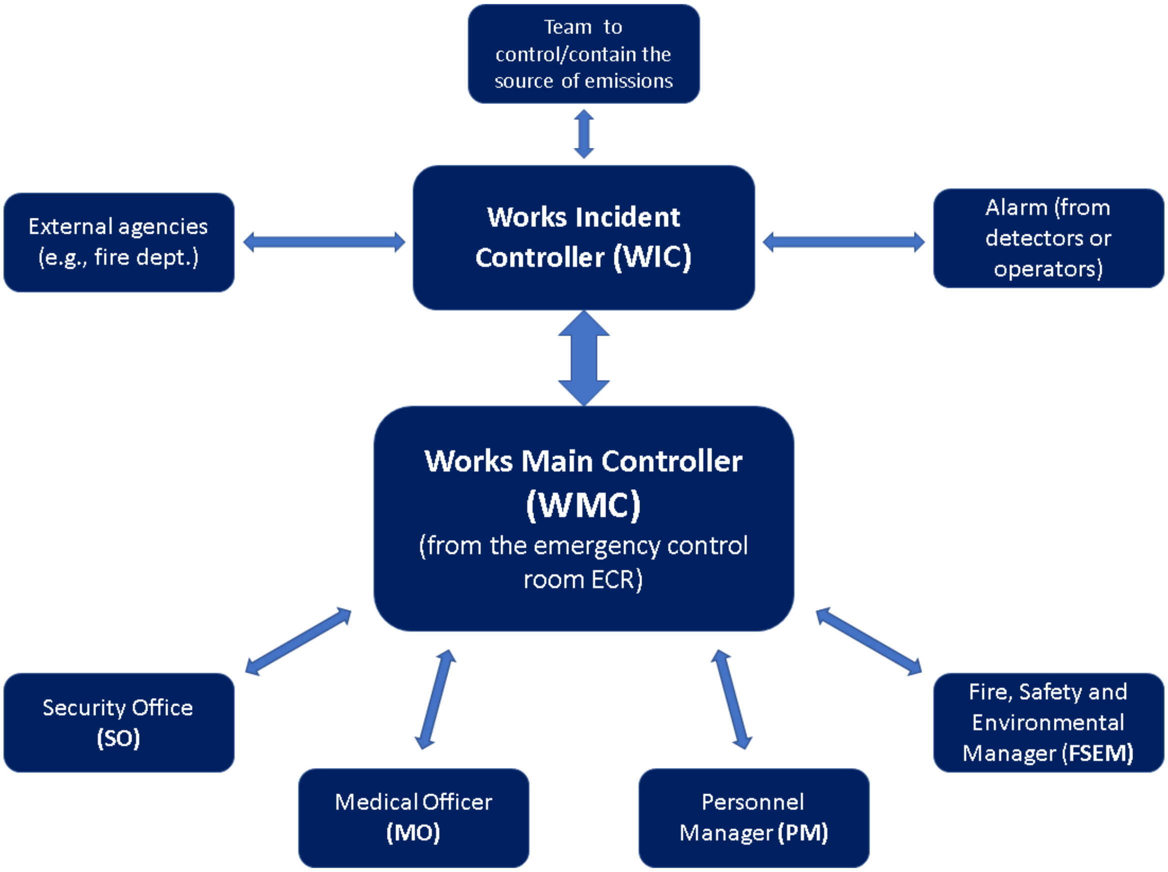


Figure 5.9: An example of communication network of the on-site emergency plan.

- Activates fire-fighting system/water curtains, etc.
- Ensures the safety of the electrical machinery.

An example of communication network between stakeholders is proposed in Figure 5.9.
The other barrier considered in the event tree (Figure 5.8) is the fire crew intervention. They can mitigate the consequences of the LOC setting, e.g., water curtains. But their intervention can be considered successful only if it happen within a limited period of time. According to Wu and Chen (2016), the time required is given by the contribution of three times:

1. Times for the receipt of information;
2. Times for preparation;
3. Times for arrival.

Moreover, for the case study considered, an intervention of the fire crew within five minutes from the call can be assumed as successful.

Chapter 6

Results

Three methods presented in Chapter 4 (REWI, Petro-HRA and TEC2O) were applied to the case study. Only the main results from each method are summarized in the next sections. The discussion of the results will be performed in the next chapter.

6.1 REWI method

The REWI method considers a set of resilience-based indicators for the prevention of accidents. As shown in Chapter 5, a selection of the most important general issues was performed. According to Øien et al. (2010), each of the three top-level CSFs (i.e., Risk Awareness, Response capacity,

CSF level 1	CSF level 2	General issues	Indicators
Risk Awareness	Risk undestanding	Information about quality of barrier support fuction	1.1.5.3: No. of procedures not up to date
Response capacity	Response	Training	2.1.1.3: No. Of emergency preparedness exercises last three months
Response capacity	Robustness	Communication between actors	2.2.4.1: No. of cases which communication between actors has been inadequate
Response capacity	Resourcefulness/ Rapidity	Adequate resource allocation and staffing	2.3.1.1: Amount of overtime worked
Support	Decision support	Adequate ICT decision support system	3.1.2.2: No. of times critical ICT systems have failed or are inoperable/down

Table 6.1: List of REWI indicators selected for the ammonia storage tank (Øien et al., 2010).

Support) should have at least one indicator allocated to cover all the resilience dimensions. To achieve this goal, a set of the most important second level CSFs with the respectives general issues was selected. Eventually, the choice of the most appropriate indicators was performed. Five indicators representing the general issues selected that could have prevented the Jonova accident were identified. These results are summarized in Table 6.1.

6.2 Petro-HRA

The evacuation barrier is taken as a representative example to show the application of the Petro-HRA method for assessing the performance of operational safety barriers. The evacuation represents one of the last barriers on the bow-tie diagram (before the Dangerous Phenomena), so its success/fail has a strong impact on the final consequences. Moreover, a strong influence from human and organizational factor by carrying out the evacuation was observed (see section 5.5.2.2).

As discussed in Chapter 4, Petro-HRA consist in 7 steps:

1. Scenario definition;
2. Qualitative data collection
3. Task Analysis
4. Human Error Identification
5. Human Error Modeling
6. Human Error Quantification
7. Human Error Reduction

In the following sections, the main results from the application of this method are presented. The HER was not performed because not relevant for the comparison with the other methods. However, HER would be the main output of HRA and its importance is acknowledged.

6.2.1 Scenario definition

The scenario is defined by the internal evacuation of the personnel. Two manager playing key roles to carry out the evacuation were found: the on-site works main controller (WMC) and the on-site works incident controller (WIC) (V. Ramabrahmam et al., 1996). To achieve a successful evacuation, both managers have to interact each other and with other stakeholders.

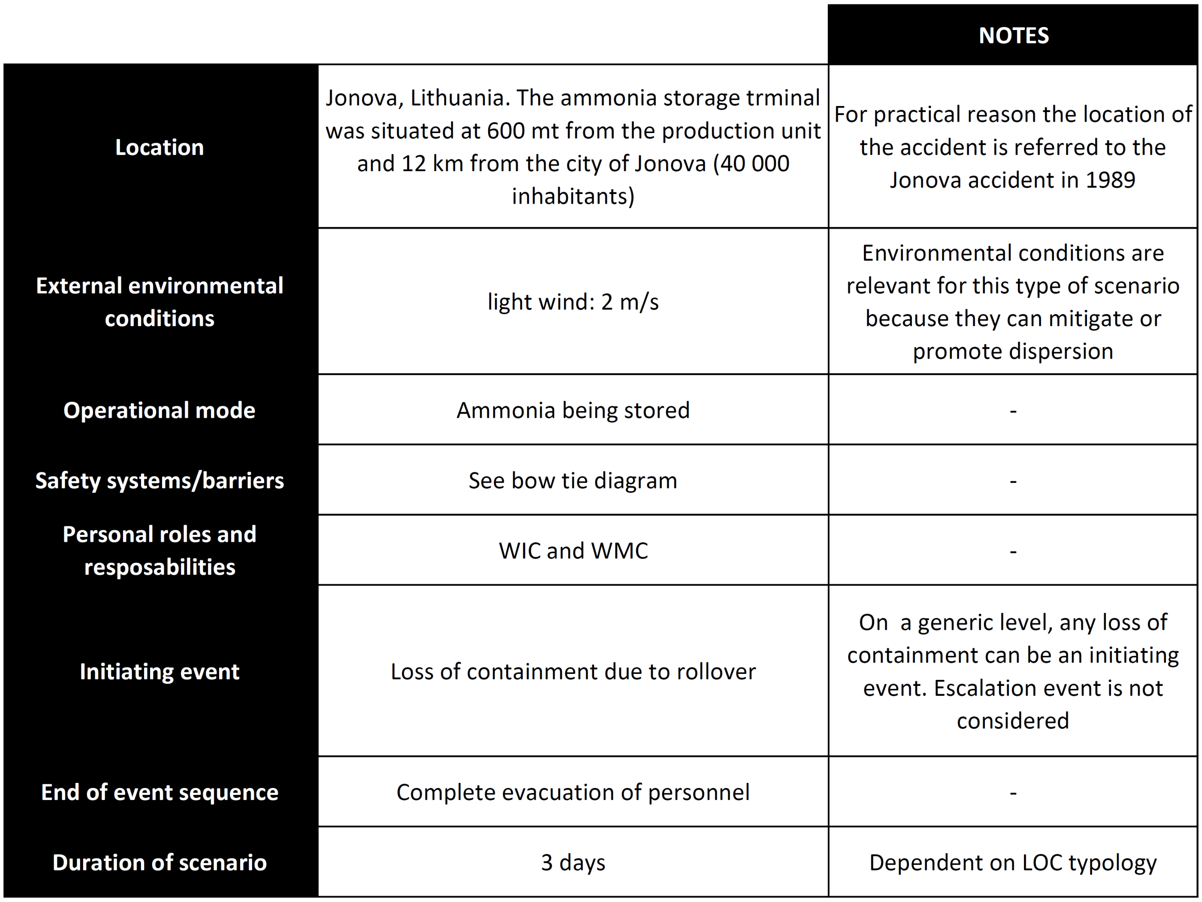
Based on information gathered from the case study (see Chapter 5) and the structure of the emergency plan given by V. Ramabrahmam et al. (1996), the scenario description can be summarized in Table 6.2.

6.2.2 Qualitative data collection

A more specific data gathering through interviews about human performance factors should be performed. In this work, this step is performed through a literature review about the organization of the emergency response plan.

6.2.3 Task analysis

The task analysis describes the steps carried out by the responsible. In this work, a Hierarchical Task Analysis for both WMC and WIC is performed. HTA is presented in Figure 6.1 and Figure 6.2 for the WIC and WMC respectively. As a starting point, a simple cognitive behavioral model to identify the main operator's actions to complete the task was adopted. It breaks down the



		NOTES
Location	Jonova, Lithuania. The ammonia storage trminal was situated at 600 mt from the production unit and 12 km from the city of Jonova (40 000 inhabitants)	For practical reason the location of the accident is referred to the Jonova accident in 1989
External environmental conditions	light wind: 2 m/s	Environmental conditions are relevant for this type of scenario because they can mitigate or promote dispersion
Operational mode	Ammonia being stored	-
Safety systems/barriers	See bow tie diagram	-
Personal roles and resposabilities	WIC and WMC	-
Initiating event	Loss of containment due to rollover	On a generic level, any loss of containment can be an initiating event. Escalation event is not considered
End of event sequence	Complete evacuation of personnel	-
Duration of scenario	3 days	Dependent on LOC typology

Table 6.2: Step 1: scenario definition.

task goal into four phases: detect, diagnose event, decide on actions and execute actions. Each phase was broken down into main task steps presented in Figure 6.1 and Figure 6.2.

6.2.4 Human Identification Error

The tasks defined through HTA are analyzed to identify the potential human error that can occur in the scenario. To support this step, a list of error taxonomy from the Systematic Human Error Reduction and Prediction Approach (SHERPA) was used. Moreover, an evaluation of the likely

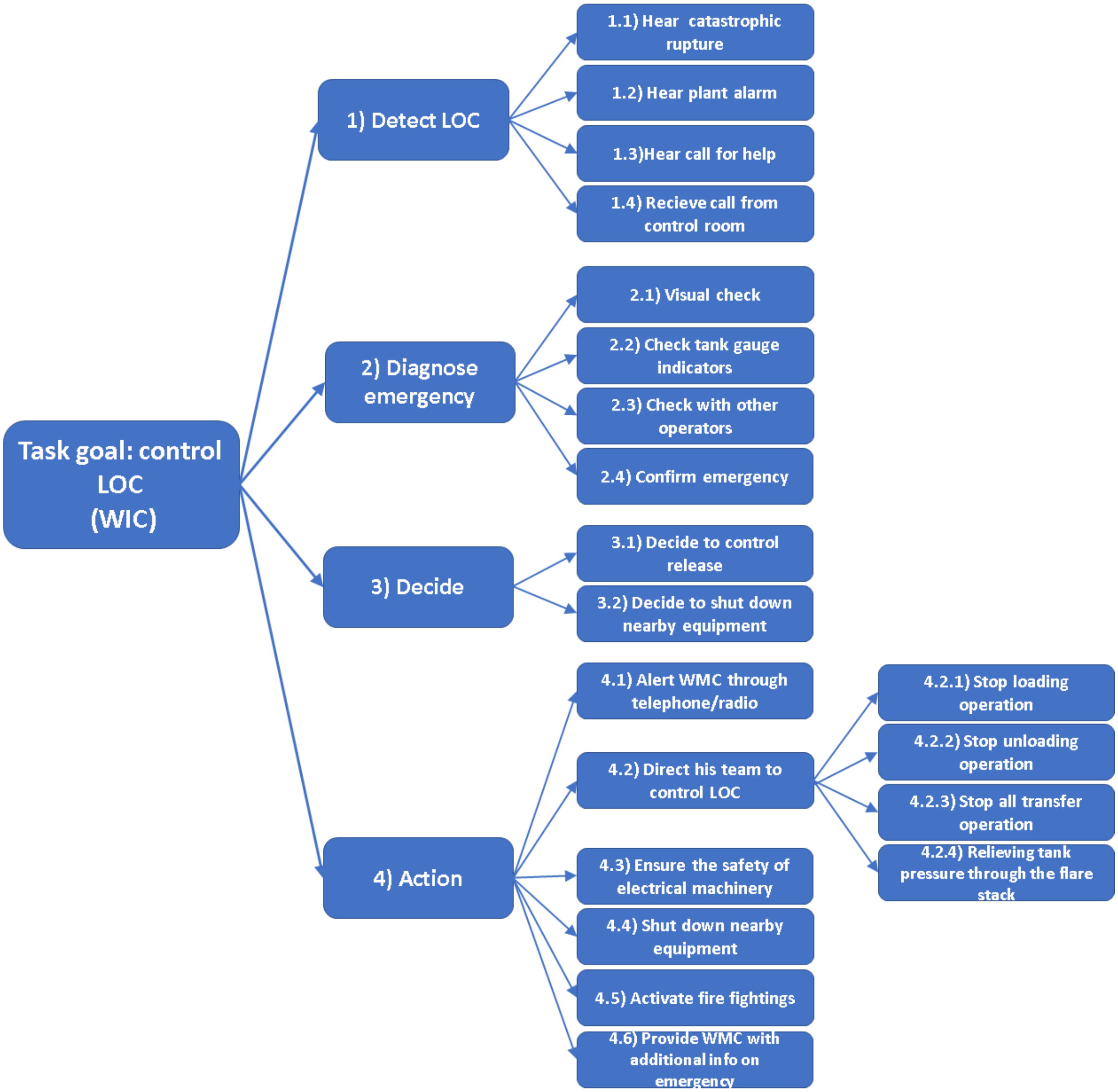


Figure 6.1: Hierarchical Task Analysis for works incident controller (WIC) .

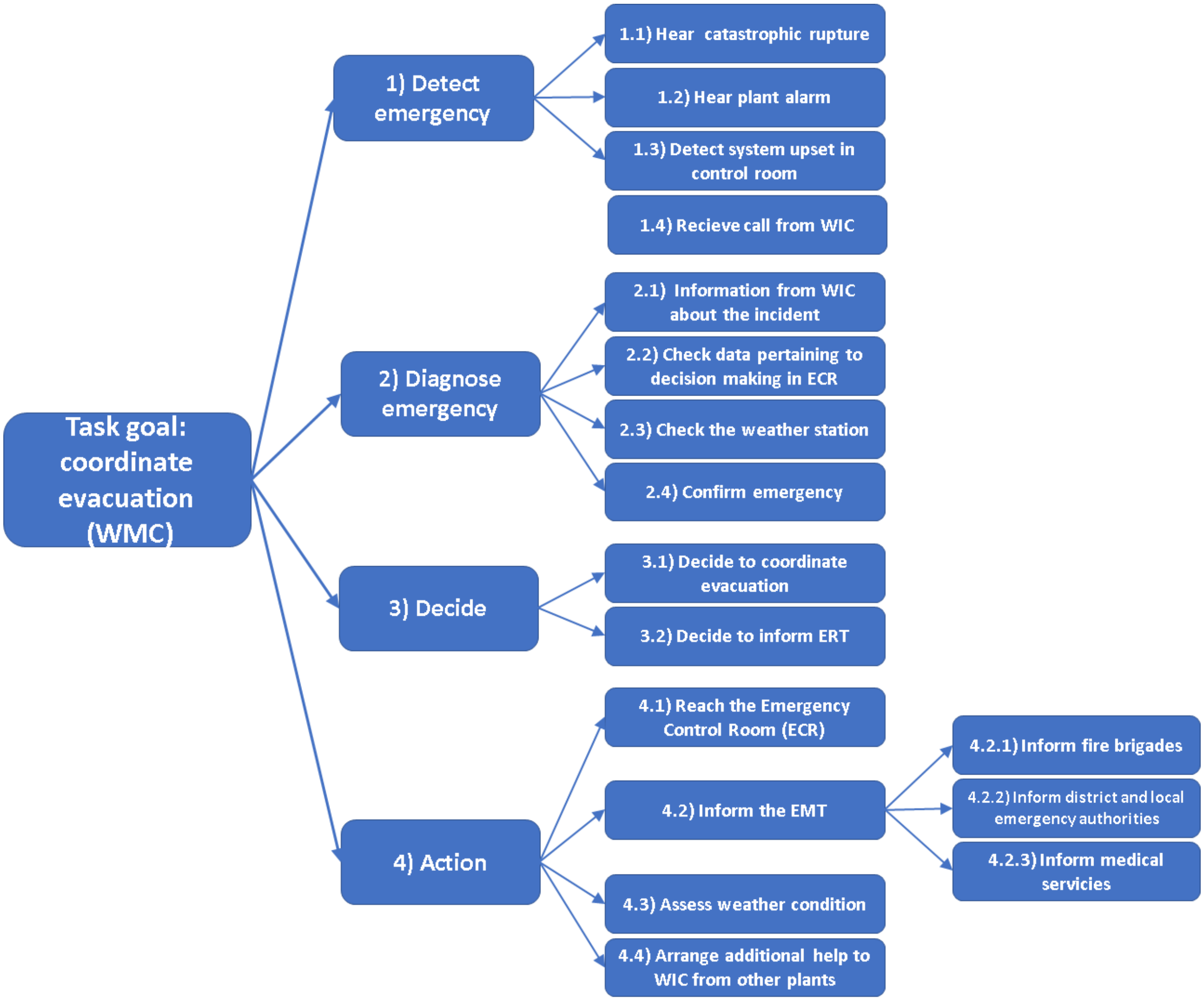


Figure 6.2: Hierarchical Task Analysis for works main controller (WMC) .

consequence and possible recovery opportunity was performed. This analysis was carried out for both WIC and WMC roles. The results are organized in Table 6.3 and Table 6.4 for the WIC and the WMC respectively.

Step No.	Description	Cue	Feedback	HMI	Person responsible	Potential error	Likely consequences	Recovery opportunity	Further analysis
1.1	hear catastrophic rupture	audible sound of catastrophic rupture			WIC	WIC does not hear the sound of catastrophic rupture	delay detection	additional indications from 1.2 to 1.4	N
1.2	Hear plant alarm	audible sound of alarms		speaker	WIC	WIC does not hear the sound of the alarms	delay detection	additional indications from 1.2 to 1.5	N
1.3	Hear call for help	audible call from operator			WIC	WIC does not hear the call	delay detection	additional indications from 1.2 to 1.6	N
1.4	Recieve call from control room	audible sound of call		telephone /radio	WIC	WIC does not hear the call	unlikely to detect catastrophic rupture in time for evacuation	none	Y
2.1	Visual check	indication from step 1			WIC	WIC does not visually check	uncertainty or delay in diagnose of event	additional check in 2.2 and 2.3	N
						WIC misdiagnoses LOC	unlikely to diagnose the catastrophic rupture in time for evacuation	additional check in 2.2 and 2.3	N
						check takes too long	delayed step 3	none	Y
2.2	check tank indicators	indication from step 1		tank gauge indicators	WIC	WIC does not visually check	uncertainty or delay in diagnose of event	additional check in 2.3	N
						WIC misdiagnoses of gauge indicators	unlikely to diagnose the catastrophic rupture in time for evacuation	additional check in 2.3	N
						check takes too long	delayed step 3	none	Y
2.3	check with other operators	indication from step 1		telephone /radio	WIC	WIC does not check with others	uncertainty and delay in diagnose of event	none	Y
						WIC misunderstands	uncertainty and delay in diagnose of event	none	Y
						check takes too long	delayed step 3	none	Y
2.4	Confirm emergency	results from step 2.1 to 2.3			WIC	WIC does not diagnose that this is a catastrophic rupture	WIC does not start LOC control procedure	none	Y
3.1	decide to control release	result from diagnosis and WIC training			WIC	WIC decides to not control LOC	uncontrolled LOC	none	Y
						WIC decides to control LOC not in time	delayed step 4	none	Y
3.2	decide to shut down nearby equipment	result from diagnosis, WIC training and system knowledge			WIC	WIC decides to not shut down the nearby equipment	escalation	none	Y
4.1	alert WMC through telephone/radio	results from step 3	answer from WMC	telephone /radio	WIC	WIC does not call WMC	WMC not informed about LOC	none (WMC would have recovery opportunity)	N
						WIC does not call WMC in time	WMC not informed in time about LOC	none (WMC would have recovery opportunity)	N
4.2.1	stop loading operation	result from 3.1	flow rate indicators		WIC	WIC does not direct his team to stop loading	increase release	none	Y
						WIC does not direct his team to stop loading in time	increase release	step 4.2.4	N
4.2.2	stop unloading operation	result from 3.2	flow rate indicators		WIC	WIC does not direct his team to stop unloading	escalation	step 4.2.3	N
						WIC does not direct his team to stop unloading in time	escalation	step 4.2.3	N
4.2.3	stop all transfer operation	result from 3.2	plant indicators	control panel	WIC	WIC does not direct his team to stop transfer operation	escalation	step 4.3	N
						WIC does not direct his team to stop transfer operation in time	escalation	step 4.3	N
4.2.4	relieving the tank pressure through the flare stack	result from 3.1	tank pressure indicator		WIC	WIC does not direct his team to relieve tank pressure	increased release	none	Y
						WIC does not direct his team to relieve in time the tank pressure	increased release	none	Y
4.3	ensure the safety of electrical machinery	result from 3.2			WIC	WIC does not ensure the safety of electrical machinery	escalation	step 4.4	N
						WIC does not ensure in time the safety of electrical machinery	escalation	step 4.4	N
4.4	shut down nearby equipment	result from 3.2	plant indicators	control panel	WIC	WIC does not shut down nearby equipment	escalation	none	Y
						WIC does not shut down nearby equipment in time	escalation	none	Y
4.5	activate fire fightings	result from 3.1			WIC	WIC does not activate fire fightings	escalation	none	Y
						WIC does not activate fire fightings in time	escalation	none	Y

Table 6.3: Human Error Identification for works incident controller (WIC).

Step No.	Description	Cue	Feedback	HMI	Person responsible	Potential error	Likely consequences	Recovery opportunity	Further analysis
1.1	hear catastrophic rupture	audible sound of catastrophic rupture			WMC	WMC does not hear the sound of catastrophic rupture	delay detection	additional indications in 1.2, 1.3, 1.4	N
1.2	Hear plant alarm	audible sound of alarms		speaker	WMC	WMC does not hear the sound of the alarms	delay detection	additional indications in 1.3 and 1.4	N
1.3	Detect syst. upset from control room	audible sound of alarms and tank indicators		panel	WMC	WMC does not hear sound of alarms or does not check indic.	delay detection	additional indications in 1.3	N
1.4	Recieve call from WIC	audible sound of call		telephone/ radio	WMC	WMC does not recieve the call	unlikely to detect in time that evacuation is required/delayed step 2	none	Y
2.1	Information from WIC about the incident	indication from step 1		telephone/ radio	WMC	WIC misdiagnoses LOC	unlikely to diagnose that evacuation is required by WMC	none	Y
						Information retrieval incomplete	uncertainty or delay in diagnose of the emergency by WMC	additional check in step 2.2	N
2.2	Check data pertaining to decision making in ECR	indication from step 1		panel	WMC	WMC misdiagnose data	uncertainty and delay in diagnose of the emergency	additional check in step 2.1	N
						check takes too long	unlikely to diagnose that evacuation is required	none	Y
2.3	Check the weather station	indication from step 1		weather station	WMC	WMC misdiagnose data	unlikely to diagnose the correct strategy for the evacuation	additional check in step 2.1	N
						WMC does not check data	uncertainty and delay in diagnose of the weather condition	none	Y
2.4	Confirm emergency	results from step 2.1 to 2.3			WMC	WMC does not diagnose that evacuation is required	WIC does not start to coordinate evacuation	none	Y
3.1	Decide to coordinate evacuation	result from diagnosis and WMC training	-		WMC	WMC decides to not coordinate evacuation	evacuation not carried out	none	Y
						WMC decides to coordinate evacuation not in time	delayed step 4	none	Y
3.2	Decide to inform ERT	result from step 2 and WMC training	-	telephone/ radio	WMC	WMC decides to not inform ERT	escalation	call to authorities by neighbours or population	N
						WMC decides to inform ERT not in time	delayed step 4.2	none	Y
4.1	Reach the Emergency Control Room (ECR)	result from step 3.1			WMC	WMC does not reach the ECR	evacuation not started	none	Y
						WMC does not reach the ECR in time	evacuation not started in time	none	Y
4.2.1	Inform fire brigades	result from step 3.2	answer from fire brigades	telephone/ radio	WMC	WMC does not inform the fire brigades	escalation	none	Y
						WMC does not inform the fire brigades in time	escalation	none	Y
4.2.2	Inform district and local emergency authorities	result from step 3.2	answer from district and emergency authorities	telephone/ radio	WMC	WMC does not inform the district and local emergency authorities	escalation	step 4.2.1 and 4.2.3	N
						WMC does not inform the district and local emergency authorities in	escalation	step 4.2.1 and 4.2.3	N
4.2.3	Inform medical services	result from step 3.2	answer from medical services	telephone/ radio	WMC	WMC does not inform the medical services	escalation	step 4.2.1 and 4.2.2	N
						WMC does not inform the medical services in time	escalation	step 4.2.1 and 4.2.2	N
4.3	Assess weather condition	result from step 3.1		weather station	WMC	WMC does not assess weather condition	escalation	comunication with WIC	N
4.4	Arrange additional help to WIC from other plants	result from step 3.1		telephone/ radio	WMC	WMC does not help WIC	escalation	ERT cooperates with WIC	N
						WMC does not cooperate with neighbour plants	escalation	ERT cooperates with neighbours	N

Table 6.4: Human Error Identification for Works Main Controller (WMC).

6.2.5 Human Error Modelling

The modeling of the task steps presented in Section 6.2.4 through an Operator Action Event Tree (OAET) was performed. In the OAET showed in Figure 6.3, two main branches can be distinguished:

- fail to control LOC: which represents the WIC role;
- fail to coordinate evacuation: which represents the WMC role.

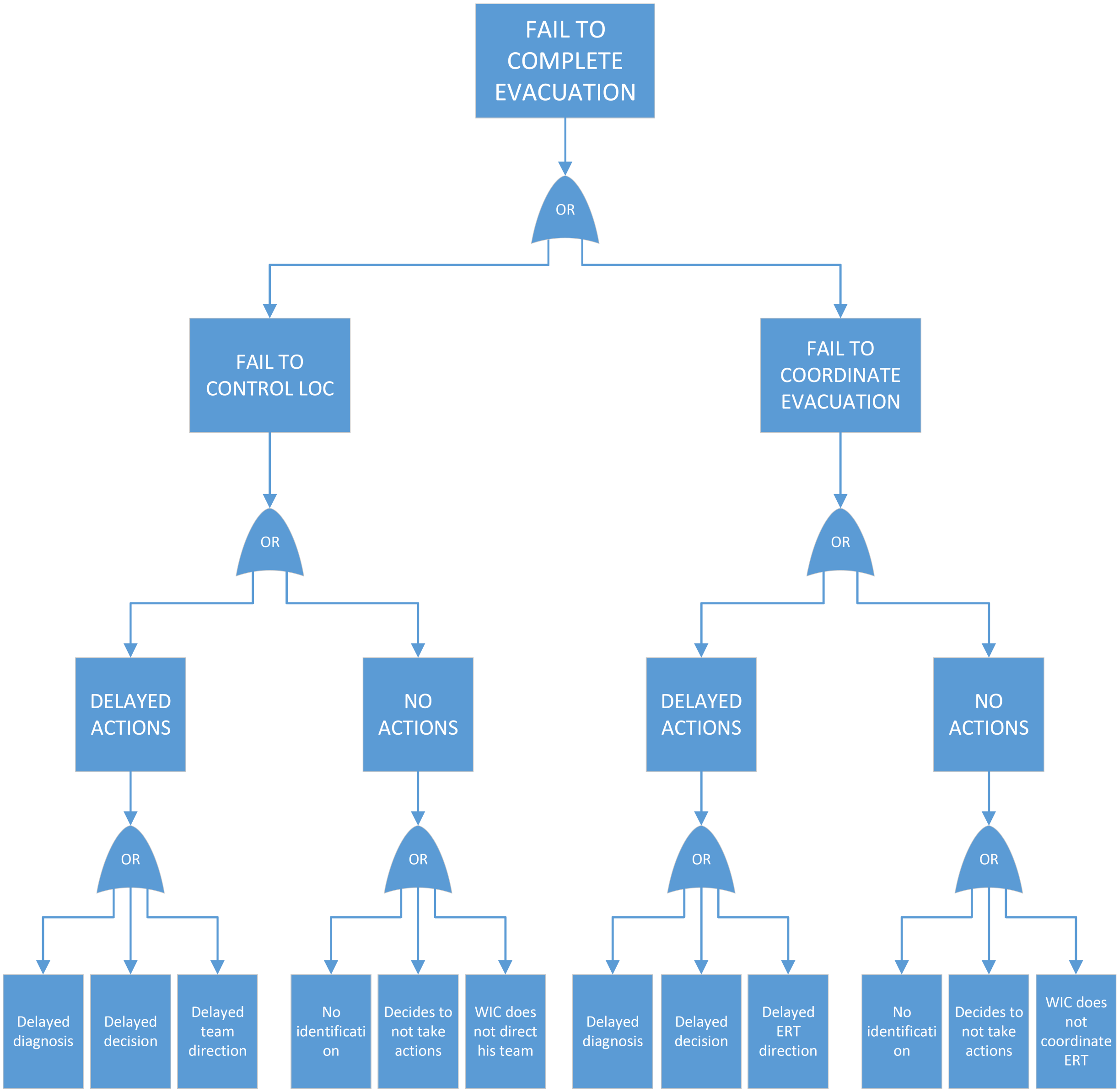


Figure 6.3: Operator Action Event Tree for the evacuation barrier.

Each basic events assigned to both branches represents groups of potential errors identified during the HEI. Then, a set of PSFs for each basic event was assigned (see Table 6.5). The choice was based on the evaluation of the results from the HTA, HEI and HEM.

6.2.6 Human Error Quantification

The quantification of each PSF selected was carried out. The scores were assigned considering the information gathered from the Jonova case study. For instance, a higher HEP to ”Fail to coordinate evacuation” (i.e., the WMC task) was assigned because, according to ARIA Database (access date: october, 2017), local authorities were informed 25 minutes after the accident. As shown in Table 6.5, the final HEP associated with the evacuation barrier is 0,34.

				PSF	Multiplier	Level	Description
FAIL TO COMPLETE EVACUATION (HEP=0,34)	**FAIL TO CONTROL LOC (HEP=0,086)**	DELAYED ACTIONS (HEP=0,078)	Delayed diagnosis (HEP=0,005)	Threat stress	5	Low negative effect on performance.	The operator(s) experiences moderate threat stress. The operator experiences that there is a threat to their own or others' personal safety or a very high threat to self-esteem or professional status.
				Experience/training	0,1	Moderate positive effect on performance.	The operator(s) has extensive experience and/or training on this task and the operator(s) has extensive knowledge and experience to be prepared for and to do the task(s) in this scenario.
			Delayed decision (HEP=0,05)	Threat stress	5	High negative effect on performance.	The operator(s) experiences very high threat stress. In this situation the operator's own or other person's life is in immediate danger.
				Procedures	1	Nominal effect on performance.	The quality of the procedures is adequate and they are followed. The quality of procedures does not affect performance either positively or negatively.
			Delayed team direction (HEP=0,025)	Teamwork	0,5	Low positive effect on performance.	The team is very good on one or more teamwork factors that have been identified as important for the task or scenario in question and teamwork increase the performance
				Threat stress	5	Low negative effect on performance.	The operator(s) experiences moderate threat stress. The operator experiences that there is a threat to their own or others' personal safety or a very high threat to self-esteem or professional status.
		NO ACTIONS (HEP=0,008)	No identification (HEP=0,0025)	HMI	0,5	Low positive effect on performance.	The HMI is specifically designed to make human performance as reliable as possible in this task/tasks of this type.
				Procedures	0,5	Low positive effect on performance.	Procedures are exceptionally well developed, they are followed, and they enhance performance.
			Decides to not take actions (HEP=0,005)	Experience/training	0,1	Moderate positive effect on performance.	The operator(s) has extensive experience and/or training on this task and the operator(s) has extensive knowledge and experience to be prepared for and to do the task(s) in this scenario.
				Threat stress	5	Low negative effect on performance.	The operator(s) experiences moderate threat stress. The operator experiences that there is a threat to their own or others' personal safety or a very high threat to self-esteem or professional status.
			WIC does not direct his team (HEP=0,0005)	HMI	0,5	Low positive effect on performance.	The HMI is specifically designed to make human performance as reliable as possible in this task/tasks of this type.
				Experience/training	0,1	Moderate positive effect on performance.	The operator(s) has extensive experience and/or training on this task and the operator(s) has extensive knowledge and experience to be prepared for and to do the task(s) in this scenario.
	FAIL TO COORDINATE EVACUATION (HEP=0,28)	DELAYED ACTIONS (HEP=0,272)	Delayed diagnosis (HEP=0,005)	Threat stress	5	Low negative effect on performance.	The operator(s) experiences moderate threat stress. The operator experiences that there is a threat to their own or others' personal safety or a very high threat to self-esteem or professional status.
				Experience/training	0,1	Moderate positive effect on performance.	The operator(s) has extensive experience and/or training on this task and the operator(s) has extensive knowledge and experience to be prepared for and to do the task(s) in this scenario.
			Delayed decision (HEP=0,25)	Threat stress	25	High negative effect on performance.	The operator(s) experiences very high threat stress. In this situation the operator's own or other person's life is in immediate danger.
				Procedures	1	Nominal effect on performance.	The quality of the procedures is adequate and they are followed. The quality of procedures does not affect performance either positively or negatively.
			Delayed ERT direction (HEP=0,025)	Teamwork	0,5	Low positive effect on performance.	The team is very good on one or more teamwork factors that have been identified as important for the task or scenario in question and teamwork increase the performance
				Threat stress	5	Low negative effect on performance.	The operator(s) experiences moderate threat stress. The operator experiences that there is a threat to their own or others' personal safety or a very high threat to self-esteem or professional status.
		NO ACTIONS (HEP=0,01)	No identification (HEP=0,0025)	HMI	0,5	Low positive effect on performance.	The HMI is specifically designed to make human performance as reliable as possible in this task/tasks of this type.
				Procedures	0,5	Low positive effect on performance.	Procedures are exceptionally well developed, they are followed, and they enhance performance.
			Decides to not take actions (HEP=0,005)	Experience/training	0,1	Moderate positive effect on performance.	The operator(s) has extensive experience and/or training on this task and the operator(s) has extensive knowledge and experience to be prepared for and to do the task(s) in this scenario.
				Threat stress	5	High negative effect on performance.	The operator(s) experiences very high threat stress. In this situation the operator's own or other person's life is in immediate danger.
			WMC does not coordinate ERT (HEP=0,0025)	HMI	0,5	Low positive effect on performance.	The HMI is specifically designed to make human performance as reliable as possible in this task/tasks of this type.
				Teamwork	0,5	Low positive effect on performance.	The team is very good on one or more teamwork factors that have been identified as important for the task or scenario in question and teamwork increase the performance

Table 6.5: Scores of PSFs and HEP of each task.

6.3 TEC2O

As mentioned in Chapter 4, this method is developed for the Dynamic Risk Assessment. Assuming the magnitude constant over time, the dynamic property is guaranteed by the frequency modification factor Ω(t), which updates the baseline frequency of a selected Dangerous Phenomena over time. In this work, also the TMF is assumed constant over time. An example of representative TMF value is given by Landucci and Paltrinieri (2016c) and considered for this study: TMF=1,18. Then, the assessment of the management modification factor (MMF) was carried out. The selection of indicators applied in TEC2O was based on the set of REWI indicators selected in Section 6.1. A score (”GOOD”=2, ”MEDIUM”=4 or ”BAD”=6) to each TEC2O indicator was assigned. The result of this operation is shown in Table 6.6.
As mentioned in Chapter 4, the Eq. 6.2 to obtain the management average score μ was applied:

$$OP = \sum_{i=1}^{M} \omega_i S_{OPE,i} = 2; \qquad ORG = \sum_{j=1}^{N} \omega_j S_{ORG,j} = 3 \tag{6.1}$$

$$\mu = \omega_{OPE} \times OP + \omega_{ORG} \times ORG = 2,5 \tag{6.2}$$

For each subfactor's indicator, all the weights were assigned as equal and for both ω_{ORG} and ω_{OP} the same weight of 0,5 was assigned. Eventually, the Management Modification Factor through Figure 4.4 can be derived. A μ=2,5 corresponds to MMF of 0,3.
Given the TMF and the MMF, the Ω(t) through Equation 6.3 and the updated frequency F(t) through Equation 6.4 can be calculated. The baseline frequency is referred to the DP selected as representative for the Jonova accident (see Figure 5.8), that is 5,31*10^{-8}.

$$\Omega(t) = TMF \times MMF = 1,18 \times 0,3 = 0,354 \tag{6.3}$$

$$F(t) = F_0 \times \Omega(t) = 5,31 \times 10^{(-8)} \times 0,354 = 1,88 \times 10^{(-8)} \tag{6.4}$$

TEC2O indic.	Description	Score
ORG 1.1.4.1	No. of procedures not up to date	MEDIUM = 4
OPE 2.1.1.3	No. Of emergency preparedness exercises last three months	GOOD = 2
ORG 2.2.1.1	Amount of overtime worked	MEDIUM = 4
ORG 2.2.2.1	No. of cases which communication between actors has been inadequate	GOOD = 2
ORG 3.1.1.1	No. of times critical ICT systems have failed or are inoperable/down	GOOD = 2

Table 6.6: Scores of the selected TEC2O indicators.

6.3.1 Variation of Management Modification Factor over time

Score indicators are changed to simulate the variation of the frequency of a DP over time. The aim is to show how TEC2O is capable to assess risk changes through a periodic revision and update of indicators. As an example, three different values of frequency about different conditions were obtained. The three condition states considered are:

Year 1. results from the case study;

Year 2. after a considerable time, the procedures may not be updated;

Year 3. increasing the amount of overtime worked and a decreasing of emergency preparedness exercises may occur.

Only the indicator scores referred to the last two events were updated. The other indicators were assumed constant and their value can be found in Table 6.6. In Table 6.7, the updated scores for each situation were presented. A simple graphical representation of the frequency trend is shown in Figure 6.4.

	TEC2O ind. updated	**Score**	μ	**MMF**
Year 1	see Table 6.6	see Table 6.6	see Eq. 6.2	0,3
Year 2	ORG 1.1.4.1	”BAD”=6	2,75	0,4
Year 3	ORG 1.1.4.1 OPE 2.1.1.3 ORG 2.2.1.1	”BAD”=6 ”MEDIUM”=4 ”BAD”=6	4	1,1

Table 6.7: MMF changes over time.

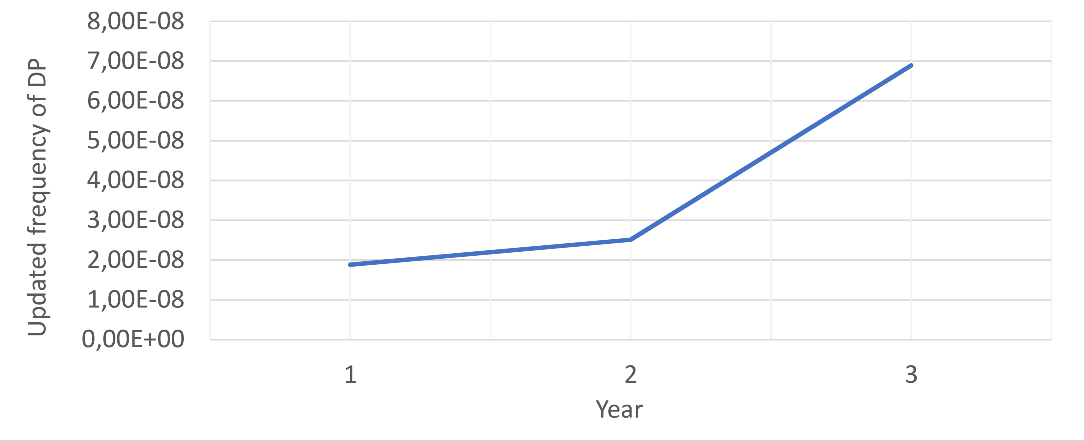


Figure 6.4: Updated frequency over time for the DP related to the case study.

Chapter 7

Discussion

The application of REWI, Petro-HRA and TEC2O to the ammonia storage terminal has shown different levels of detail of these methods.

The REWI method is, first of all, a method for establishing a set of early warning indicators for the prevention of accidents. Its aim is to early identify poor knowledge management or deficient hazard identification, in order to awake risk awareness in the company and implement corrective actions. It mainly addresses organizational aspects related to the entire installation and to all its risks. The selection of the CSF performed in the previous Capter 6. The resilience property of the method accounting all the first level CSF was ensured. More specific second-level CSFs that could have early identified system upset were selected. For instance, a better system knowledge could have prevented the introduction of the warm ammonia into the tank. At least, it could have detected the possibility that rollover occurred (the overpressure occurred 60 min after the warm ammonia introduction). Also, a timely response of the personnel could have mitigated the consequences of the accident (e.g., local authorities were alerted 25 min after the accident (ARIA Database (access date: october, 2017)). Moreover, REWI indicator's system can be reviewed and updated regularly, taking into account changes of the system conditions. As suggested by Øien et al. (2010), to ensure the dynamic characteristic of the method, indicators that are not changing over time anymore should be replaced with others more representative of system conditions.

The main result given by the Petro-HRA method is the HEP for the evacuation barrier of 0,34. This error probability can be used within a QRA giving a more detailed overall risk assessment. It is worth to mention that this result is given assuming a condition of ”low positive effect on performance” or ”Nominal effect on performance” for the most of the PSFs. An exception was made for the ”threat stress” of the event ”delayed decision” of the WMC, where worst score was assigned. This exception was made to stress the responsibility of the WMC in the Jonova accident, where local authorities were alerted 25 minutes after the catastrophic rupture. Despite these ”not-so-conservative” assumptions, the HEP seems to be over-conservative respsct to the

probability of failure estimated through ARAMIS (i.e. 0,1). This can be due to the fact that Petro-HRA is a novel technique in its early stage, still needing thorough validation. For this reason, some tuning of the scores could be necessary. However, the real strength of this method is the support to rigorous human error reduction. It is done providing a systematic approach which points out factors and systems that can be improved to reduce the HEP and the overall system risk. The quantification can highlight where the human error reductions are necessary.
The TEC2O method has shown how the frequency modification factor Ω(t) changes during the lifetime of the plant, giving a dynamic variation of the DP frequency. It is worth to mention that the magnitude of the DP is assumed constant over time. But magnitude in a storage tank can vary significantly due to the quantity of the substance stored. To assess risk in a more realistic way, also the modeling of consequences has to be performed. In this work, dynamic dimension is only addressed to the MMF. This method was capable to assess risk changes over time updating the selected indicators. Moreover, the set of indicators employed in this work proposed by Landucci and Paltrinieri (2016c) is not "closed". Also, it is possible to change weights of each indicator to penalize more critical aspects, even during the process life-cycle. To get more accurate results, indicators and their weights should be modified by a preliminary workshop with the company. However, the TEC2O method has proved capable to represent the risk picture accounting technical, human and organizational factors, combining the strength of the HRA methods (i.e. systematic way to assess human and organizational factors) as Petro-HRA to the dynamic and resilience characteristic of the REWI methodology. However, a preliminary HRA for a better selection of indicators can be performed. But HRA techniques are typically time-consuming, so its application depends on the trade-off between the level of accuracy desired and time available.

Eventually, the REWI indicators and the PSF from Petro-HRA were compared to find out relationship between the REWI indicator's structure and the construction of the performance shaping factors. A similar work was carried out by Landucci and Paltrinieri (2016c), where TEC2O

PSF	**CSF**	**REWI indic.**	**Description**
Procedures	Risk Awareness	1.1.5.3	No. of procedures not up to date
Experience/ training	Response capacity	2.1.1.3	No. Of emergency preparedness exercises last three months
Teamwork	Response capacity	2.2.4.1	No. of cases which communication between actors has been inadequate
Threat stress	Response capacity	2.3.1.1	Amount of overtime worked
HMI	Support	3.1.2.2	No. of times critical ICT systems have failed or are inoperable/down

Table 7.1: Association between PSF and REWI indicators applied for the case study.

indicators were associated with SPAR-H Performance Shaping Factors. They showed how each PSFs can have influence on technical, human and organizational aspects. In Table 7.1, an association of the REWI indicators found in Section 6.1 and the PSF found in Section 6.2 is proposed. According to Table 7.1, a set of PSFs to each CSF can be assigned (Table 7.2).

	CSF 1: Risk Awareness	**CSF 2: Response Capacity**	**CSF 3: Support**
PSF (Petro-HRA)	Procedure, Stress	Experience/Training, Stress	HMI

Table 7.2: Association between CSF and Petro-HRA indicators.

Chapter 8

Conclusion

The importance of human and organizational factors to prevent major accidents was already outlined for the nuclear and afterwards for the petroleum industry. Several techniques were developed and adapted to these sectors. With the present work, the necessity to study the human and organizational factors also for the chemical process industry is pointed out. As an example, the ammonia production plant was analyzed and the main concerns related to each section of the plant were discussed. The incident database analysis on ammonia plant has shown that human and organizational factors are the second cause of accidents, incidents or near misses, right after technical failures. A selection among different models to better represent these aspects was performed. Indicator-based methods are well established in industries being easy to apply and update. So, the application of REWI, Petro-HRA and TEC2O to a selected case study focusing on human and organizational factors was carried out. A real case study (i.e., rupture of the cryogenic ammonia storage tank in Lihuania,1989) to evaluate accomplishments of these models was considered.The REWI outcome is a list of indicators being the operationalization of resilience concept. Their monitoring could have early identified the system upset preventing the accident. The Petro-HRA step-method was applied to the internal evacuation barrier to clarify and quantify the roles and responsibilities of the personnel involved. The probability of failure of the evacuation barrier seems to be over-conservative. An additional tuning of the PSFs scores could be required. Despite that, Petro-HRA was capable to point out where more corrective actions are necessary, in order to reduce the overall risk. The TEC2O application demonstrates how human and organizational factors can accounted whith technical factors to give a more complete and realistic risk assessment. It shows how a systematic update of the resilience-based indicators can manage the risk in a proactive way, showing the variation of the risk related to a specific DP over time. Moreover, a preliminary HRA technique (e.g., Petro-HRA) to make a more appropriate selection of the indicators may be carried out.

Appendix A

Acronyms

AIChE American Institute of Chemical Engineers

API American Petroleum Institute

APSRF Ammonia Plant Safety and Related Facilities

ARIA Analysis, Research and Information on Accidents

BARPI Bureau for Analysis of Industrial Risk and Pollution

BBN Bayesian Belief Networks

BORA-Release Barrier and Operational Risk Analysis of hydrocarbon releases

CE Critical Event

CSF Contributing Success Factor

DC Direct Cause

DDC Detailed Direct Cause

DEA Diethanolamine

DGS Dry Gas Seal

DP Dangerous Phenomena

DRA Dynamic Risk Assessment

ERT Emergency Response Team

ET Event Tree

FT Fault tree

HCL Hybrid Causal Logic

HEI Human Error Identification

HEM Human Error Modelling

HEQ Human Error Quantification

HFE Human Failure Events

HRA Human Reliability Analysis

HSE Health and Safety Executive

HTA Hierarchical Task Analysis

HTHA High Temperature Hydrogen Attack

ICT Information and Communication Technology

IFE Institute for Energy Technology

LC Level of Confidence

LIOH Leading Indicators of Organizational Health

LNG Liquefied Natural Gas

LOC Loss Of Containment

LPI Loss of Physical Integrity

MACHINE Model of Accident Causation using Hierarchical Influence NEtwork

ME Major Event

MEA Monoethanolamine

MHIDAS Major Hazard Incident Data Service

MIMAH Methodology for the Identification of Major Accident Hazards

MIRAS Methodology for the Identification of Reference Accident Scenarios

MMF Management Modification Factor

NPK nitrogen, phosphorus, and potassium

NRC National Response Center

NSC Necessary and Sufficient Cause

NTNU Norwegian University of Science and Technology

OAET Operator Action Event Tree

PSA Pressure Swing Adsorption

PSF Performance Shape Factor

QRA Quantitative Risk Assessment

RAS Reference Accident Scenarios

REWI Resilience Based Early Warning Indicator

SCC Stress Corrosion Cracking

SCE Secondary Critical Event

SHERPA Systematic Human Error Reduction and Prediction Approach

SLIM Success Likelihood IndexMethod

TCE Tertiary Critical Event

TEC2O TECnical Operational and Organizational factors

TMF Technical Modification Factor

TSA Temperature Swing Adsorption

TTA Tabular Task Analysis

TTS Technical Condition Safety

UE Undesirable Events

VCE Vapour Cloud Explosion

WIC Works Incident Controller

WMC Works Main Controller

Appendix B

Ammonia plant incident database

Date	Location	Substance	Incident type	Origin	General cause	Specific cause	Injured	Evacuated	Killed	Damage	Section	Quantity (ton)
11/07/1959	Ube, Japan	Oxygen, Syngas	EXPLODE; FIRE	PROCESS - PVESSEL	PROCOND	GENERALOP	44	0	11	240 M yen	CO2 REMOVAL	
1965	Pasadena, TX	Hydrogen; Ammonia	FIRE				3	0	2			
29/12/1966	LUDWIGSHAFEN; GERMANY	AMMONIA, HYDROGEN	RELEASE	PROCESS-PIPEWORK; HEATXCHANG	HUMAN; MECHANICAL	DESIGN	62	0	0			
18/02/1970	DEER PARK; TEXAS; USA	HYDROGEN	EXPLODE	PROCESS-PVESSEL	INSTRUMENT; HUMAN	DESIGN	1	0	0		REFORMING	
21/12/1971	ELLESMERE PORT; CHESHIRE; UK	SYNGAS	RELEASE, FIRE	PROCESS-PUMP	MECHANICAL - EXTERNAL	FLANGCOUPL - EXTNLFIRE	1	0	0	US$ 0.50 x 10E6	REFORMING	
09/07/1972	SAKAI CITY; OSAKA; JAPAN	Ammonia	RELEASE	PROCESS-PIPEWORK	MECHANICAL	CORRODE	0	0	0		AMMONIA SYNTHESIS	
26/09/1973	Kawasaki, Kanagawa, Japan	Hydrogen	RELEASE; FIRE	PROCESS - PVESSEL	HUMAN; MECHANICAL	MAINTAIN; FLANGCOUPL	0	0	0		DESULFURIZATION	
02/10/1973	CAMROSE; ALBERTA; CANADA	HYDROGEN SULPHIDE	RELEASE	PROCESS-PIPEWORK	MECHANICAL	OVERPRES	0	800	0			
16/09/1978	Immingham, UK	Syngas	RELEASE; EXPLODE				0	0	0			
01/04/1980	Tokuyama City, Yamaguchi Pref.	Nitrogen	EXPLODE	PROCESS - PVESSEL	MECHANICAL; HUMAN	BRITTLE; MAINTAIN; COMPAIR	0	0	0		DESULFURIZATION	
01/09/1981	Czechoslovakia	Syngas	RELEASE; EXPLODE				0	0	0			
01/10/1981	CZECHOSLOVAKIA	SYNGAS	RELEASE, FIRE	PROCESS-PVESSEL	HUMAN; MECHANICAL	MAINTAIN; OVERPRES	29	0	6		REFORMING	12
05/01/1982	FEDMIS; SOUTH AFRICA	HYDROGEN, AMMONIA	EXPLODE; FIRE	PROCESS-PVESSEL			0	0	0		REFORMING	
11/11/1982	LAKE CHARLES; CALIFORNIA; USA	NITROGEN, HYDROGEN	EXPLODE; FIRE	PROCESS-PIPEWORK			1	0	0			
01/07/1984	CHICAGO; ILLINOIS; USA	MEA	RELEASE, EXPLODE	PROCESS-PVESSEL	MECHANICAL; HUMAN	WELDFAIL - DESIGN	17	0	17	US$ 100.00 x 10E6	H2S REMOVAL	<85
07/06/1905	NORWAY	HYDROGEN	EXPLODE, FIRE	PROCESS-PUMP	HUMAN, MECHANICAL	GENERAL OP, DESIGN	1	0	2		CO2 REMOVAL	7
06/07/1985	Clinton, IA	Syngas	RELEASE; EXPLODE				0	0	0	14,7 M $		
21/01/1986	Kawasaki, Kanagawa, Japan	Fuel	RELEASE; EXPLODE	PROCESS - FIREDEQUIP	HUMAN	GENERALOP; VALVE; DESIGN	1	0	0		REFORMING	
November, 1986	LOUISIANA	SYNGAS		PROCESS-PVESSEL	MECHANICAL		0	0	0		REFORMING	
November, 1986	CANADA	SYNGAS	EXPLODE	PROCESS-PVESSEL	MECHANICAL	OVERHEAT	0	0	0		REFORMING	
04/10/1987	Sakai, Osaka, Japan	Syngas; Naphta	RELEASE; FIRE	PROCESS - PIPEWORK	MECHANICAL	FLANGCOUPL	1	0	0		REFORMING	
23/12/1987		Syngas; Natural gas; Ammonia	EXPLODE; FIRE; RELEASE	PROCESS - PIPEWORK	MECHANICAL	METALLURG	0	0	0	0,65 M euro	CO2 REMOVAL	
09/06/1988		Hydrogen; Nitrogen	EXPLODE	PROCESS - PVESSEL	HUMAN; MECHANICAL	MAINTAIN; OVERPRES	1	0	1		AMMONIA SYNTHESIS	
23/02/1989		Hydrogen; Nitrogen	RELEASE; EXPLODE	PROCESS - PIPEWORK	MECHANICAL	MAINTAIN; INCOMPAT	0	0	2		AMMONIA SYNTHESIS	
20/03/1989	Jonova, LITHUANIA	Ammonia	RELEASE, FIRE	STORAGE-TANKCONTNR	HUMAN	GENERAL OP	57	32000	7		STORAGE	7000
13/09/1989		Ammonia	RELEASE	STORAGE - PSVESSEL			6	0	0		STORAGE	
28/03/1990		Ammonia	RELEASE	PROCESS - PIPEWORK	HUMAN	MAINTAIN; GENERAL	1	0	0			

Date	Location	Substance	Incident type	Origin	General cause	Specific cause	Injured	Evacuated	Killed	Damage	Section	Quantity (ton)
29/05/1990	Columbus, GA	Ammonia	RELEASE		HUMAN	GENERAL	0	0	0			
06/06/1990	Pollock, LA	Ammonia	RELEASE	PROCESS - PUMP	MECHANICAL		0	0	0			0,159
17/08/1990	Arita, Wakayama, Japan	Syngas; Naphta	RELEASE; FIRE	PROCESS - PIPEWORK	MECHANICAL	FLANGCOUPL	0	0	0	1 M yen	REFORMING	
31/08/1990		Ammonia	RELEASE	STORAGE - PSVESSEL	HUMAN	GENERAL	3	3 (operators evacuated the tower and washed themselves)	0		STORAGE	
02/11/1990	Enid, OK	Ammonia	RELEASE	PROCESS - PUMP	MECHANICAL	GLANDSEAL	0	0	0			1,06
03/01/1991	Luling, LA	Syngas		PROCESS - PVESSEL			0	0	0		REFORMING	
25/01/1991	Donaldsonville, LA	Ammonia		PROCESS - PIPEWORK	MECHANICAL		0	0	0			0,068
13/06/1905	FRANCE	Ammonia	RELEASE	PROCESS-PVESSEL	MECHANICAL, HUMAN	WELDFAIL	0	0	0		AMMONIA SYNTHESIS	
04/02/1991	Bayonne, NJ	Ammonia	FIRE				0	0	0			
19/02/1991	Geismar, LA	Ammonia		PROCESS - PVESSEL	MECHANICAL		0	0	0			
13/06/1905	GERMANY	Ammonia	RELEASE	PROCESS-PVESSEL	MECHANICAL, HUMAN	WELDFAIL	0	0	0		AMMONIA SYNTHESIS	
19/03/1991	Kawasaki, Kanagawa, Japan	Syngas	RELEASE; EXPLODE; FIRE	PROCESS - HEATXCHANG	PROCOND; MECHANICAL	FLANGCOUPL	0	0	0			
02/04/1991	Westwego, LA	Ammonia	RELEASE				0	0	0			
09/04/1991	Lake Charles, LA	Ammonia	RELEASE				0	0	0			0,068
26/04/1991	Enid, OK	Ammonia	RELEASE	PROCESS - PUMP	MECHANICAL		0	0	0			0,103
05/05/1991	Montebello, CA	Syngas					0	0	0			0,045
08/05/1991		Ammonia	FIRE; RELEASE	PROCESS - PIPEWORK	MECHANICAL	CORRODE; VALVE	0	0	0		AMMONIA SYNTHESIS	20
11/05/1991	Beaumont, TX	Syngas	RELEASE	PROCESS - PUMP	MECHANICAL		0	0	0			2,268
17/05/1991	Donaldsonville, LA	Ammonia	RELEASE	PROCESS - PUMP	MECHANICAL		0	0	0			0,68
24/05/1991	Donaldsonville, LA	Ammonia		PROCESS - PIPEWORK	MECHANICAL		0	0	0			0,068
13/08/1991	Enid, OK	Ammonia	RELEASE				0	0	0			0,053
06/11/1991	Catoosa, OK	Ammonia	RELEASE	HOSE	MECHANICAL		0	0	0			0,204
19/03/1992	Geismar, LA	Ammonia					0	0	0			
09/04/1992	Geismar, LA	Ammonia		PROCESS - PIPEWORK	PROCOND		0	0	0			
01/06/1992		Ammonia	FIRE; RELEASE	PROCESS - PIPEWORK	MECHANICAL	METALLURG	0	0	0		AMMONIA SYNTHESIS	0,6
19/06/1992	Geismar, LA	Ammonia	RELEASE				0	0	0			0,045
August, 1992	ENGLAND			PROCESS-PVESSEL	MECHANICAL	MAINTAIN, DESIGN	0	0	0		REFORMING	

Date	Location	Substance	Incident type	Origin	General cause	Specific cause	Injured	Evacuated	Killed	Damage	Section	Quantity (ton)
03/08/1992	Geismar, LA	Ammonia	RELEASE	PROCESS - PIPEWORK			0	0	0			0,045
02/09/1992	Donaldsonville, LA	Ammonia		PROCESS - PIPEWORK			0	0	0			
16/10/1992	Sodegaura-city, Chiba prefecture	Syngas	RELEASE; EXPLODE; FIRE	PROCESS - HEATXCHANG	HUMAN; MECHANICAL	MAINTAIN; FLANGECOUPL	7	0	10			
21/12/1992	Waggaman, LA	Ammonia	FIRE; RELEASE	PROCESS - PVESSEL		INTNLFIRE	0	0	0		REFORMING	
08/02/1993	GERMANY			PROCESS-PIPEWORK	MECHANICAL	DESIGN, WELDFAIL	0	0	0		AMMONIA SYNTHESIS	
05/05/1993	PAKISTAN	SYNGAS	RELEASE	PROCESS-HEATXCHANG	MECHANICAL	METALLURG	0	0	0		AMMONIA SYNTHESIS	
01/08/1993	IJMUIDEN; NETHERLANDS	Ammonia	EXPLODE	PROCESS			0	0	0	US$ 3.80 x 10E6		
14/09/1993	NETHERLANDS	HOT AIR		PROCESS-PIPEWORK	PROCOND	MAINTENANCE	0	0	0		AMMONIA SYNTHESIS	
29/09/1993	GERMANY	SYNGAS	RELEASE	PROCESS-PIPEWORK	MECHANICAL	METALLURG, MAINTAIN	0	0	0		AMMONIA SYNTHESIS	
July, 1994	CANADA	SYNGAS	RELEASE	PROCESS-PVESSEL	MECHANICAL	OVERHEAT	0	0	0		REFORMING	
18/08/1994	Kawasaki, Kanagawa, Japan	HYDROGEN, AMMONIA	RELEASE; FIRE	PROCESS - PIPEWORK	HUMAN; MECHANICAL	MAINTAIN; FLANGECOUPL	0	0	0	10000 yen	DESULFURIZATION	
19/11/1994	TEXAS	SYNGAS	RELEASE	PROCESS-PUMP	MECHANICAL	VALVE, DESIGN	0	0	0		REFORMING	
01/12/1994	Ribercourt.dreslincourt, FRANCE	Ammonia	RELEASE	PROCESS-PIPEWORK	HUMAN	MAINTAIN, DESIGN	2	0	1			5
25/04/1995	INDIA	SYNGAS, AMMONIA	RELEASE, FIRE	PROCESS-PVESSEL	MECHANICAL	WELDFAIL	0	0	0		AMMONIA SYNTHESIS	
18/06/1905	GEORGIA, USA			PROCESS-PVESSEL	MECHANICAL	METALLURG	0	0	0		AMMONIA SYNTHESIS	
05/03/1996	INDIA	OIL	RELEASE, FIRE	PROCESS-MACDRIVE, PIPEWORK	MECHANICAL		0	0	0		AMMONIA SYNTHESIS	
19/04/1996		Ammonia	RELEASE	STORAGE - PIPEWORK	HUMAN	MAINTAN	0	0	2		STORAGE	
01/05/1996	LA, USA	SYNGAS	RELEASE, FIRE	PROCESS-PIPEWORK	HUMAN	MAINTAIN, GENERAL OP	0	0	0		AMMONIA SYNTHESIS	
14/05/1996	PORT LISAS; TRINIDAD & TOBAGO	Ammonia	RELEASE	PROCESS			13	0	0			
13/04/1997	NORWAY	SYNGAS	EXPLODE	PROCESS-PIPEWORK	HUMAN	GENERAL OP, MAINTAIN	0	0	0		CO2 REMOVAL	
09/05/1997	QUATAR	SYNGAS		PROCESS-MACDRIVE	PROCOND; MECHANICAL		0	0	0		REFORMING	
July, 1997	MALAYSIA	CATALYST	RELEASE	PROCESS-PVESSEL	MECHANICAL	METALLURG	0	0	0		AMMONIA SYNTHESIS	
01/08/1997	OTTMARSHEIM, FRANCE	Ammonia	RELEASE	PROCESS-PIPEWORK	PROCOND	ELECTRIC	0	0	0		AMMONIA SYNTHESIS	
04/08/1997	Toluouse, FRANCE	SYNGAS	RELEASE		EXTERNAL	ELECTRIC	0	0	0		AMMONIA SYNTHESIS	
October, 1997	SOUTH AFRICA	FUEL	EXPLODE	PROCESS-PVESSEL	HUMAN	GENERAL OP, DESIGN	2	0	0		REFORMING	
07/11/1997	INDIA	WATER	RELEASE	PROCESS-PIPEWORK	MECHANICAL	MAINTAIN, GENERAL OP	0	0	0		REFORMING	
01/12/1997	LOUISIANA	SYNGAS	FIRE	PROCESS-PVESSEL	MECHANICAL	OVERHEAT, WELDFAIL	0	0	0		REFORMING	

Date	Location	Substance	Incident type	Origin	General cause	Specific cause	Injured	Evacuated	Killed	Damage	Section	Quantity (ton)
21/12/1997		Fuel; Oxygen; Steam; Syngas	RELEASE; FIRE	PROCESS - PVESSEL	MECHANICAL	FLANGCOUPL	2	0	0		REFORMING	Hydrocarbon: 42; Oxygen: 46; CO: 9; Hydrogen: 26
27/03/1998	Toluouse, FRANCE	Ammonia	RELEASE	PROCESS-HEATXCHANG	HUMAN	DESIGN	0	0	0		STORAGE	10
20/06/1905	PAKISTAN	CATALYST	RELEASE	PROCESS-PVESSEL	MECHANICAL		0	0	0		AMMONIA SYNTHESIS	
27/05/1998	Kashima, Ibaragi, Japan	Syngas	RELEASE; EXPLODE; FIRE	PROCESS - PVESSEL			6	0	1	18 M yen	DESULFURIZATION	
08/07/1998	INDIA	MDEA, HYDROGEN	RELEASE, FIRE	PROCESS-PIPEWORK	MECHANICAL, INSTRUMENT	METALLURG	0	0	0		CO2 REMOVAL	
29/07/1998	CANADA	NATURAL GAS	FIRE	PROCESS-PIPEWORK	PROCOND; MECHANICAL	DESIGN	0	0	0		REFORMING	
31/08/1998	BANGLADESH	WATER, AMMONIA, SYNGAS		PROCESS-PVESSEL	MECHANICAL	DESIGN, METALLURG	0	0	0		CO2 REMOVAL	
16/11/1998	CANADA	SYNGAS		PROCESS-PIPEWORK	HUMAN	GENERAL OP, WELDFAIL	0	0	0		REFORMING	
24/04/1999	INDIA	SYNGAS	FIRE	PROCESS-PIPEWORK	PROCOND; MECHANICAL	DESIGN	0	0	0		REFORMING	
01/05/1999		CATALYST	RELEASE	PROCESS-HOSE	PROCOND		0	0	0		AMMONIA SYNTHESIS	8500
17/06/1999	INDONESIA	SYNGAS	FIRE, EXPLODE	PROCESS-PVESSEL	PROCOND	BRITTLE,DESIGN	0	0	0		AMMONIA SYNTHESIS	
20/08/1999	ALASKA	SYNGAS	FIRE, EXPLODE	STORAGE	HUMAN	GENERAL OP, DESIGN	3	0	0		CO2 REMOVAL	
09/05/2000	QUATAR	STEAM		PROCESS-PUMP	EXTERNAL; MECHANICAL		0	0	0		REFORMING	
24/05/2000		Syngas	EXPLODE; FIRE	PROCESS - PVESSEL	MECHANICAL; HUMAN	WELDFAIL; MAINTAIN	8	0	3		CO2 REMOVAL	
03/09/2000		Hydrogen; Hydrogen sulfide	EXPLODE; FIRE; RELEASE	PROCESS - PUMP	HUMAN; PROCOND	GENERAL; DESIGN; GENERALOP	1	0	0	13,72 M euro (material damage); 68,6 M euro (production loss)	DESULFURIZATION	
02/02/2001		Natural gas; Syngas	RELEASE; FIRE	FIREDEQUIP	HUMAN	MAINTAIN	5	0	2			
15/04/2002	Tomokomai, Hokkaido, Japan	Hydrogen sulphide; Hydrogen	RELEASE; FIRE	PROCESS - PIPEWORK	MECHANICAL	CORRODE	0	0	0	7-8 billion yen	DESULFURIZATION	
11/08/2002	Büttel, Schleswig-Holstein	Ammonia	RELEASE	STORAGE - PSVESSEL	PROCOND; INSTRUMENT	DESIGN; GENERAL; OVERPRES	0	0	0		STORAGE	450
17/11/2002		Syngas; Fuel	RELEASE; FIRE	PROCESS - HEATXCHANG	HUMAN	CONSTRUCT	1	0	0	4,3 M euro (material damage); 1,7 (production loss)	REFORMING	
11/04/2003		Ammonia	EXPLODE; FIRE; RELEASE	PROCESS - PVESSEL	PROCOND	OVERPRES	0	100	1		AMMONIA SYNTHESIS	
28/05/2003	Köln-Worringen, Nordrhein-Westfalen	Arsenic oxide	RELEASE	PROCESS - HEATXCHANG			0	0	0			0,75
17/03/2004	Büttel, Schleswig-Holstein	Ammonia	RELEASE	PROCESS - PIPEWORK	MECHANICAL		0	0	0			9

Date	Location	Substance	Incident type	Origin	General cause	Specific cause	Injured	Evacuated	Killed	Damage	Section	Quantity (ton)
26/06/2004		Hydrogen sulfide; Sulfur dioxide	FIRE	PROCESS - FIREDEQUIP	MECHANICAL	METALLURG	2	600	0	6 M euro (material damage); 22,5 M euro (production loss)	DESULFURIZATION	
16/08/2004	Köln-Worringen, Nordrhein-Westfalen	Arsenic oxide	RELEASE	PROCESS - PIPEWORK	MECHANICAL; HUMAN	DESIGN	0	0	0			0,22
04/01/2005		Ammonia	EXPLODE; RELEASE	STORAGE - PSVESSEL	PROCOND	GENERALOP	1	0	1	1 million $	STORAGE	
19/02/2005	Coffeeyville, KS	Ammonia	RELEASE	PROCESS - HEATXCHANG			0	0	0			0,045
23/05/2005	Fort Dodge, IA	Ammonia	RELEASE	PROCESS - PIPEWORK		OVERPRES	0	0	0			
31/05/2005	Claremore, OK	Ammonia	RELEASE	PROCESS - PIPEWORK		OVERPRES	0	0	0			0,161
11/06/2005	Claremore, OK	Ammonia	RELEASE	PROCESS - PIPEWORK			0	0	0			0,063
24/06/2005	Fort Dodge, IA	Ammonia	FIRE				0	0	0			0,045
28/06/2005	Coffeeyville, KS	Ammonia	RELEASE				0	0	0			1,113
12/07/2005	Fort Dodge, IA	Ammonia	RELEASE	PROCESS - PIPEWORK			0	0	0			
31/08/2005	Donaldsonville, LA	Ammonia	RELEASE	PROCESS - PIPEWORK			0	0	0			0,227
12/09/2005	Claremore, OK	Ammonia	RELEASE	PROCESS - PIPEWORK			0	0	0			0,506
20/11/2005	Salt Lake City, UT	Hydrogen sulfide	RELEASE				0	0	0			0,045
24/04/2006	Gonfreville l'orcher, FRANCE	SYNGAS	RELEASE	PROCESS-PIPEWORK	HUMAN	FLANGCOUPL,MAINTAIN	0	0	0	300000 euro	REFORMING	
01/06/2006		Syngas	RELEASE; FIRE; EXPLODE	PROCESS - PIPEWORK	human	glandseal	2	0	0	2 M euro	REFORMING	1,45
26/11/2006	GRANDPUITS-BAILLY-CARROIS, FRANCE	Ammonia	RELEASE	PROCESS-PIPEWORK	HUMAN	GENERAL OP, MAINTAIN	0	0	0		STORAGE	
29/11/2006	GRANDPUITS-BAILLY-CARROIS, FRANCE	SYNGAS	EXPLODE	PROCESS-PIPEWORK	HUMAN	FLANGCOUPL, GENERAL OP	0	0	0		REFORMING	
23/08/2007		Syngas	RELEASE	PROCESS - PIPEWORK	HUMAN; INSTRUMENT	DESIGN; GENERAL	0	0	1		REFORMING	
26/06/2009		Natural gas	EXPLODE	PROCESS - FIREDEQUIP	EXTERNAL; HUMAN	GENERAL; DESIGN	2	0	0		REFORMING	
03/07/2009	NANCY, FRANCE	Ammonia	RELEASE		INSTRUMENT	CONTROL	0	0	0		AMMONIA SYNTHESIS	2,5
22/07/2009	GRANDPUITS-BAILLY-CARROIS, FRANCE	Ammonia	RELEASE	PROCESS-HOSE	INSTRUMENT	CONTROL	35	0	0		STORAGE	
07/11/2009	Gonfreville l'orcher, FRANCE				EXTERNAL, HUMAN	ELECTRIC, DESIGN	0	0	0		ALL	
11/04/2010	Vatva GIDC	Ammonia	EXPLODE	PROCESS - PVESSEL	PROCOND; INSTRUMENT	OVERHEAT; OVERPRES	12	0	1			
15/04/2010	GRANDPUITS-BAILLY-CARROIS, FRANCE	NATURAL GAS	FIRE	PROCESS-PIPEWORK	MECHANICAL		0	0	0		REFORMING	
28/06/2010		Steam	EXPLODE	PROCESS - PIPEWORK	MECHANICAL	METALLURG	0	0	0	2 M euro	REFORMING	
24/07/2010		Syngas; Natural gas	EXPLODE; FIRE; RELEASE	PROCESS - PIPEWORK	MECHANICAL	GLANDSEAL; VALVE	5	0	0	12 M euro	AMMONIA SYNTHESIS	Hydrogen: 2,5; Natural gas: less than 10

Date	Location	Substance	Incident type	Origin	General cause	Specific cause	Injured	Evacuated	Killed	Damage	Section	Quantity (ton)
02/04/2011	Brunsbüttel, Schleswig-Holstein	Ammonia	RELEASE	PROCESS - PIPEWORK	MECHANICAL	CORRODE	0	0	0			25
09/11/2011	Ludwigshafen, Rheinland-Pfalz	Syngas; Natural gas	FIRE	PROCESS - PIPEWORK	HUMAN	MAINTAIN	0	0	0	500000 euro	REFORMING	0,22
07/12/2012	Rostock-Peez, Mecklenburg-Vorpommern	Ammonia	RELEASE	STORAGE - PSVESSEL			0	0	0		STORAGE	0,3
14/01/2014		Syngas	RELEASE; FIRE	PROCESS - PIPEWORK	INSTRUMENT; MECHANICAL	CORRODE	0	0	0		REFORMING	Hydrogen: 0,7
09/05/2014	Enid, OK	Ammonia	RELEASE	PROCESS - PIPEWORK	PROCOND		0	0	0			0,045
14/07/2014	Garyville, LA	Hydrogen; Hydrogen sulfide	RELEASE	PROCESS - PIPEWORK			0	0	0			
02/09/2014	St.James, LA	Ammonia	RELEASE	PROCESS - PIPEWORK			0	0	0			
28/10/2014	Dodge City, KS	Ammonia	RELEASE	PROCESS - PIPEWORK			0	0	0			0,045
31/03/2015	Enid, OK	Ammonia	RELEASE	PROCESS - PIPEWORK	MECHANCAL		0	0	0			
05/11/2015	St.James, LA	Ammonia	RELEASE				0	0	0			
13/07/2016	Sulphur, LA	Hydrogen sulphide; Sulfur dioxide	RELEASE; FIRE	PROCESS - PIPEWORK	MECHANICAL		0	0	0		REFORMING	

Appendix C

Fault trees for the ammonia storage tank

Undesirable event		**Detailed direct causes**		**Direct causes**		**Necessary and sufficient causes**		**Critical event**
Human error	or	Wrong connection procedure	or	external HP source connected causes overpressure	or	internal overpressure	or	(large) breach on shell or leak from pipe
Badly designed procedure								
Wilfull disobedience	or	Source should not be connected						
Human error								
vessel filled by design has blocked inlet and outlet	or	filled vessel containing liquid	and	thermal expansion of liquid filled vessel causes overpressure				
vessel left in overfilled condition								
refrigeration fails	or	temperature rise						
warmed up externally								
excessive liquid transfer in batch system (due to human or command error)	or	filled beyond normal level		Overfilling vessel causes overpressure				
insufficient capacity available in batch system (design error, defective maintenance)								
Loss of utilities								
blocked internals leads to overfilling of continuous system(defective maintenance, unexpected reaction)								
blocked outlet leads to overfilling of continuous system (defective maintenance, unexpected reaction (crystallisation))								
filling of a vessel	or	difference in temperature between layers (temperature inversion)		roll-over of vessel contents causes overpressure				
fail of refrigeration system								
internal flammable or explosive mixture	and	internal combustion/explosion		combustion/explosion causes overpressure				
ignition source								
Conception error (insufficient release or mitigation of weight)	or	Natural causes (snow, ice, water, wir	or	Overloading	or	Rupture tied to an excessive mechanical stress due to		
Installation error								
Lacking or defective maintenance								
Wilful disobedience	or	Loads placed on the equipment						
Malicious intervention								
Manipulation error								
Other human error								
		Overfilling						

Undesirable event		Detailed direct causes		Direct causes	Necessary and sufficient causes	Critical event
Lacking or defective maintenance	or	Support fails				
Installation error						
Conception error						
Manufacturing error				High amplitude vibrations (e.g.,earthquake)		
Lacking or defective maintenance	or	Due to external causes (furnace, boilers,..)	or	Dilatation		
Conception error						
Manufacturing error						
Installation error						
Incorrect command and/or control signal						
Incorrect sensor signal						
Interpretation error						
Transmission error						
Wilful disobedience						
Malicious intervention						
Manipulation error						
Other human error						
Lacking or defective maintenance	or	Due to internal cause (overheating of the content)				
Conception error						
Manufacturing error						
Installation error						
Incorrect command and/or control signal						
loss of utilities						
Incorrect sensor signal						
Interpretation error						
Transmission error						
Wilful disobedience						
Malicious intervention						
Manipulation error						
Other human error						
		Domino effect (fire)				
		Domino effect (explosion)		External overpressure		
Lacking or defective maintenance	or	Torque	or	Domino effect (explosion)		
Conception error						
Manufacturing error						
Installation error						

Undesirable event		Detailed direct causes		Direct causes		Necessary and sufficient causes	Critical event
Conception error	or	Lacking or defective support					
Installation error							
Lacking or defective maintenance							
Defective maintenance (not replaced like with like)	or	Low resilience material	or	Brittle structure		Brittle rupture	
Design error							
Manufacturing error							
Installation error (wrong material used)							
Wrong material delivered							
Hydrogen cracking sensitive material	and	Hydrogen or other chemical causes of enbrittlement					
Contamination by hydrogen							
Wrong material	or	Embrittlement due to welding					
Wrong welding procedure							
Unauthorized welding							
Sensitive material	and	Embrittlement due to other thermal clycles					
Heating followed by fast cooling							
Design error	or	Wrong material used	or	Inappropriate material	or	Insufficient initial mechanical properties of the structure	
Wrong material ordered Size of the leak: Large							
Wrong material delivered							
Human error							
Bad quality resulting from transport or storage conditions	or	Bad quality material used					
Bad quality delivered							
Lacking or deficient checking procedure							
Manufacturing error							
				Inappropriate dimensions			
Design error	or	Wrong assembling procedure	or	Inappropriate assembling			
Transmission/information error							
Human error	or	Non respect of assembling procedures					
Impossibility to apply the procedures							

Undesirable event		Detailed direct causes		Direct causes		Necessary and sufficient causes	Critical event
Incorrect or lacking information from the process	or	Bad information	or	Valve left open by mistake	or	Functional opening	(medium) breach on shell or leak from pipe
Incorrect instruction given by other operator/staff member							
Incorrect or lacking procedure							
Incorrect or lacking information from other operator/staff member							
Right information from the process/human environment but misunderstood by operator	or	Bad interpretation of signal					
Misunderstanding of the procedure							
Human error : valve operated in the wrong direction	or	Other error					
Human error : wrong valve opened							
Incorrect or lacking information from the process	or	Bad information	or	Valve opened by mistake			
Incorrect instruction given by other operator/staff member							
Incorrect or lacking procedure							
Incorrect or lacking information from other operator/staff member							
Right information from the process/human environment but misunderstood by operator	or	Bad interpretation of signal					
Misunderstanding of the procedure							
Human error : valve operated in the wrong direction	or	Other error					
Human error : wrong valve opened							
Corrosive environment	or	Corrosion	or	Valve blocked			
Corrosive product							
Electrical origin							
Stress related corrosion							
Inappropriate material							
Lacking or defective protection							
Internal friction with erosive material	or	Erosion					
Flow pattern favours erosion							
External friction with erosive material (dust, structure)							
Lacking or defective maintenance	or	Electrical failure					
General electrical failure							
External cause (water creates a short circuit, electrical cable is sectioned)							

Undesirable event		Detailed direct causes		Direct causes	Necessary and sufficient causes	Critical event
Defective software	or	Command failure				
Defective hardware						
Defective transmission system						
Excessive conditions created by the environment	or	Aging	or	Seal, joint loss of effectiveness		
Excessive conditions created by the process						
Lacking or defective maintenance						
Wrong material delivered	or	Improper material				
Wrong material used						
Wrong dimension	or	Bad design				
Wrong material						
Not replaced like with like	or	Bad installation or maintenance				
Bad installation or maintenance procedure						
Normal use/storage of aggressive chemical	or	Physical or chemical aggression				
Contamination						
		Normal functioning of the safety valve	or	Safety valve, safety relief device		
		Too sensitive safety valve				
Operator error	or	inadequate isolation procedure	or	fail to clear out contents before opening containment		
Wilful disobedience						
Incorrect procedure						
Lacking or defective maintenance	or	leaking isolation equipment				
Conception error						
Manufacturing error						
Installation error						
Human error	or	Disconnected by operator	or	disconnect during filling		
Wrong information about process						
Wilful disobedience						
impact	or	Disconnected by other cause				
moving parts						
Incorrect sensor signal	or	Lacking or wrong information about the content	or	wrong part (containing hazardous material) worked on		
Interpretation error						
Transmission error						
Human error						

Undesirable event		Detailed direct causes		Direct causes	Necessary and sufficient causes	Critical event
Wilful disobedience	or	Conscious work on part containing hazardous material				
Malicious intervention						
Incorrect sensor signal	or	Lacking or wrong information about containment	and	operation started when containment open		
Interpretation error						
Transmission error						
Human error						
Incorrect command and/or control signal	or	Containment closing procedure failed				
Incorrect sensor signal						
Human error						
Flow stop control not accessible	or	flow stop control not operated in time	or	uncontrolled flow during sampling/draining		
Flow stop control difficult to operate						
Manipulation error						
Other human error						
Lacking information induces delayed action						
Lacking or defective maintenance	or	flow stop control inoperable				
Flow stop control not accessible						
Operator error	or	flow stop control operated in wrong direction				
Wrong information on flow stop control						

Undesirable event		Detailed direct causes	Direct causes	Necessary and sufficient causes	Critical event
Human error	or	Fast Emptying	Fast emptying of the vessel	Underpressure (pressure below the containment limit of the vessel)	Vessel collapse
Incorrect command or control signal					
Incorrect sensor signal					
Transmission error					
Normal situation					

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Acknowledgment

First of all, I would like to thank the Norwegian University of Science and Technology which hosted me during the development of this thesis. In particular, I would express my gratitude to my supervisor Professor Nicola Paltrinieri for his patience and support during the elaboration of this work. Many thanks to Eng. Sarah Bonvicini from the University of Bologna, she supported me despite the distance. I would also thank Yara International ASA and OCI Nitrogen for their contribution to the development of this work.
Finally, I am also very thankful and grateful to my family and my friends, which are always present, even in the most difficult moments.