Material Degradation: Findings from Historical Accident Analysis in Process Industries

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Material degradation: Findings from historical accident analysis in process industries

Morena Vitale *, Huxiao Shi, David J. Castro Rodriguez, Antonello A. Barresi, Micaela Demichela

Department of Applied Science and Technology, Politecnico di Torino, Corso Duca Degli Abruzzi 24, 10129 Torino, Italy

A R T I C L E I N F O

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Safety of process
Bayesian networks

A B S T R A C T

Material degradation represents a source of risk in the process industry, being responsible for 30% of loss of containment events. This investigation focuses on the analysis of historical events related to material degradation to gain awareness and enhance preparedness in the process industry. A database containing 3,772 records was built. Data collection was performed using industrial-accident open access databases, classifying the information according to macro-sector, type of equipment, substance involved, scenario, age of the plant, actions taken after the event and type of losses. Corrosion emerged as the main failure mechanism, followed by vibration and fatigue. This phenomenon occurs predominantly in plants with more than 25 years of operation, where prolonged exposure to chemical and environmental agents accelerates the degradation of materials. In contrast, more recent plants are more prone to failures caused by vibration. Corrosion events were frequently associated with environmental contamination episodes, with Event Tree Analysis showing it as the most likely scenario, representing approximately 50% conditional probability in documented corrosion incidents. To complete the analysis, two representative case studies were chosen for the application of the quantitative risk assessment. Conditional relationships among the variables of the database were found using Bayesian networks after the first frequentist analysis. This method allowed the investigation of uncertain data revealing a notable rise in the frequency of LOC and toxic gas dispersion. The analysis of past events highlighted the critical failure factors, which can be considered for the adoption of more effective preventive measures.

List of abbreviations

API	American Petroleum Institute
BNs	Bayesian networks
CPT	Conditional probability table
DAG	Directed acyclic graph
E	Explosion
EC	Environmental contamination
EC&I	Electrical, control, and instrumentation
ETA	Event tree analysis
F	Fire
HE	Hydrogen embrittlement
HF	Hydrofluoric acid
HTHA	High-temperature hydrogen attack
LOC	Loss of containment
MF	Multiple fatalities
MI	Multiple injuries
MM	Multi-prediction with multi-results
MMD	Minor or moderate damages
MS	Multiple scenarios
MSR	Multi-prediction with single result
NH	Non-hazardous substances
ND	Absence of environmental contamination
NI	No injuries
NF	No fatalities
PC	Peter-Clark algorithm
PCS	Primary containment system
PSM	Process safety management
QRA	Quantitative risk analysis
RBI	Risk based inspection
RMP	Risk management plan
R-NFC	Release without further consequences

* Corresponding author.
E-mail address: morena.vitale@polito.it (M. Vitale).

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SED	Severe environmental damage
SI	Single injury
SF	Single fatality
S	Single prediction
TGD	Dispersion of toxic gases

1. Introduction

Sixty per cent of major loss-of-containment (LOC) incidents are attributable to technical integrity issues, and nearly half of these are exacerbated by ageing infrastructure [11]. Horrocks et al. [32] highlighted that ageing is not simply a matter of the chronological age of equipment, but rather a process that reflects the overall state and evolutionary transformations that occur over time. It manifests itself through progressive deterioration and material damage that increases the probability of failure over the operational life of the component. This progression is not linear, but it depends on several variables, including management and maintenance methods, as well as the operating conditions to which the equipment is subjected.

Ageing is a universal process that affects all equipment categories. It begins in the manufacturing or construction phase and continues throughout the entire life cycle. Although adequate maintenance interventions can slow down this process, it cannot be stopped completely [34]. It is important to distinguish ageing from obsolescence. The first one, refers to a gradual deterioration of the physical properties of a component or system, leading to an increased risk of failure or loss of containment [7]. On the contrary, obsolescence is related to the advancement of technical knowledge, industrial standards and safety regulations that render equipment non-compliant with new technological or regulatory requirements [42]. This issue is particularly relevant in Europe, the USA and the Scandinavian countries, where many industrial infrastructures have surpassed their intended operating cycle. In Europe, for example, 50% of industrial plants continue to operate beyond the time initially planned for their use [54]. Wintle et al. [60] performed a retrospective analysis of previous incidents, with the aim of identifying the underlying causes and effects associated with each event. Their research results showed that 60% of the incident reports with an outcome of loss of containment were attributable to problems related to the technical integrity of the equipment. Of these, approximately half of the events were related to material degradation. The challenge of ageing management is thus ensuring the safety and efficiency of plants, for which one requires adequate monitoring, maintenance and technical updating strategies. Legislative Decree 105/2015[1], known as Seveso III, has given complete transposition in Italy to European Directive 2012/18/EU[2] [36], concerned with regulations concerning the control of hazards due to major accidents involving dangerous substances [4].

The Seveso III Directive focuses on accident prevention and safety management at sites storing and handling dangerous substances. Although it does not directly address the management of ageing of industrial plants, it requires each site to identify and describe the deterioration mechanisms of materials, thus making the monitoring of ageing processes mandatory. A strong point is made in Annex 3 of the Seveso III Directive: the aspects to consider during inspections are clearly laid out, stating that ageing and corrosion are two main factors for the control of risk. Then, Annex B lays emphasis on the surveillance of deterioration of materials being perpetuated, thus emphasizing the preventive strategies to curb the risk of accidents in relation to structural deterioration. In the end, Annex H, although it does not provide operational details on the assessment procedures, introduces a useful checklist to support auditors during inspections. However, despite the importance given to these aspects, the Directive does not specify detailed operational methodologies for the assessment of degradation, leaving operators the task of implementing tools and techniques appropriate to their needs [9]. The mechanism advocated by Seveso III serves the purpose of ensuring industrial safety by such measures as controlling risks stemming from the degradation of materials. The function is retaining the integrity of structures and lowering the opportunity for accidents caused by structural deterioration; thus, improving the overall safety of regulated sectors [8]. In the United States, although there is no direct equivalent to the European Seveso III Directive, two major regulatory frameworks address process safety and the management of hazardous substances: OSHA's Process Safety Management (PSM) standard and EPA's Risk Management Plan (RMP) standard [47,53]. The PSM standard, which was introduced in 1992, focuses on preventing the release of hazardous chemicals, with safety programs that include hazard analysis, mechanical integrity, and change management. The RMP standard, introduced in 1996, complements the PSM standard and requires process facilities to evaluate release scenarios and potential consequences and implement prevention programs and emergency response plans [5]. Although these regulations do not explicitly address ageing infrastructure and material degradation, they implicitly require management of these issues through inspection, maintenance, and risk-based decision-making.

A study done by Hansler et al. [30] indicated that industrial facilities still lack very much in identifying degradation mechanisms and hazards even though they fulfil the regulatory framework. The study showed that most of the time, ageing management and control are inadequate concerning some very essential parts: safety studies, failure analysis, routine preventive maintenance, regular inspection, and application of tolerability criteria are most disregarded. The regulatory directive includes provisions to ensure regular checks on facilities, aimed at assessing and improving operational safety. However, several studies suggest adopting qualitative and quantitative approaches to explore ageing processes in more detail.

According to Milazzo and Bragatto [42], three key elements are essential for effective management of ageing. First, a comprehensive knowledge of the deterioration mechanisms, both chemical and physical, is needed, which can be internal or external, continuous or occasional, and which could compromise the integrity of the equipment during its operational life. Horrocks et al. [32] delved into the main deterioration mechanisms, such as corrosion, erosion and cracking, describing in detail how these phenomena develop and affect the materials commonly used in the process industry. Second, it is essential to have detailed documentation on the history of the equipment, including the materials of construction, the operating conditions and all maintenance and modifications performed over time. In the end, it is important to collect specific data on the deterioration mechanisms through non-destructive testing; these data allow the integrity and functionality of the systems to be monitored over time. Ageing has been considered a key hazard factor in multi-risk analysis of industrial plants; however, it is recognized that further research is required to characterize its behaviour with vulnerable items within the process industry [15].

Several methods for quantifying the risk associated with ageing are present in the literature, including the Ageing Fishbone, an indicator-based approach that has been subsequently updated to include applications to dynamic systems. Although the use of an indexed method involves some uncertainty, this approach offers a clearer and more structured view of deterioration processes than other qualitative methodologies [8,41,43].

Over the years, the literature has increasingly focused on data-driven and hybrid approaches to the modelling of degradation phenomena. For instance, multivariate degradation modelling was recognized as a powerful tool to implement the dependences among multiple degradation indicators, particularly when they share environmental or

[1] Legislative Decree No. 105 of June 26, 2015, "Implementation of Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances." Italian Official Gazette General Series No. 161 14/07/2015-Suppl. Ordinary No. 38 (In Italian language).

[2] Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances, amending and subsequently repealing Council Directive 96/82/EC.

operational conditions. These models consider dependencies via stochastic processes [23,61]. Furthermore, nonlinear mixed-effects models integrating dynamic covariates and Bayesian P-splines have been suggested to improve predictions of degradation pathways for systems exposed to variable environments [38]. In the hydrogen sector, machine learning methods including the Random Forest and Deep Neural Networks have been in use to predict the hydrogen-induced fatigue of structural materials, where emphasis was laid on microstructural and environmental parameters rather than the classical mechanical ones [10]. Moreover, a physics-informed neural network was proposed with stochastic processes to model degradation under uncertainty, enabling real-time updates, and improving the data available and the accuracy of the predictions [31]. To deepen the understanding of failure and breakdown mechanisms in the process industry, several studies have conducted historical analyses to draw lessons from past experience, providing useful information for risk assessment and inspection planning. However, previous analyses [9,28,30] have often been based on a limited number of documented incidents and on data that is not always complete, making it more difficult to obtain an in-depth view of the phenomenon, thus reducing the reliability and representativeness of the conclusions obtained and the completeness and reliability of the available information [57]. This limitation may affect the precision of the conclusions drawn, narrowing the scope of the results.

In this context, the present study aims to analyse the incidents where ageing plays a direct role or contributes to the escalation of events, reported in the main industrial open-source databases up to 2023. Our preliminary investigation [57], which collected 546 reports from the ARIA database, was limited to part 1 of phase 2 of the analysis methodology described in the following, that is to comprise only data collection and characterization, with the study of the frequencies of the raw data. The study was expanded and deepened with the use of additional accident databases, along with data modelling and prediction, to obtain a more in-depth view of the phenomenon of material degradation in the process industry. This analysis focuses on the most affected categories and the most frequent incident scenarios.

The primary objective of this work is to deepen the knowledge of material degradation and failure mechanisms in the process industry. To this end, the approach proposed in Castro Rodriguez et al. [14] was used, conducting an overall analysis of the raw data in order to identify trends and relative frequencies of the different scenarios. Given the high uncertainty in the collected data, a modelling part is then conducted using the quantitative risk analysis (QRA) techniques, which allows a second view of the data by addressing the challenge of unknown data. The use of this methodology allows to address the challenge of dealing with uncertain and incomplete data, often present in accident records, with the use of BNs that allow the discovery of the dependencies between the key variables and the calculation of the conditional probabilities of the scenarios in which the data is not available. This twofold approach provides for a more robust interpretation of historical data and allows a prediction of the data in cases of uncertainty. The reason for the work lies in the need for better knowledge of material degradation in the process industry, to identify the priority of the cases, thus offering support to inspections and maintenance activities overcoming a gap in the legislative framework. An increasingly popular methodology for managing material ageing and degradation in process plants is the Risk Based Inspection (RBI), described in API Recommendation Practice 580 [2]. The RBI practice bases inspections on the risk of failure, so the probabilities of the degradation mechanisms and the consequences are considered. The effectiveness of this methodology is limited by the knowledge of the failure mechanisms and the consequent scenarios that can occur in a plant. For this reason, the study aims to investigate past incidents, to better understand the causes and consequences of material degradation in the process industry. The use of predictive models, the management of uncertainty and the practical applicability of the results contribute to an improvement of the tools available for reliability assessment and safety management in the process industry.

Furthermore, this study contributes to providing quantitative data useful for integration into multi-hazard analysis within a resilient framework, aiming to increase awareness of system vulnerability and knowledge of the possible damages the system could incur following unexpected events [16].

2. Materials and methods

This research includes two significant phases.

Phase 1: Initial data collection involves various accident databases. Database from different countries were considered, selecting records related to industrial events and accidents across various macro-sectors of the process industry.
Phase 2: Data analysis is divided into two parts. Part 1 includes an exploratory phase, which involves examining raw data to identify trends, seasonality, and relative frequencies. This step serves to understand the nature of the data, detect patterns and repetitive behaviours over time, and analyse the distribution of values to identify any anomalies. Next, Part 2 involves predictive modelling, which aims to predict future behaviours based on historical data. In this phase, quantitative risk analysis techniques are applied, which serve to assess uncertainties and predict future scenarios.

2.1. Source of data

To conduct the analysis, the main open-source industrial databases from both the United States and Europe were consulted, collecting all the records in which ageing and degradation of the material played a key role or secondary role in the escalation of accidental events. Each record documents a single event, including information such as location and data, detailed explanation, human losses and environmental impact in case of pollution. Among the main databases consulted were: **i)** Analysis, Research and Information on Accidents (ARIA) database [3], **ii)** the Major Accident Reporting System [25], **iii)** the National Response Center database [45] and **iv)** Chemical Safety and Hazard Investigation Board database [21]. A detailed explanation of the different databases is reported by Castro Rodriguez et al. [14]. From this consultation, a data-driven repository was built and aligned with the architecture of previous research [13].

2.2. Data collection

The search was conducted using specific keywords shown in Table 1. The keywords used for data collection were chosen to reflect degradation mechanisms in the process industry, ensuring alignment between previously conducted studies and the objectives of the current one. These keywords were intentionally combined with terms such as "plant", "industry" and "establishment" to obtain a more complete and specific view of the context. Through this approach, a total of 3772 relevant incidents were identified. This large collection of data allowed the creation of a data-driven repository, which constituted the cornerstone to

Table 1
Keywords used in database search analyses.

Keyword in English	Keyword in French
Ageing	*Vieillissement*
Corrosion	*Corrosion*
Erosion	*Erosion*
Vibration	*Vibration*
Wear	*Usure*
Embrittlement	*Fragilisation*
Creep	*Fluage*
Fatigue	*Fatigue*
Degradation	*Dégradation*

analyse the material degradation factors in the process industry.

The classification was structured as follows:

Source: the source of the information or report. In this context, the source indicates the place where the report was found, including the name of the database consulted, and the identification number of the document within that database, for traceability purposes.

Macro sector: the type of plant where the event occurs. In line with previous studies, process plants have been divided into different macro-categories, including Chemical and Petrochemical, Manufacturing, Pipeline, Power Production, Storage and Warehouse, Transportation and Water Treatment [50].

Outcome: type of industrial event that occurred. Accident or Incident. Loss of containment (LOC) were also considered following Ricci et al. [50], adding Near-miss, according to Gnoni et al. [29]. In detail:

i) Accident: an event that has the intrinsic capacity to generate extremely serious consequences, such as human losses, permanent damage to the health of the people involved and significant economic damage. Therefore, it is an event of significant relevance that can have long-term impacts on both the human, environmental and economic levels.
ii) Incident: an event with the potential to cause considerable damage or loss, characterized by the possibility of generating significant impacts in various sectors. This includes serious health consequences or injuries, localized damage to property and the surrounding environment, a considerable loss of production and a significant impact on the reputation of the company involved.
iii) Loss of containment (LOC): an event that involves the release of material; therefore a situation in which substances or materials, usually contained within a plant or structure, are unintentionally released into the surrounding environment.
iv) Near-miss: a dangerous context in which the sequence of events could lead to an accident if it had not been interrupted by a planned or random intervention. In this situation, a series of circumstances occurs that, if not stopped promptly, could lead to an accident.

Final scenario: the impacts generated by the event; it includes the dispersion of toxic gases (TGD), environmental contamination (EC), release without further consequences (R-NFC), fire (F), explosion (E) or multiple scenarios (MS) [50]. Multiple scenarios imply the combination of different types of scenarios among those previously mentioned.

Cause: the most common degradation mechanisms in the process industry identified by Hansler et al. [30] were considered in the analysis. This choice ensures consistency with previous studies on the vulnerability related to the ageing of plants. Therefore, the causes identified are the following:

i) Corrosion is a process that occurs on the surface of the material due to chemical reactions with the surrounding environment, leading to its degradation. The degree of susceptibility of the material to corrosion is influenced by the type of environment to which it is exposed, while the corrosiveness of an environment is determined by the material that is exposed to it [22]. This category also includes events due to High-Temperature Hydrogen Attack (HTHA). This phenomenon occurs when steel is exposed to hydrogen at high temperatures causing surface, or even bulk, decarburization, due to the high temperature at which the carbon can react with hydrogen-forming gases, such as methane [48]. The phenomenon of HTHA can affect several mechanical properties of the material in an irreversible way. In the study, it is included in the corrosion category due to its chemical nature and the internal degradation mechanism of the material involving reactions between hydrogen and carbon. Furthermore, the choice to include HTHA in this category is in line with the classifications present in previous studies [30].
ii) Fatigue is the process of deterioration of a material caused by cyclic loading or repetitive stresses. During cyclic loading, materials may undergo a series of stress and strain cycles. Over time, this cyclic loading can lead to the formation and growth of cracks in the material. It is often influenced by changes in temperature, pressure and loads. The phenomenon of embrittlement is also included in this category.
iii) Embrittlement is a concept that refers to the reduction in toughness and increased susceptibility to fracture of a material due to factors, such as exposure to high temperatures, ionizing radiation or prolonged stress.
iv) Erosion is caused by the removal of part of the surface material by external agents, such as solid particles carried by moving fluids (liquids or gases) [32]. Erosion is often associated with systems in which fluids containing solid particles flow through pipes, ducts or equipment. Also included in this category is material wear, a deterioration process that occurs when two surfaces in relative contact slide or move against each other. During this contact, friction and abrasion occur, causing the progressive removal of material from the surface of one or both of the objects in contact. This phenomenon can lead to a gradual loss of material, causing changes in the shape, size and surface properties of the objects involved.
v) Hydrogen embrittlement has been considered as a separate class. This process can cause a decrease in both macroscopic and microscopic tensile strength, fatigue resistance and fracture toughness of steel, because of the penetration of hydrogen atoms in the crystalline lattice of the metal. Despite a number of studies conducted in the past on Hydrogen embrittlement (HE) in metals, the fundamental mechanisms of this phenomenon are still not fully understood [37].
vi) Vibrations can be generated by various sources, including moving machinery, rotating equipment, motors or other mechanical processes. Vibrations can have various effects on equipment, including wear of equipment, structural deterioration, unwanted noise and, in some cases, represent a source of safety risk.
vii) Unspecified material degradation is the category that includes reports where it was not possible to identify the specific type of degradation, therefore classified as "unknown".

In some events, more than one of the causes just described acted as a triggering factor; for this reason, they were defined as multiple causes. It is recognized that other mechanisms may exist and could be relevant. The API Recommended Practice 571 [1] provides a comprehensive taxonomy of damage mechanisms that can occur in process industry equipment, an aspect that will be explored in future work.

Equipment involved: types of equipment vulnerable to material degradation according to Horrocks et al. [32]:

i) Primary containment system (PCS) are the elements and devices specifically designed to safely contain and preserve hazardous substances within an industrial plant. These elements may include static or rotating components, such as vessels, pipes, pumps and turbines.
ii) Control & mitigation system refers to a set of components, devices and procedures designed to control and manage unwanted or critical situations within an industrial plant. These systems are crucial for the safety and operational efficiency of the plants and are designed to prevent, limit or mitigate the effects of unwanted events.
iii) Electrical, control, and instrumentation (EC&I) system, refers to a set of systems, equipment and procedures associated with the electrical aspects, control systems and instrumentation present in industrial plants. EC&I systems can be considered as a form of safeguard, including safety, detection, and response systems to ensure the integrity and availability of key services.

iv) Structures. These elements include the structural components of the plant infrastructure and provide support for operational activities.

Classification of substances involved: the classification adopted follows the guidelines of the Globally Harmonized System of Classification and Labelling of Chemicals [52]. This system organizes substances into categories based on the physical hazards (such as flammable or corrosive substances, like methane or acetic acid), health hazards (such as toxic or carcinogenic substances, like benzene or asbestos) and environmental hazards (such as those harmful to aquatic and terrestrial life, like pesticides or heavy metals). The category NH has been added for non-hazardous substances indicating that the substance cannot be included in the categories considered. Substances that present more than one hazard were defined as multiple hazards. Classification according to multiple hazards is regulated by note 6 of Annex I of European Directive 2012/18/EU.

Action taken: the actions taken following an accidental event [40]. In particular, the following are considered:

i) Inspections. When the frequency of inspections increased after the accident because it was not sufficient before the event.
ii) Treatments. In this case, after the event, specific treatments on the materials are implemented. These treatments are designed to improve the properties or resistance of the materials, reducing the risk of future accidents or similar failures.
iii) No action implemented. When there are no changes to the maintenance plan (ordinary inspection) after the event.

Losses can be categorized into three main types: human, economic and environmental.

i) Human losses can be divided into injuries and fatalities. Injuries involve people who have been injured due to the event and can be single or multiple in nature, depending on the number of people involved. Fatalities represent the number of people who have died due to the event and can also be single or multiple, depending on the number of people involved. The category "NI" has also been added for all events where there are no injuries, and NF for no fatalities.
ii) Economic losses include all expenses necessary to restart operations after an incident. These are all direct and indirect financial costs associated with restoring normal operations after an incident, including those for repairing material damage, environmental clean-up and recovery, and compensation for lost production or income [51]. These economic losses were divided into: i) losses up to $100,000; ii) losses between $100,000 and $1 million; iii) losses between $1 million and $10 million; and iv) losses greater than $10 million, following a classification consistent with previous studies.
iii) Environmental pollution is divided into two main categories: SED (Severe Environmental Damage) and MMD (Minor or Moderate Damages), as also reported in Annex VI of the Seveso III Directive and introduced with the environmental vulnerability criteria. The consequences of environmental pollution can be permanent and long-term in the case of SED, indicating serious and lasting damage to the environment. On the other hand, in the case of MMD, the consequences on the environment are considered moderate or minor, indicating less serious or temporary damage. The ND category was added to indicate the absence of environmental contamination.

Age of the installation is the age of the specific facility or infrastructure involved in the event. The division is based on the study conducted by Hansler et al. [30]: **i)** old, for facilities that have been in operation for more than 25 years; **ii)** medium, for facilities that have been in operation for 5 to 25 years; **iii)** new, for facilities that are less than 5 years old. However, this information is not always available in reports. Therefore, further research using other sources of information, such as site typology and facility location, is needed to obtain the age of the infrastructure involved.

In selecting the reports, only those corresponding to the previously defined macro-sector categories and associated with specific scenarios were included. The other reports were excluded from the analysis. The causes of the accidents identified in these reports are always attributable to the ageing of the infrastructures, with the related degradation mechanisms explained in detail.

2.3. *Repository structure*

Fig. 1 shows the diagram of the repository structure containing the 3772 reports related to material degradation, from 1966 to 2023. This repository has been organized to facilitate the collection, analysis, and consultation of material degradation data [58].

2.4. *Data quality*

It should be noted that the data obtained from these records are often characterized by incompleteness or inaccuracies. To address this limitation and ensure consistency with previous studies, the category "Unknown" was introduced to allow for a more detailed analysis of cases where information is limited or not entirely clear [20,35,50]. This additional categorization allows for accurate data treatment and consistency with analysis methodologies used in previous studies. When compiling the database, special care was taken to avoid repetition, focusing on the date of the incident, its geographical location, and the specific type of event reported, ensuring that the most accurate and clear records available were selected. This meticulous care in selecting records helped ensuring the quality and integrity of the information contained in the repository.

2.5. *Data analysis*

The second phase of the research, related to data analysis, is divided into:

Part-1. An overall analysis of the data using tables, graphs and drawings. This visual method allows for the quick identification of correlations between the analysed variables.
Part-2. The modelling and quantitative risk assessment (QRA) follows the preliminary overall analysis. The use of advanced tools of QRA such as the event tree analysis (ETA) and Bayesian networks will be outlined.

The ETA is a graphical tool used to analyse sequences of events that can lead to failures or accidents, allowing to assess risks and improve safety [18].

Bayesian networks (BNs) are further used to calculate the conditional probabilities between different variables and predict occurrence modes [27]. This method provides an estimation of the failure frequencies and helps to better understand the risk factors and their interactions. In this study, the Peter-Clark (PC) algorithm has been adopted to explore the structural framework in the BNs model. The skeleton was obtained based on conditional independence tests while casual rules embedded with the algorithm and expert knowledge support learning edge directions. By establishing the BNs model based on a large collected dataset, it is possible to reveal the conditional interdependencies among attributes and thus support the predictive modelling and probabilistic reasoning under conditions of uncertainty in the realm of NaTech [14].

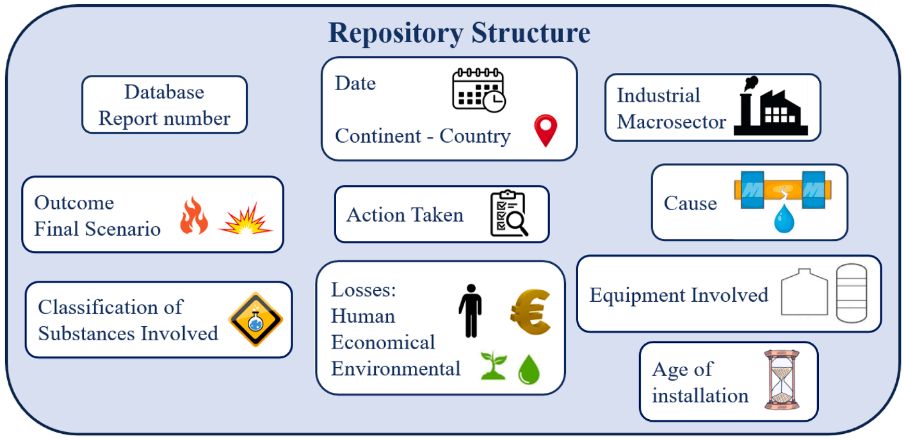


Fig. 1. Repository structure containing 3772 events on material degradation.

3. Results and discussion

Fig. 2 shows the source of the collected reports: 84.7% come from the NRC database, 15% from ARIA, 3% from eMars and only 0.3% from CSB. The NRC database collects a very large number of reports because it collects voluntary calls from American citizens, so the data is often incomplete with limited information. Considering the large number of reports from NRC, the results are presented separately for: i) NRC and ii) other sources, such as ARIA, CSB and eMars. It should be noted that the events collected by the NRC database are all from North America, while the other sources have an incidence of 95% of events from Europe. Indeed, the geographical distribution of the events shows that 86% occurred in North America, while 14% in Europe. The choice to analyse European and US databases reflects the availability, accessibility and coherence with the study by Castro Rodriguez et al. [14]. However, this entails a geographical limitation, in particular regarding the Asian and African contexts. Future developments of the work may include the integration of databases from other regions, such as the Failure Knowledge Database developed in Japan [33], or data published by Indian bodies such as the National Data and Analytics Platform [44] and the data.gov.in portal [46], which present government datasets potentially relevant for the process industry. The inclusion of these data may contribute to improving the understanding of regional risk patterns and to further validate the proposed models.

The temporal trend is reported in Fig. 3.

The NRC database became operational in 1990, indeed there is only one previous event dating back to 1988. From 1990 to 2023 NRC data show a generally stable trend over time, with a slight reduction in the average number of cases recorded in the period 2016-2023. This last period temporally coincides with the improvement of regulations and safety standards, technological advances and increased investments. In recent years, indeed, in the United States, significant improvements in regulations regarding material degradation have been implemented to promote the safety and reliability of infrastructure. For example, the Pipeline and Hazardous Materials Safety Administration (PHMSA) has introduced more stringent requirements for inspection, maintenance, and corrosion management [17]. Additionally, the American Society of Mechanical Engineers (ASME) has updated the Boiler and Pressure Vessel Code to improve corrosion management by introducing new materials and methods of protection against degradation [26].

With respect to the other sources, approximately 95% of these reports were registered in Europe. There has been an increase in the number of reports since 2000. This phenomenon coincides with the rise of the fourth industrial revolution, which has made it easier to document events thanks to the advent of the internet in the industrial context. Additionally, many European facilities were built after World War II and have now been in operation for over 50 years, which can cause structural and functional problems due to the natural ageing process of the infrastructure.

Between 2000 and 2016, the trend remained substantially constant, but since 2016, an increase has been observed, with the peak reached in 2019. This increase was observed a few years after the introduction of the Seveso III Directive (2012/18/EU) in Europe; this directive has emphasized the importance of material degradation and ageing in the industrial context, leading to an increased attention in the detection of this type of failure. In 2020, the advent of the COVID-19 pandemic led to the blocking of many activities worldwide, and in that year a decrease in ageing-related accidents was observed. Furthermore, this decrease also temporally coincides with the introduction of several guidelines to assess material degradation and prevent accidents, as by Milazzo and Bragatto [42].

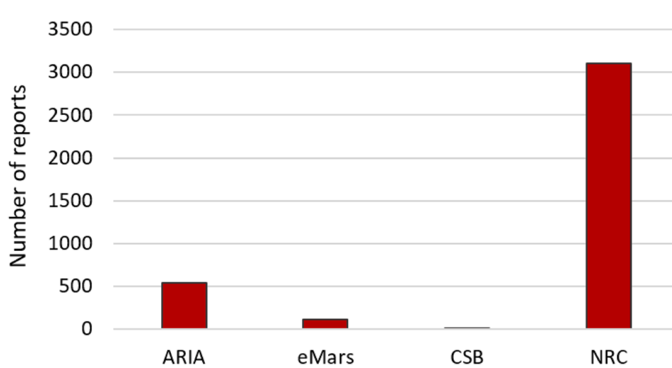


Fig. 2. Number of records for each database analysed.

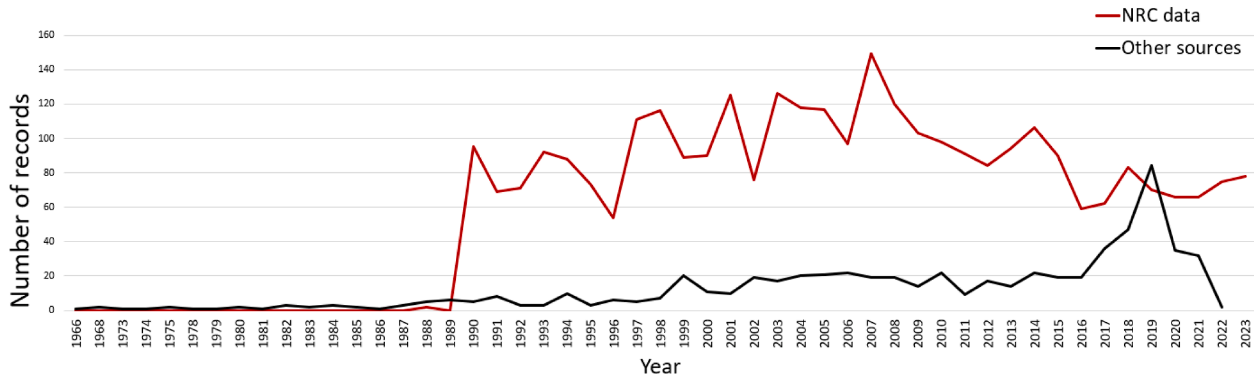


Fig. 3. Number of events over time.

3.1. *Characterization of industrial events and frequency of functional attributes*

The 3772 records were classified by failure mechanism. Fig. 4 shows the number of events for each mechanism and source. The figure shows that corrosion is the most recurrent failure mechanism, underlining the importance of more rigorous control and more adequate treatments. Vibration and fatigue follow as other relevant mechanisms. The records classified as multiple causes are 42. In particular, the most frequent degradation mechanisms in these events are corrosion, which appears in 3186 events, and erosion, in 141.

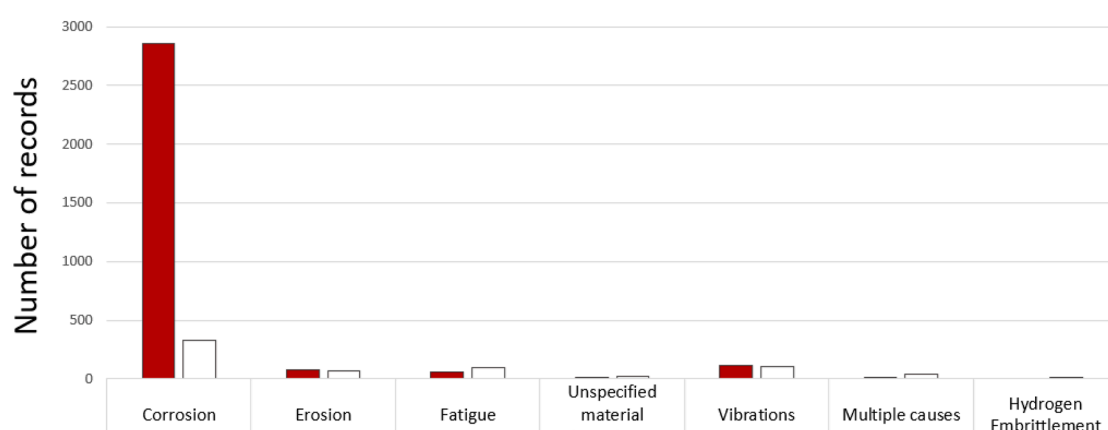
Another aspect analysed concerns the industrial macro-sectors and the equipment involved in the incidents. Fig. 5 clearly shows that the most involved sectors are chemical and petrochemical, pipelines, and, subsequently, storage and warehousing.

In the chemical and petrochemical sector, process conditions, such as temperature and pressure gradients, can contribute to mechanical stresses. As for pipelines, these stresses strongly depend on the environmental conditions to which they are exposed, such as cold or hot waves, or particularly aggressive environments depending on geography.

The analysis of the macro sectors revealed a different trend depending on the continent where the plants are located. In America, the Chemical & Petrochemical and Pipeline categories are the most affected, with events that are distributed almost equally between these two categories, with 40% and 39% of the incidents that occurred in America, respectively. Next comes the Storage & Warehousing category, with approximately 20% of the events. However, in Europe the Chemical & Petrochemical category is the most affected, with 55% of the incidents, followed by the Manufacturing category with 15% and lastly Storage & Warehousing with 7%. These data highlight how, in America, transport via pipelines is more frequently involved in events due to material degradation than in Europe.

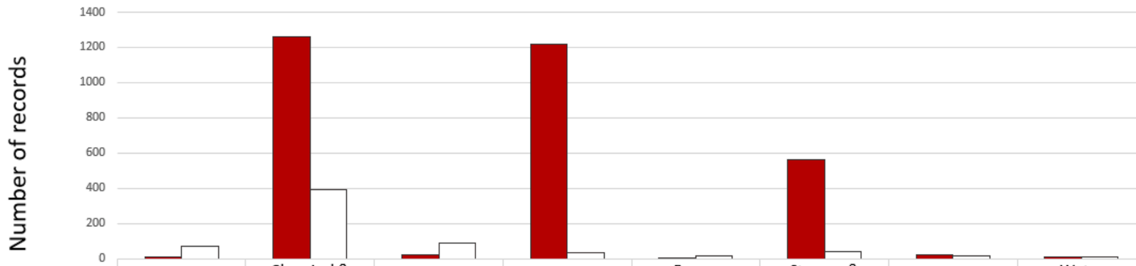
As for the type of equipment involved, it is important to note that primary containment systems are the most affected (Fig. 6). There are several reasons why primary containment systems are particularly vulnerable. Primarily, the nature of the substances contained in these systems is a determining factor in the vulnerability of these systems. The physical-chemical characteristics, reactivity and type of substances themselves significantly influence the risk of failure of the containment system. Then, primary containment systems are subjected to changing process conditions, such as temperature and pressure variations, which can compromise their structural integrity over time. These constant mechanical stresses can weaken the materials and reduce the effectiveness of the containment systems in preventing accidents or leaks. It is observed that the number of events related to the equipment classified as "Control & mitigation system" is higher than that of "Structures".

This phenomenon suggests that material degradation affects more significantly the equipment intended for process control and mitigation, compared to that intended to support operations. Indeed, control and mitigation equipment is frequently exposed to intense and variable conditions of use that accelerate its deterioration. This type of equipment is also subject to interactions with the fluids or gases treated, which can contribute to the deterioration of the materials, leading to



	Corrosion	Erosion	Fatigue	Unspecified material degradation	Vibrations	Multiple causes	Hydrogen Embrittlement
N. Events NRC	2855	77	54	1	112	4	0
N. Events other sources	331	64	98	24	107	38	7

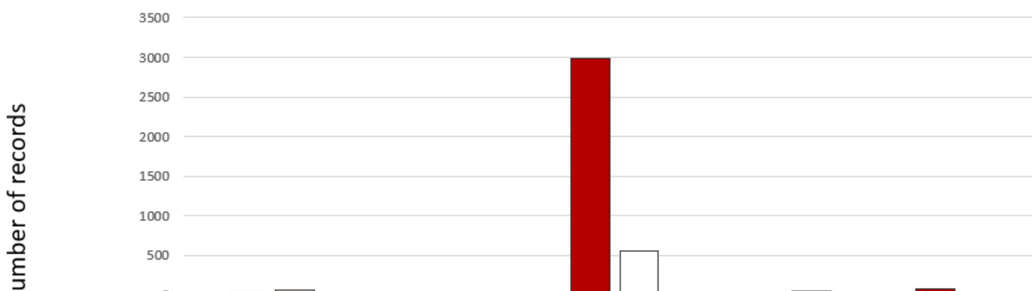
Fig. 4. Failure mechanisms in the 3772 records. The red bar represents the NRC database records, the white bar represents ARIA, CSB and eMars database.



	Bioprocesses	Chemical & Petrochemical	Manufacturing	Pipeline	Power Production	Storage & Warehousing	Transportation	Water treatment
N. Events NRC	10	1259	20	1216	3	565	22	8
N. Events other sources	69	395	89	36	14	39	17	10

N. Events NRC N. Events other sources

Fig. 5. Macro sectors involved in the events studied. The red bar represents the NRC database records, the white bar represents ARIA, CSB and eMars.



	Control & mitigation system	EC&I System	Primary containment system	Structures	Unkown
N. Events NRC	31	4	2985	10	73
N. Events other sources	55	14	555	44	0

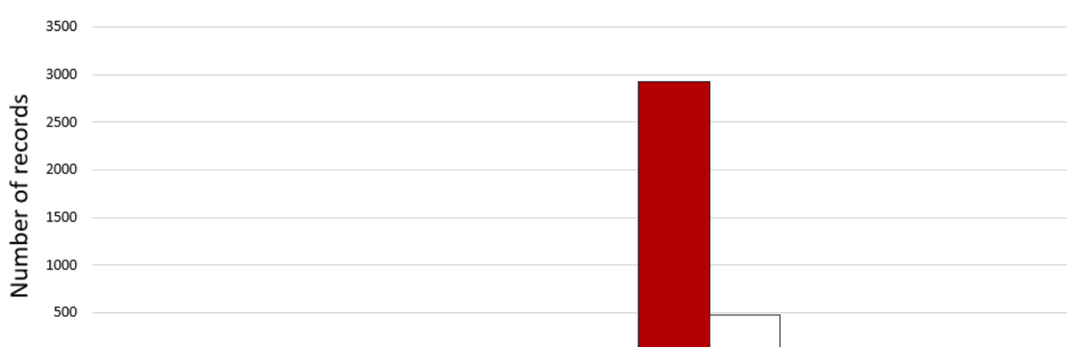
N. Events NRC N. Events other sources

Fig. 6. Equipment involved in the analysed events. The red bar represents the NRC database records, the white bar represents ARIA, CSB and eMars.

more frequent failures or malfunctions. Conversely, the equipment least affected by degradation is classified as "EC&I system", which is specifically designed to ensure the safety of the plant. This category of equipment seems to have a longer lifespan than control and mitigation systems. Furthermore, this equipment is frequently subjected to more rigorous preventive maintenance, further reducing the probability of failures due to degradation.

Regarding the equipment involved in the events, an in-depth analysis was carried out in relation to the location of the plants. The analysis revealed similar trends for both continents, Europe and America.

Regarding the outcome, it is remarkable to observe that over 90% of the events result in LOC, while 2% and 3% in accidents and incidents respectively, and finally 1% in cases of near misses. These results are illustrated in Fig. 7, which clearly shows that material degradation most frequently led to loss of containment. It is interesting to note that, in the case of American records, LOC has an occurrence rate of 94%, while



	Accident	Incident	LOC	Near Miss
N. Events NRC	0	11	2926	6
N. Events other sources	78	90	479	22

N. Events NRC N. Events other sources

Fig. 7. Outcome of the 3772 records studied. The red bar represents the NRC database records, the white represents ARIA, CSB and eMars.

events classified as accident and incident have a rate of 0.5% each, respectively. On the contrary, European events show an outcome of LOC with an occurrence rate of 74%, while accidents of 7.6% and incidents of 14%. Thus, in America, the rate of accidents and incidents is 172 times lower than that of LOC. On the contrary, in Europe, the rate of LOC is about 5 times higher than that of incidents and 10 times higher than that of accidents. It should be noted that operational practices, safety management systems, and plant infrastructure differ between Europe and America, contributing to the mitigation of escalation toward major incidents. These discrepancies may contribute to the observed differences in incident data. In particular, differences in regulatory and compliance frameworks governing the situation, as the NRC relies on voluntary reporting which can lead to a higher percentage of events classified as LOC, while European systems under the Seveso III Directive require structured mandatory reporting for some industrial plant, which can lead to a higher number of incidents and near misses. Indeed, it is generally observed in the literature that near misses tend to occur more frequently than loss of containment or serious incidents [19]. However, in the dataset, near misses are significantly fewer. This discrepancy may be attributed to the lack of specific regulatory requirements for reporting these events in some jurisdictions, variability in data collection systems between operators and competent authorities, and the perception by operators that these events are less relevant, resulting in under-recording. This aspect represents an inherent limitation of the available data and highlights the need to promote a reporting culture also for minor events, in order to improve the understanding of the precursors to serious incidents in order to limit their escalation.

It is important to note that major accidents in the process industry are often caused by containment losses, as highlighted by Casal [12]. This underlines the importance of implementing preventive strategies to avoid such losses, in order to prevent the escalation of accidents.

In Fig. 8a and b, the different final scenarios related to the failure mechanisms are shown, to conduct a more in-depth analysis. The choice to represent the results in two separate figures is motivated by the fact that the number of events due to corrosion is significantly higher than the other mechanisms; therefore, this subdivision provides a clearer and more detailed graph. Significant differences in the results emerge based on the nature of the different mechanisms. Corrosion mainly leads to environmental contamination (58%) and is often caused by the substances contained that can damage the materials and accelerate the deterioration of the equipment. The second scenario concerning corrosion, with a rate of 10%, is characterized by the release of the substances without causing significant consequences on the surrounding environment. This occurs when the contained substances are not harmful to the environment or when, despite the presence of such properties, the release is promptly and effectively managed to prevent environmental damage. When the contained substances are not classified as hazardous, corrosion is due to external conditions and does not lead to contamination. Timely management measures may include containment of the release, neutralization of the substances, securing the affected areas and implementing preventive actions to avoid the propagation of damage. However, this scenario has a significantly lower occurrence rate than environmental pollution, highlighting the need for timely interventions. Therefore, it is necessary to improve such management through more

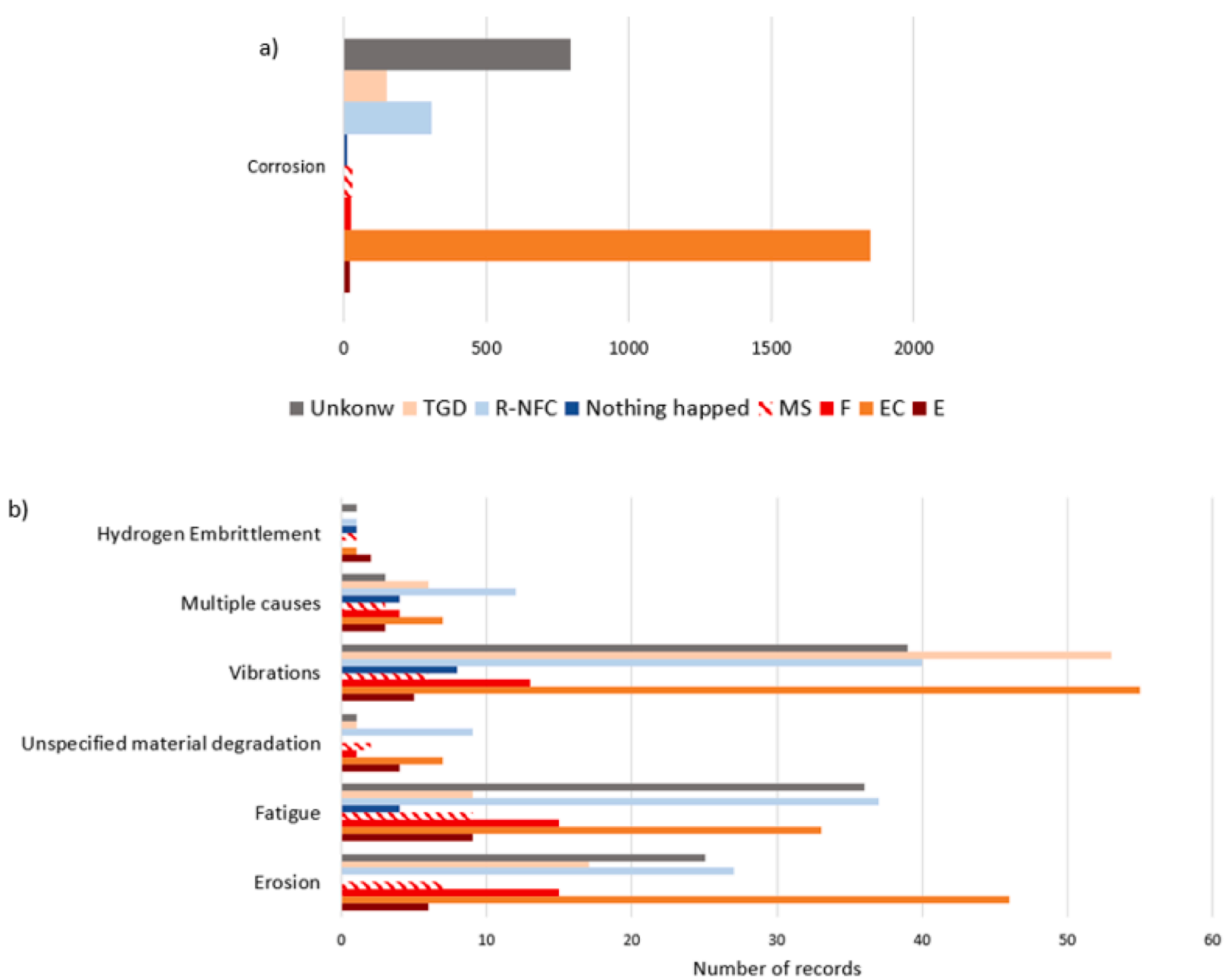


Fig. 8. Final scenario for each failure mechanism. a) Corrosion. b) All other mechanisms.

frequent inspections and the implementation of specific treatments where necessary.

Vibrations also mainly lead to environmental contamination, in 25% of reports, but it is interesting to notice that there is also a significant number of toxic gas dispersion (24%), since vibrations can cause small losses of gas containment through small holes in equipment generated by this phenomenon.

When we talk about fatigue and erosion in an industrial context, we are referring to mechanical phenomena that cause the deterioration of materials over time. Fatigue occurs when a material is subjected to repeated stresses over time, while erosion is caused by external agents. When fatigue phenomena occur in a plant, the most common outcome is a release without significant consequences, accounting for 24% of the cases. This can be attributed to two main factors. First, the mechanical nature of such phenomena is not influenced by the substance contained in the plant. Second, optimal management of losses, thus preventing any adverse consequences. On the contrary, release without significant consequences represents only the second most frequent event associated with the erosion mechanism, while the first one is environmental contamination, accounting for 32% of cases, although erosion is not directly related to the contained substance. It is interesting to note that a good part of the events that lead to fires and explosions, approximately 40%, are associated with the phenomenon of fatigue and erosion. Vibrations, which also present a high number of fire events, can produce sparks that, if flammable substances are present, trigger fires and/or explosions. Finally, it is observed that events due to hydrogen embrittlement evolve in explosions in 29% of the reports, while no case of fire is recorded. This phenomenon can be attributed to the dynamics of hydrogen release in cases of structural failure; indeed, this result suggests that, in cases of hydrogen embrittlement, the structural failure leads to a release of hydrogen in quantities sufficient to trigger an explosion, rather than a fire.

It can be observed that the number of missing data is significantly high; an example is the corrosion phenomenon, where the second most frequent scenario is classified as “Unknown”.

Fig. 9 shows the substances involved in each incident, classified according to risk categories. It can be observed that most of the substances involved present multiple hazards, representing almost 75% of the total. Many of these substances are aggressive towards the materials with which they come into contact, promoting the degradation of the material itself. Table 2 shows the substances classified as having more than one hazard. Interestingly, 92% of incidents involving substances classified in more than one hazard category are related to physical hazards.

It is interesting to note the presence, although in a very small number, of substances classified as non-hazardous (NH). This phenomenon can be explained by the degradation of the material, which is not caused exclusively by the substances contained in the system but can also be influenced by other external or operational factors, by the environmental conditions to which the materials are exposed and by the physical stresses they undergo. For instance, atmospheric corrosion, which can occur due to exposure to humidity in the air, pollutants, or proximity to the sea, or the corrosion under insulation, which develops when the material is covered by insulation and water, due to humidity or rain, remains trapped, promoting corrosion, are both recurring mechanisms even in the absence of hazardous substances.

For a more in-depth analysis, the age of the plant was also collected where possible. It was possible to trace the date of construction of the plant, or the age of the equipment involved for 457 events. Fig. 10 shows the trend of these data, showing that more than 70% of the incidents involve "old" plants, therefore plants older than 25 years; indeed, according to Vairo et al. [54], in Europe a substantial proportion of industrial installations, around 50%, continue to operate beyond their expected lifespan, often exceeding 25 years. This partly explains the high percentage of accidents that occurred in plants classified as "old" in the dataset. However, a small percentage of events equal to 5% involve plants that are less than 5 years old. This indicates that operating time is not the only factor in preventing material degradation, but there are

Table 2
Substances presenting more than one hazard according to UNECE [52].

Multiple hazard	N. Events	%
Health hazard and Environmental hazard	220	7.8
Health hazard, Environmental hazard and Physical hazard	2341	83.3
Health hazard and Physical hazard	233	8.3
Physical hazard and Environmental hazard	15	0.5

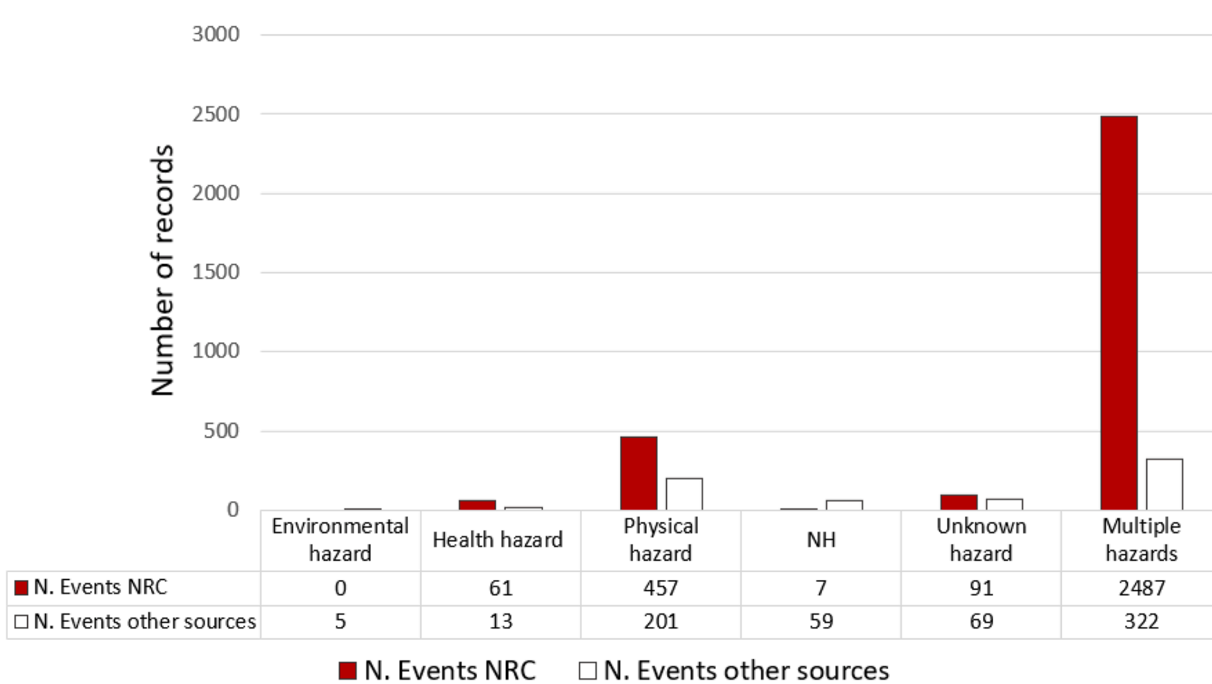


Fig. 9. Classification of the substance involved. Number of events associated with each category of substances, with the indication of the database from which the record comes.

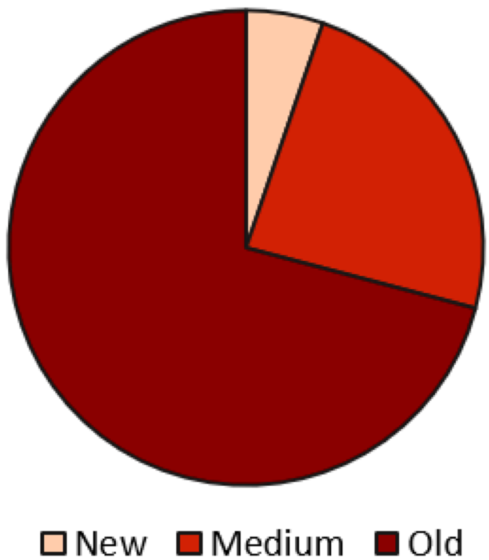


Fig. 10. Age of the plants involved in 457 records for which it was possible to trace the data. Age distribution for old, medium, and new installations.

multiple complex variables that must be considered.

An in-depth analysis was conducted on the age of the installations involved in accidents, in relation to the continent where they are located. However, a limitation emerged due to the fact that European databases often provide data on the age of the installations, while the main American database, the NRC, does not include this information. For this reason, only a small number of American records, those from the CSB, present data on the age, compared to the greater number of European reports from Aria and eMars. The analysis revealed an expected and common trend in Europe and America: the oldest installations are more frequently involved in accidents, followed by those of medium age, while the youngest installations are the least affected.

For the reports that provided the data, we also collected the actions taken after the event, to analyse the effectiveness of the inspection plans. This information was found for 360 events. The trend is shown in Fig. 11, where it is observed that in 90% of the cases, the inspection plan was revised after the event, increasing the frequency of inspections. This data highlights that current inspections are often still not sufficient, indicating the need to implement more frequent inspection plans. This highlights the need for a risk-based inspection (RBI) approach, rather than continuing with the traditional method of periodic inspections, which does not take into account the most vulnerable components of the equipment [6,49]. Consequently, a more effective management and control system is needed.

However, in 7% of the events, no action was implemented after the event. This suggests that, although the inspection plan was already set up with a high frequency, the event still occurred, indicating that ongoing inspections are not yet fully adequate. This evidence highlights the need to develop specific guidelines and procedures to ensure that thorough and effective inspections are performed. Therefore, it is essential to develop new inspection methodologies that not only increase the frequency but also improve the ability to identify potential problems and intervene promptly to avoid them. It was observed that in 2% of the events, a specific treatment was integrated into the material to increase its resistance to degradation. The treatments must be carefully chosen from the beginning of the commissioning of the plant or implemented if absent.

The absence of adequate treatments also highlights a deficiency at the risk analysis level, which had underestimated the degradation of the material, preventing the adoption of the necessary protective treatments. To effectively address this issue, it is crucial to develop a greater knowledge of both the deterioration mechanisms and the methods of monitoring and preventive maintenance. Improving the understanding of how and why these phenomena occur allows for the implementation of more effective strategies for their management, reducing the risk of failures and production losses. Furthermore, the adoption of advanced prevention systems and the continuous updating of inspection and maintenance techniques can help mitigating the negative effects of deterioration. This approach not only improves the safety of the plants but also their long-term reliability, ensuring continuous production and reducing the costs related to repairs and unplanned interruptions.

One aspect examined concerns the losses caused by the incidents; Fig. 12 shows the results, divided into human (orange), economic (dark red) and environmental losses (red).

The acronyms shown in the figure represent the different categories of events, while the numbers indicate the number of events that fall into each category. It is evident that the number of available data is significantly lower than the total number of events analysed. Only 4% of the cases document economic losses, 7.3% report impacts on people and 28.2% report environmental pollution. This distribution could reflect both a lack of detailed data in the available sources and greater attention to some types of consequences compared to others.

For economic losses, it is observed that the four categories are almost equivalent in number, with the exception of losses exceeding ten million dollars, which are slightly lower.

For environmental contamination, most cases have no contamination (ND), followed by moderate or minor contamination (MMD). Events with severe contamination (SED) are significantly lower in number.

In terms of human losses, the category with the highest occurrence rate is the one with no fatalities (NF), followed by the category with no injuries (NI) and multiple injuries (MI). The following are the single injury (SI), multiple fatalities (MF) and single fatality (SF) categories.

These results highlight that most of the events involve releases

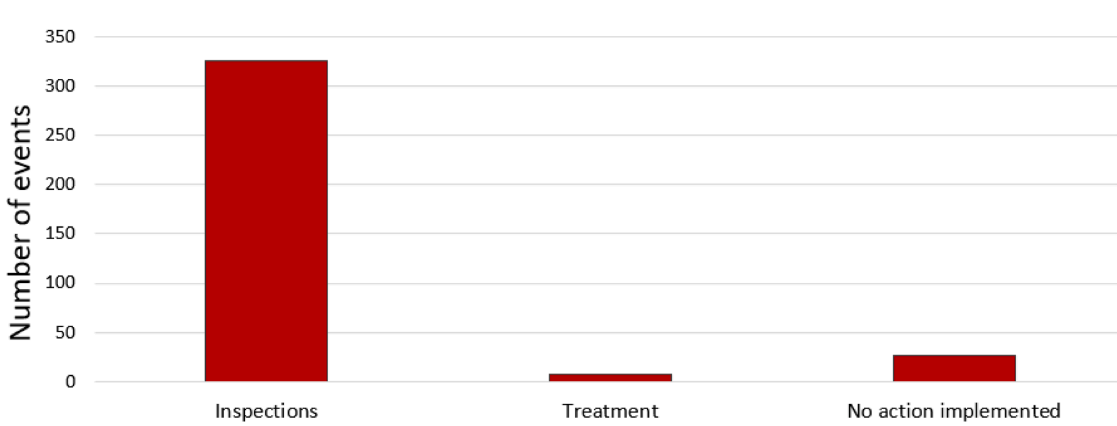


Fig. 11. Action taken after the event for records for which it was possible to trace the data.

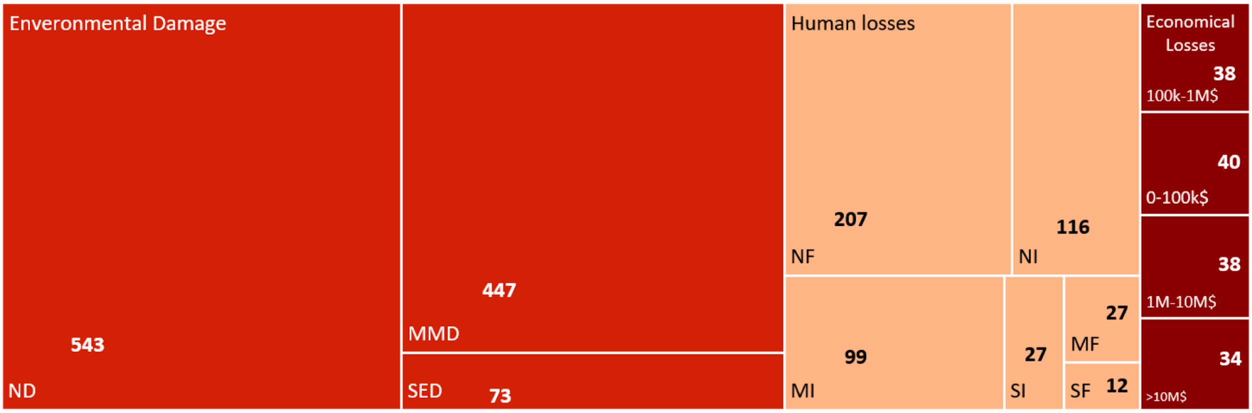


Fig. 12. Losses caused by the accidental event. Environmental pollution is red, human losses are orange, and economic losses are dark red.

without further consequences. However, the economic impact can vary greatly, with some losses exceeding ten million dollars, although less frequent than other categories.

For human losses, to contextualize these results, a comparison was conducted with the historical analysis of Ricci et al. [50], which collected a database of 9100 NaTech events, also including information on human losses. NaTech event (Natural Hazard Triggering Technological Accidents) refers to technological accidents triggered by natural hazards [55]. In this study, the number of events where human loss data is available amounts to 210, corresponding to 2.3% of the total, while in the material degradation study, the data is reported in 281 reports, equal to 7.4%. Fig. 13 presents the results of this comparison, with the percentage of events where losses are documented. The figure also presents the results for single and multiple injuries and for single and multiple fatalities, distinguishing between the two studies: the red bars represent the results of the material degradation study, while the white bars correspond to the NaTech study. From this comparative analysis it emerges that, in absolute terms, the number of reports containing information on human losses is similar in the two studies. However, in percentage terms compared to the total number of events analysed, the study on material degradation presents a greater availability of data, suggesting that this type of event may have slightly more detailed documentation than the NaTech cases.

3.2. Quantitative risk assessment

This section illustrates the results obtained using the event tree and Bayesian networks, tools that model the behaviour of complex systems considering the dependencies between variables. The use of the event tree allows for the systematic representation of possible sequences of events that can arise from an initial failure, while Bayesian networks allow for the calculation of the conditional probabilities of the functional attributes, providing a quantitative representation of the uncertainties. This approach is particularly useful for managing the intrinsic uncertainty of data coming from open-source databases, often incomplete or uncertain.

3.2.1. Event tree analysis

Since 85% of the events were caused by corrosion, the event tree analysis (ETA) was developed from this type of phenomenon. When equipment in a plant corrodes, a leak may occur, which, depending on the material released, can then ignite and lead to a fire or explosion; however, the ignition may happen immediately or be delayed. Depending on the timing of the trigger, a different scenario can emerge [56]. From the ETA in Fig. 14 it is observed that when a release happened, immediate ignition has a frequency of occurrence of 1%, almost equal to events with delayed ignition, which amounts to 1.5% (the frequency in this case is obtained by multiplying the frequency of no immediate ignition by the frequency of delayed ignition). The estimated frequency of occurrence for the events considered in the dataset is indicated on the connecting branch of the event tree. Each branch represents a distinct sequence of possible events.

It is possible to calculate the conditional probability of a specific scenario. For example, the probability that the specific fire scenario P(F|II), belonging to the upper branch of the event tree, occurs after an immediate ignition (II), can be calculated as:

$$P(F|II) = F(F|II) \times F(II) \times F(R) \times F(C)$$

where:

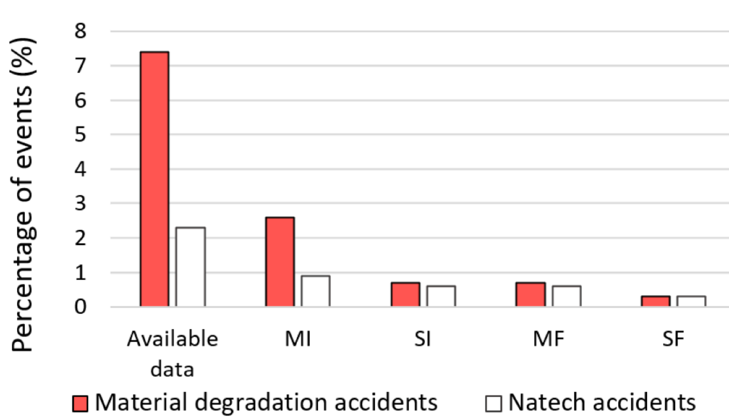


Fig. 13. Comparison between the material degradation study and the NaTech study [50] in terms of availability of human loss data. The red bars represent the material degradation study, while the white bars represent the NaTech study, highlighting differences in occurrence rate.

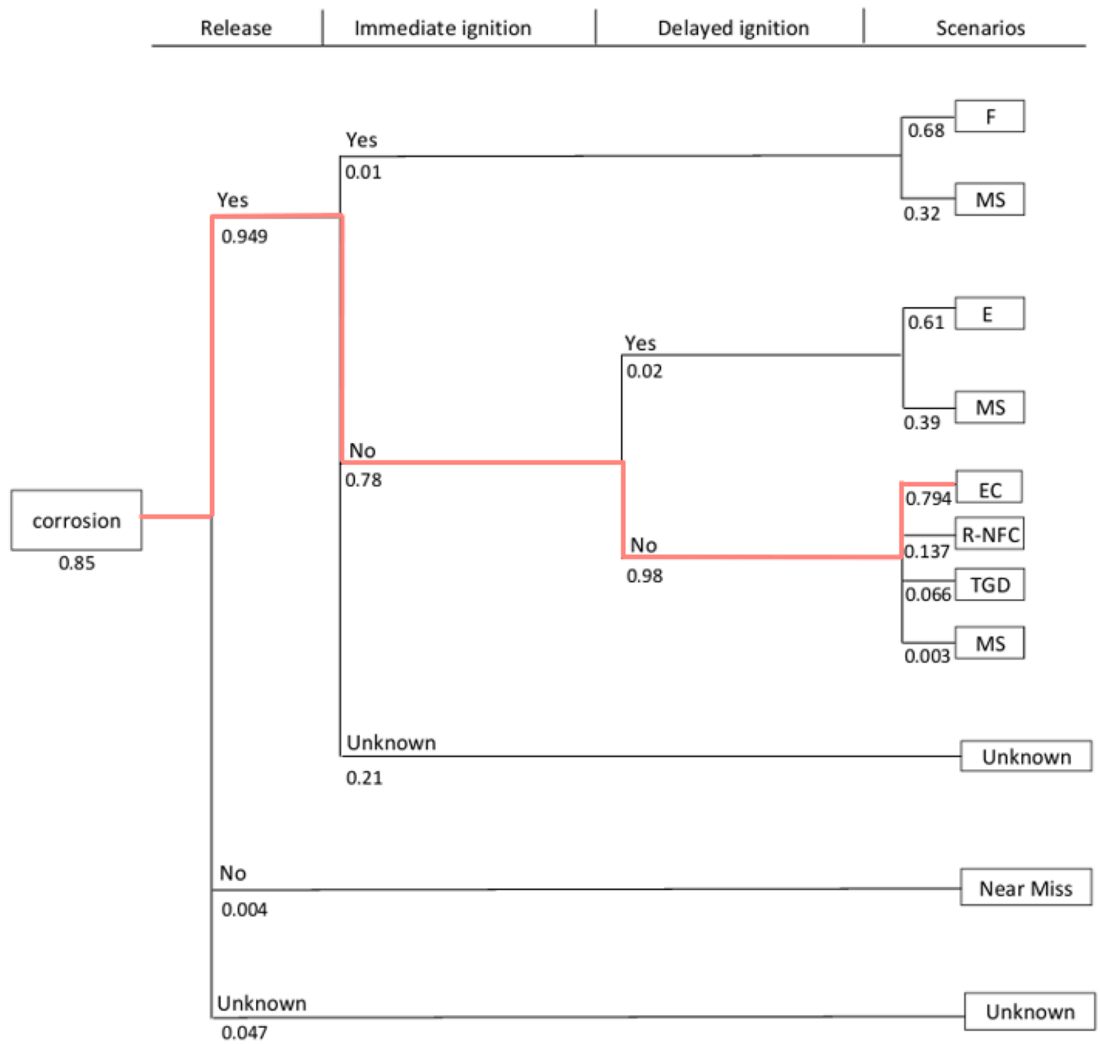


Fig. 14. Event Tree Analysis (ETA) for corrosion mechanism with all possible scenarios. Environmental contamination in the absence of a trigger, highlighted in red, is the scenario with the highest occurrence frequency.

$P(F|II)$ is the probability that a fire will occur due to an immediate ignition of a release due to corrosion.
$F(F|II)$ is the frequency of occurrence of the ignition scenarios after an immediate ignition.
$F(II)$ is the frequency of occurrence of immediate ignition.
$F(R)$ is the frequency of occurrence of a release.
$F(C)$ is the frequency of occurrence of corrosion.

Substituting the corresponding values:

$$P(F|II) = 0.68 \times 0.01 \times 0.949 \times 0.85 = 0.006$$

Similarly, it is possible to calculate the probabilities of all other scenarios. The most likely event, as also highlighted by the graphical analysis, is environmental contamination (the red line in Fig. 14). The occurring probability of this event can be calculated using the following equation:

$$\begin{aligned} P(EC|\overline{DI}) &= F(EC|\overline{DI}) \times F(\overline{DI}) \times F(\overline{II}) \times F(R) \times F(C) \\ &= 0.794 \times 0.98 \times 0.78 \times 0.949 \times 0.85 = 0.49 \end{aligned}$$

where:

$P(EC|\overline{DI})$ is the probability of environmental contamination, assuming there is no delayed ignition, occurring as a result of a release due to corrosion.
$F(EC|\overline{DI})$ is the frequency of occurrence of environmental contamination, if there is no delayed ignition.
$F(\overline{DI})$ is the frequency of non-occurrence of a delayed ignition.
$F(\overline{II})$ is the frequency of non-occurrence of an immediate ignition.

Analysis of the dataset indicates that, in cases where industrial components were affected by corrosion, environmental contamination was observed in approximately 50% of the incidents. This value represents a conditional probability, calculated on the total of corrosion-caused events documented in the database, and not an absolute probability referred to all equipment in operation. Specifically, it represents the percentage of corrosion-related events in which a leak occurred leading to environmental contamination. Therefore, this value is calculated based on reported events, and not per year, per plant or per equipment. It does not reflect the probability of failure in a general population of components, but rather the frequency observed within a subset of real incidents where corrosion has been identified as the trigger mechanism. It is important to underline that the analysed data are based on events in real plants; for this reason, the probability reflects a mitigated risk, that is the residual risk after the application of the safety measures existing at the time of the event. A validation could be pursued in future work by comparing this value with failure rate data from industry-specific reliability databases or probabilistic risk assessments. This value highlights the need to focus on optimizing inspection plans and risk analyses related to material degradation.

For the application of the method, two real case studies were selected, taken from the developed accident database, in order to validate the model and demonstrate its applicability. The selected case studies are:

Case Study 1: Report number 44683 is taken from the ARIA database and describes how on 9 December 2013, abnormal noises and vibrations occurred in the black liquor steam generator in a paper mill, which normally operates at negative pressure, but at that time recorded a positive pressure between 20 and 30 mbar. After some disturbances, the parameters returned to normal. An external visual inspection did not reveal any anomaly, but it was assumed that the cause was a falling block of sodium sulphate. The fuel oil supply was then activated to dissolve the deposits. During the night, a water leak was detected in the boiler, accompanied by abnormal humidity and low temperature. The water level became unstable and a sudden increase in flow was recorded. Therefore, the boiler was ordered to be emptied, and the building was isolated. All production facilities were stopped. The inspection, repair and restart operations took several weeks, with losses estimated between 2 and 3 million euros. The inspection reported a hole in a coated steel pipe, among the causes a corrosion-erosion due to air turbulence. The SIR department decided to review the boiler inspection plan, increasing the frequency of inspections.

Therefore, the case study reports corrosion and erosion with consequent release of water into the surrounding environment, but this was classified as release without further consequences. There were significant economic losses, but there were no cases of human losses or injured people, and there was no environmental contamination. In Fig. 15 the event tree with the case study highlighted in red:

$$P(R-NFC|\overline{DI}) = F(R-NFC|\overline{DI}) \times F(\overline{DI}) \times F(\overline{II}) \times F(R) \times F(C) = 0.137 \times 0.98 \times 0.78 \times 0.949 \times 0.85 = 0.084$$

where:

$P(R-NFC|\overline{DI})$ is the probability of release without further consequences, assuming there is no delayed ignition, occurring as a result of a release due to corrosion.

$F(R-NFC|\overline{DI})$ is the frequency of occurrence of release without further consequences, if there is no delayed ignition.

The conditional probability of the reported case study was found to be 0.084.

Case Study 2: CSB report number 2019-04-I-PA describes how on the morning of June 21, 2019, a pipe elbow in the hydrofluoric acid (HF) alkylation unit ruptured, releasing a cloud of flammable vapours composed primarily of propane and HF. The cloud ignited two minutes later, causing a large fire and three explosions, the largest of which involved a tank, sending metal fragments flying up to 600 meters away. The fire was not extinguished until the following day. The CSB investigation determined that the primary cause was accelerated corrosion of the elbow made of carbon steel with high nickel and copper content, materials known to be more vulnerable to HF. This led to the pipe becoming thinner and eventually breaking. The accident was caused by a lack of thorough inspection of all carbon steel components, the absence of remotely activated emergency isolation valves to shut off the flow of hydrocarbons, the failure of the water mitigation system, which could not be activated in a timely manner due to electrical and structural damage, and a lack of safety measures.

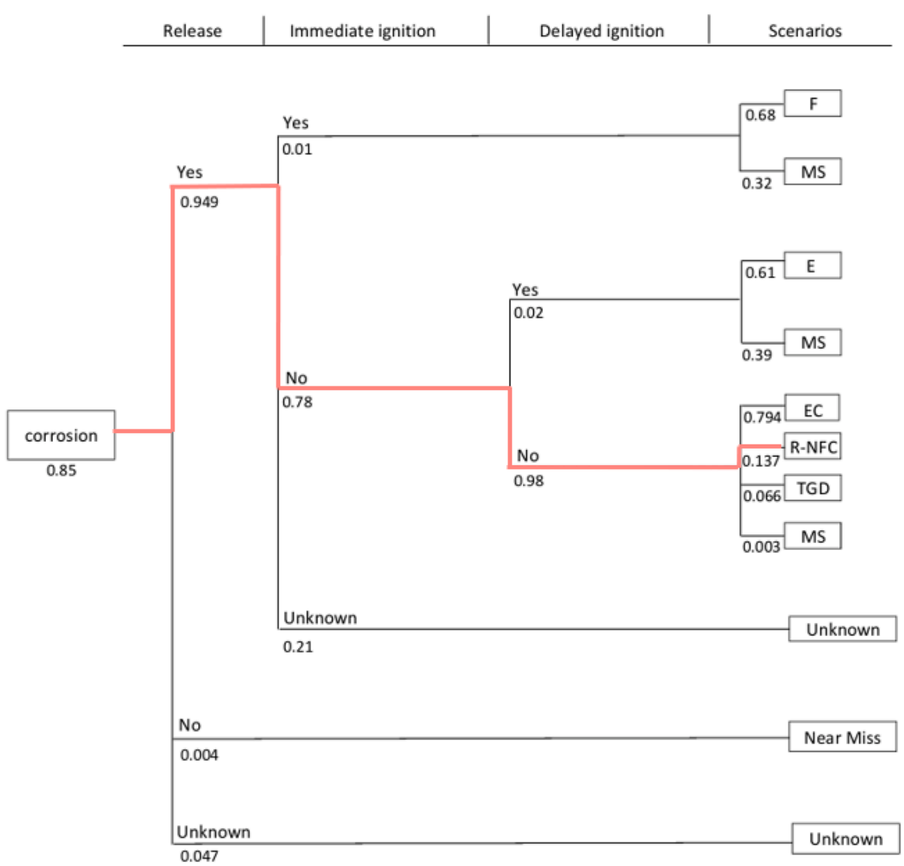


Fig. 15. Event tree analysis (ETA) for the first case study highlighted in red. The scenario reported corrosion of a component, resulting in the release of water into the environment and it is classified as release without further consequences.

The accident released approximately 5,239 pounds of HF, of which 3,271 pounds were released into the atmosphere, and 676,000 pounds of hydrocarbons, of which 608,000 were combusted. Five workers and one firefighter were injured. Metal fragments landed near tanks containing toxic and flammable substances, increasing the risk of escalation. The unit was severely damaged, with material damage estimated at $750 million, making the event the third most expensive refinery accident worldwide since 1974.

Therefore, the case study reports corrosion with the consequent release of flammable propane and HF vapours into the surrounding environment, generating fire and explosion. There were very high economic losses, and there were no cases of human losses, but several people were injured and there was moderate environmental contamination. Fig. 16 shows the event tree with the case study highlighted in red:

$$P(MS|II) = F(MS|II) \times F(II) \times F(R) \times F(C)$$
$$= 0.32 \times 0.01 \times 0.949 \times 0.85 = 0.003$$

where:

P(MS|II) is the probability of multiple scenarios, assuming there is immediate ignition, occurring as a result of a release due to corrosion.
F(MS|II) is the frequency of occurrence of multiple scenarios, if there is immediate ignition.
F(II) is the frequency of immediate ignition.

The conditional probability of the reported case study was found to be 0.003.

To integrate the results into a practical decision-making system, a 3 × 3 risk matrix was developed, combining:

- Conditional probability of the event (obtained from the ETA model)
- Severity of the consequences estimated based on economic damages, human losses, and environmental impacts.

The risk matrix developed in this study represents an integrative tool for qualitative and quantitative risk assessment, based on the intersection between the conditional probability of occurrence of an event and the severity of its consequences [24]. The thresholds adopted are:

- Probability: Low ($P < 0.01$), Medium ($0.01 < P < 0.05$), High ($P > 0.05$).
- Consequences: Low (limited economic losses, no deaths or injuries, no environmental impact), Medium (significant economic losses, no deaths but with injuries, moderate environmental contamination), High (high economic losses, with deaths and injuries, severe environmental contamination).

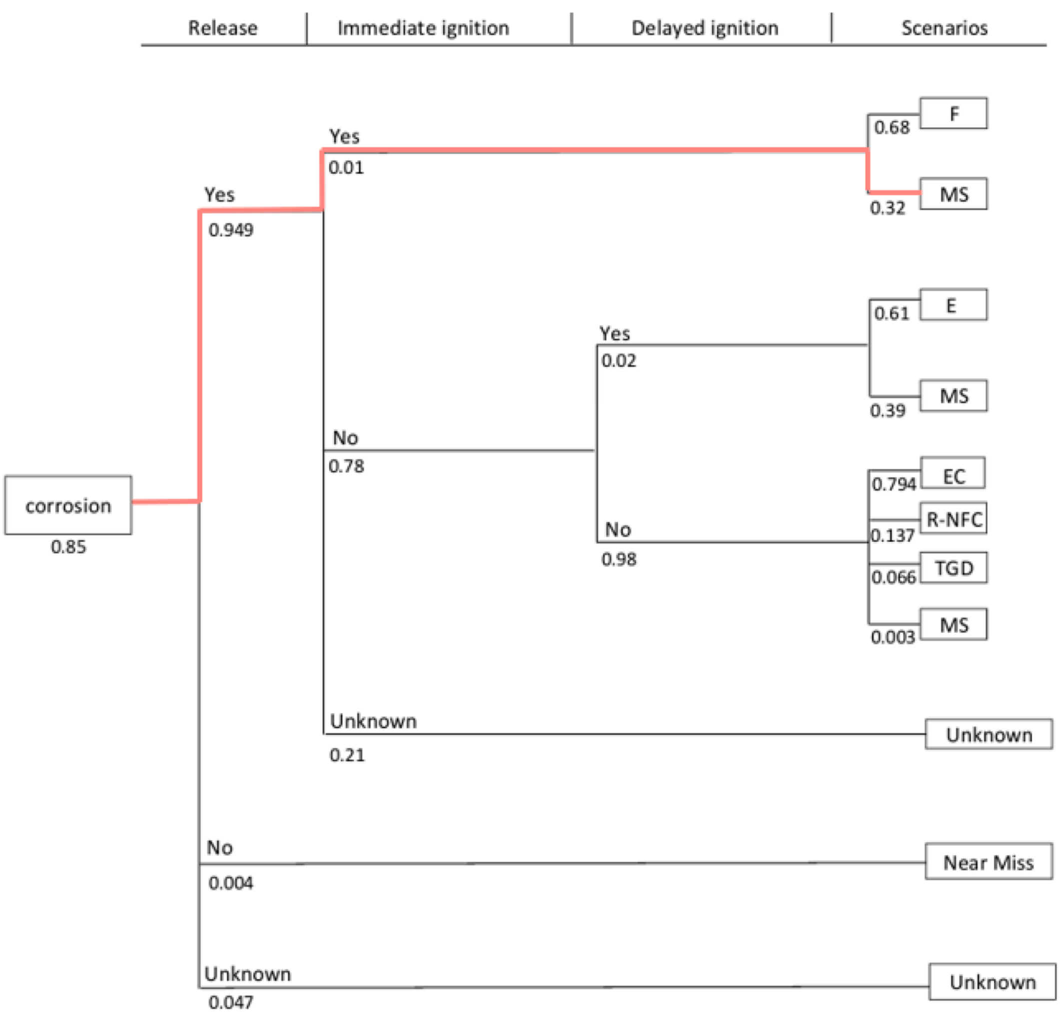


Fig. 16. Event tree analysis (ETA) for the second case study highlighted in red. The scenario reported corrosion of a component, resulting in the release of flammable vapours in the environment with consequent fire and explosion, classified as multiple scenarios.

The intersection of the two dimensions allows each scenario to be classified into one of three risk categories: low, medium or high. This classification can be used to support operational decisions, such as defining the frequency of inspections, prioritizing maintenance interventions or designing mitigation measures. Unlike the thresholds proposed by Duijm [24], which are based on absolute frequencies of occurrence, in this study more permissive thresholds have been adopted for the classification of the probability. This choice is motivated by the fact that the probabilities used do not derive from deterministic models or annual frequencies, but from conditional probabilities calculated from a historical dataset of industrial accidents. These probabilities reflect the probability of occurrence of a scenario given a certain operational context and are already influenced by the presence of active and passive safety barriers. Then, the dataset itself is subject to selection bias, as it includes only events that occurred and were reported, potentially excluding numerous avoided or undocumented cases. Therefore, the adoption of more permissive thresholds allows a more realistic classification of the residual risk and greater coherence with the objective of the BN-ETA model, which is to support operational decisions in complex and highly uncertain contexts.

In this study, the two selected cases were placed within the matrix, as shown in Fig. 17:

- Case ARIA 44683 exhibits a conditional probability that falls within the high-probability range. However, the associated consequences are limited to economic impacts, which are categorized as low severity. As a result, the overall risk level is assessed as medium.
- Case CSB 2019-04-I-PA involving a refinery explosion with estimated damages of $750 million, multiple serious injuries to personnel, and environmental contamination, is characterized by a low probability of occurrence. Nevertheless, the severity of the consequences places it in the high-impact category. Consequently, this case is also classified as medium risk.

The integration of conditional probabilities and consequences within the risk matrix allows for a systematic assessment of the risk associated with specific incident scenarios. This approach provides a synthetic but informative representation of the criticality, useful for prioritizing inspection and maintenance activities, and assigning greater attention to assets or scenarios that fall into the medium or high-risk bands.

The analysis highlights some relevant aspects:

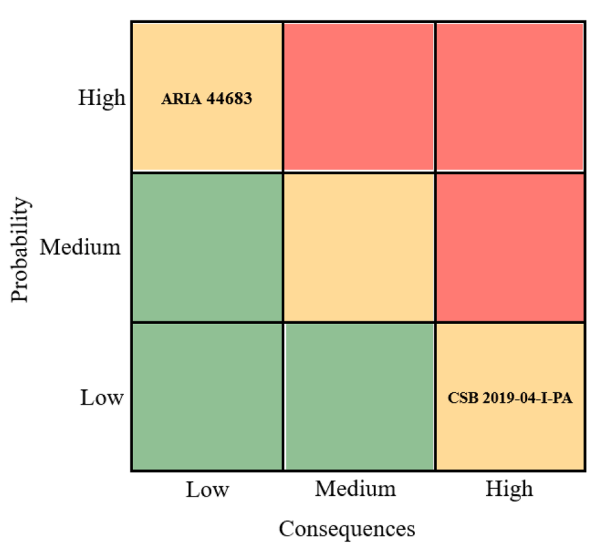


Fig. 17. Risk matrix applied to the two case studies chosen. In green the risk is low, in orange it is medium, in red it is high.

i) Despite the substantial differences between the two cases in terms of type of plant, scale of the accident, and probability, both are classified as medium risk. This shows that rare but catastrophic events can have a comparable impact, in terms of risk, to more frequent but less serious events.
ii) Both cases include safety measures already implemented (technical barriers, inspections, mitigation systems). However, the residual risk remains non-negligible, highlighting the need for more robust prevention strategies, especially in high-risk contexts such as process plants.
iii) The probabilities used do not derive from historical frequencies or deterministic models but from conditional probabilities calculated on a dataset of accidents. This introduces some uncertainties; indeed, the data may contain errors or omissions, the reports are often not standardized, with variability in the quality and detail of the information and there is a certain degree of subjectivity in the classification and narration of the events.
iv) Despite the uncertainties, the proposed model allows the integration of expert knowledge and historical data, modelling complex scenarios with multiple interdependent variables, and providing a quantitative basis for inspection prioritization and risk management.

It is important to highlight that, in the present study, the severity of the consequences was assessed based on real data from past events. However, in a predictive application, the magnitude of the consequences could be estimated using surrogate indicators, such as the type of equipment involved, the hazardous properties and the quantity of the released substance, as well as the proximity to sensitive targets (personnel or environment). This approach would allow the use of the risk matrix even in the absence of detailed historical data, making it a tool to support operational decisions in the preventive phase.

3.2.2. *Bayesian networks analysis*

To address the high level of uncertainty and missing data in the historical accident records, as also shown in the previously ETA analysis, Bayesian Networks (BNs) were introduced as a complementary modelling tool. The aim is to provide a second layer of analysis that can infer conditional relationships between key variables even when information is incomplete or unavailable. The approach supports a more robust understanding of the vulnerabilities of the system in the context of material degradation. This structure enables predictive reasoning and helps prioritizing inspection and maintenance strategies based on probabilistic insights. In detail, each node on the graph represents one interested variable, called a functional attribute, and edges between node pairs reflect their conditional independence relations.

This section targets NRC database, selecting “Equipment involved”, “Cause”, “Outcome”, “Macro-Sector”, “Substance involved”, and “Final Scenario” as the interesting variables to establish the BNs model. As mentioned in Section 2.5, both structure learning approaches and expert knowledge are combined in the structure learning process. To train the BNs model, the database was divided into training and validation sets. In this study, K-fold cross-validation with K equal to 5 has been adopted, meaning that the dataset has been split into 5 folds. According to Marcot and Hanea [39], the choice with $K = 5$ suffices with BNs model in most cases, particularly with the consideration of time consumption and computational complexity. In each of the 5 iterations of training and validation, there are four folds used for training, while the last fold is used for model validation. Each iteration provided a performance score as evaluation result, the average score from all iterations is considered as the overall performance of the BNs model, which is denoted as K validation score. Fig. 18 shows the adopted BNs model structure using the training set. In each training iteration, the learnt structure is stable.

As highlighted by a first analysis, shown in Fig. 18, the cause of the event occurrence appears to be influenced by the industrial macro-sector and the equipment involved. This influence is linked to the substances

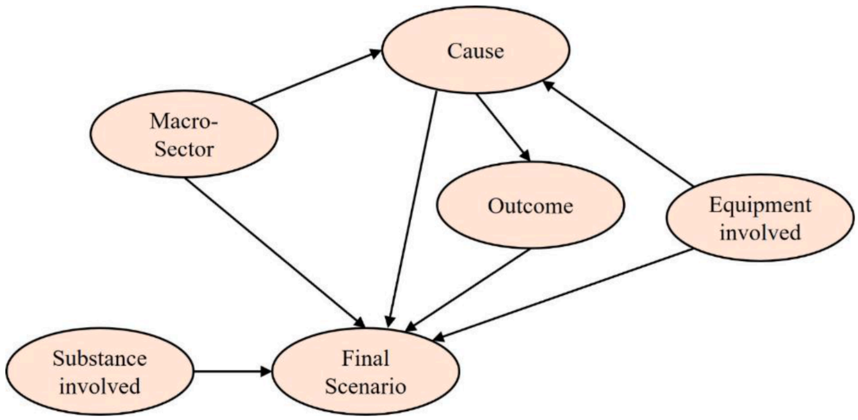


Fig. 18. Bayesian network of ageing.

present and the operating conditions to which the equipment is exposed, which vary depending on the macro-sector and the types of production. The event scenario, on the other hand, is influenced not only by the macro-sector and the equipment but also by the degradation mechanism in progress and the nature of the substance involved.

The analysis revealed a large number of Bayesian network configurations, but to simplify the approach, only the most evident dependencies were considered. This allowed us to focus on the main links that significantly influence the event, simplifying the interpretation and modelling of the system.

To validate the established BNs model in each iteration, the accuracy of predicting the "Final Scenario" given the evidence of other variables is considered as the evaluation index. However, some variables have more than one value. For example, equipment may involve substances with both "Health hazard" and "Physical hazard", this increases the complexity of the database. In this event, a multi-prediction is achieved by respectively considering "Health hazard" and "Physical hazard" as the input of the model. Thus, the validation of the established model considers three cases, which are also shown in Table 3:

- Single prediction (S): In this case, each input variable contains only one value, which makes prediction straightforward. According to Table 3, the number of events for this case is highest compared with others. The prediction accuracy performs stable in five iterations, resulting in the final score of 85.58%.
- Multi-prediction with single result (MSR): as shown in the example, equipment may involve a substance associated with multiple hazard categories, for instance "Health Hazard" and "Physical Hazard". In BNs, these categories are treated as distinct input nodes, each of which can influence the output variables. This case allows the model to evaluate multiple risk assessment paths at the same time, generating a multi-output prediction. This is more aligned to practical situations and thus increases the output interpretability. However, by conducting multi-predictions, the prediction result could remain the same. The number of events is much less than the case S, but with a higher score (90.71%).
- Multi-prediction with multi-result (MM): in multi-predictions, prediction results could be different when selecting different values as input. Few numbers of events for this case have been found. In this case, whether multi-predicted results involve the true reference value (involvement) is considered as the evaluation index.

Table 3 shows that, in the case of a single prediction, the data accuracy was approximately 86%, while in the case of multiple predictions with a single result, the accuracy increased to approximately 91%. The result of relatively high accuracy is positive and indicates that the model based on Bayesian networks has a good ability to generate reliable predictions even in the presence of uncertainties or variability in the data. An accuracy value higher than 80% is generally considered satisfactory, especially in complex contexts where information may be incomplete or uncertain.

Table 4 and Table 5 present the results of the analysis, with a probabilistic estimate of the risk scenarios and a representation of the probability distribution associated with the functional attributes. Table 4 reports the conditional probability tables (CPT) related to the cause of occurrence and the final scenario, while Table 5 shows the probabilities associated with the equipment involved and the final scenario. The occurrence frequencies, previously obtained from the analysis shown in Section 3.1, are indicated in parentheses, in order to facilitate the comparison between the results. Some probabilities in the tables are reported as zero because their value was less than three

Table 4
Conditional probability table (CPT) of cause and final scenario.

Cause/Final scenario	Corrosion	Erosion	Fatigue	Vibrations
Near miss	0.002 (0.004)	0 (0)	0 (0.037)	0.005 (0.046)
EC	0.875 (0.782)	0.644 (0.414)	0.675 (0.308)	0.511 (0.316)
F	0 (0.011)	0 (0.135)	0 (0.14)	0 (0.075)
R-NFC	0.055 (0.131)	0.104 (0.243)	0.036 (0.346)	0.103 (0.23)
TGD	0.067 (0.064)	0.252 (0.153)	0.289 (0.084)	0.380 (0.305)
E	0 (0.008)	0 (0.054)	0 (0.084)	0 (0.029)

Table 3
Validation results of K fold cross-validation (K is 5).

Case	Iteration	I1	I2	I3	I4	I5	Score
S	Event No.	782	770	783	752	736	85.58%
	Accuracy	85.29%	86.49%	85.95%	84.18%	86.01%	
MSR	Event No.	162	170	159	167	187	90.71%
	Accuracy	91.98%	92.94%	87.42%	89.22%	91.98%	
MM	Event No.	4	2	6	9	1	100%
	Involvement	100%	100%	100%	100%	100%	

Table 5
Conditional probability table (CPT) of equipment involved and final scenario.

Equipment/Final Scenario	Control & mitigation system	EC&I system	Primary containment system	Structures
Near miss	0 (0.030)	0 (0)	0.002 (0.008)	0.091 (0.077)
EC	0.304 (0.348)	1 (0.267)	0.875 (0.724)	0 (0.231)
F	0 (0.045)	0 (0.067)	0.001 (0.023)	0.545 (0.179)
R-NFC	0.036 (0.303)	0 (0.333)	0.055 (0.150)	0 (0.282)
TGD	0.661 (0.258)	0 (0.333)	0.067 (0.077)	0.364 (0.154)
E	0 (0.015)	0 (0)	0 (0.017)	0 (0.077)

decimal places; this choice was made to reduce the complexity of the model and facilitate the interpretation of the results, while maintaining consistency with the available data. However, it is recognized that such simplification could reduce the visibility of extremely rare but at the same time high-risk scenarios. In the future, it will be useful to evaluate approaches that allow the representation of these low probabilities to preserve the relevance of low-frequency but high-impact events. Therefore, they were rounded to zero, being considered of negligible relevance in the context of the study. The data reprocessed through Bayesian networks highlight an increase in the probabilities of environmental contamination and release of toxic gases compared to the data previously examined for all the causes analysed. In particular, compared to the initial data, the probability of environmental contamination increases by around 60%, while the release of toxic gases increases by about 80%. In contrast, scenarios where no damage actually occurs (defined as near misses), fires, explosions, and releases with no further consequences, show a decrease in probability. Regarding the equipment involved, the results are consistent with those observed for the causes of incidents, but it is interesting to note that, in the case of structures, the probability of near misses, fires and the dispersion of toxic gases increased, while that of environmental contamination decreased. Similarly, for Control and Mitigation Measures, a decrease in the probability of environmental contamination was recorded. Finally, for the EC&I system, the environmental contamination probability has been approximated to 1, while for all other scenarios, the frequency values were three orders of magnitude lower, which is why they have been approximated to zero.

Bayesian networks enable the prediction of the scenario following specific events, as illustrated in Table 6, which presents an example. Considering “Pipeline”, “Primary containment system”, “Environmental hazard”, “Corrosion”, “LOC”, the joint probability of the different “Final Scenario” can be calculated, and the value with the highest probability, “EC”, is considered as the result of the prediction.

Additional results are shown using heatmaps, which provide a visual representation of the conditional probabilities, as illustrated in Fig. 19. These heatmaps are particularly valuable as they visually reveal complex, age- and sector-specific degradation patterns, thereby pinpointing specific areas for future in-depth causal investigation. This visualization technique enables the immediate identification of areas with higher probability values to be clearly and immediately highlighted, making it easier to interpret the data and identify significant trends.

Fig. 19a shows the heatmap of the conditional probabilities of plant age in relation to the causes of failure. It is observed that, for older and medium-aged plants, the predominant failure mechanism is corrosion, indicating that the process is slow and persistent over time. In contrast, newer plants are more susceptible to vibration-related failures, due to the immediate nature of this process that does not require a long period to manifest itself. In older plants, in addition to corrosion, failures are mainly due to vibration, erosion and fatigue, with an almost equal distribution between these mechanisms. For plants aged between 5 and 25 years, classified as Medium-aged, after corrosion, failures are mainly due to fatigue and vibration, while erosion has a lower frequency of occurrence, suggesting that this mechanism occurs less frequently in medium-aged plants, contrary to older and newer facilities where this mechanism has a higher frequency of occurrence. Fig. 19b shows the conditional probabilities of the industrial macro-sectors involved, in relation to the degradation of the material. The figure shows that the sectors most affected by corrosion are those of pipelines and storage and warehousing, while the process industries, such as energy production and transport, are less affected by corrosion. However, in all sectors, corrosion is the most frequent phenomenon, with the exception of the energy production sector, where corrosion and fatigue occur with the same probability. For the bioprocess and transport macro-sectors, the second most recurrent phenomenon is represented by vibrations. Future work may further investigate the relationship between plant age and the occurrence of fatigue phenomena, investigate the reasons why vibrations occur less frequently in older plants, and analyse the sectoral differences that make this phenomenon less relevant in the chemical and petrochemical sector compared to bioprocesses.

These new observations offer a probabilistic reinterpretation of incomplete historical data, which would otherwise have remained unexplored. By providing an additional perspective, they allow to shed light on aspects that may not have been taken into account, thus strengthening the decision-making process to address the management of industrial vulnerability due to material degradation. However, it should be noted that, despite efforts to ensure data quality, the dataset used has some significant limitations. In particular, the installation age, the economic losses, the human losses and environmental pollution are available only in a fraction of events. The limited availability of complete data may limit the depth of the analyses for some key variables. The use of Bayesian Networks (BNs) enabled the management of uncertainty, but it is recognized that the lack of complete data may affect the robustness of the inferences in some specific areas.

Lastly, it is important to highlight that the probabilities used in the model, both in the event tree analysis and in the Bayesian networks, are derived from historical data covering a wide time range. Consequently, they represent an empirical synthesis of the frequency with which certain events have occurred in the past. As also highlighted in Fig. 3, the number and nature of accidents vary over time together with regulatory, technological and organizational factors. Therefore, the probabilities obtained cannot be interpreted as time-invariant estimates but must be considered as historical indications useful for understanding general trends and supporting comparative analyses between scenarios.

Table 6
A prediction example through BN.

Input	Joint probability of the Final Scenario		Prediction result
	Value	Probability	
{*Pipeline, Primary containment system, Environmental hazard, Corrosion, LOC*}	Near miss	0	EC
	EC	**0.976**	
	F	0.001	
	R-NFC	0.014	
	TGD	0.009	
	E	0	

4. Conclusion

The analysis of 3772 historical events from 1966 to 2023 has allowed

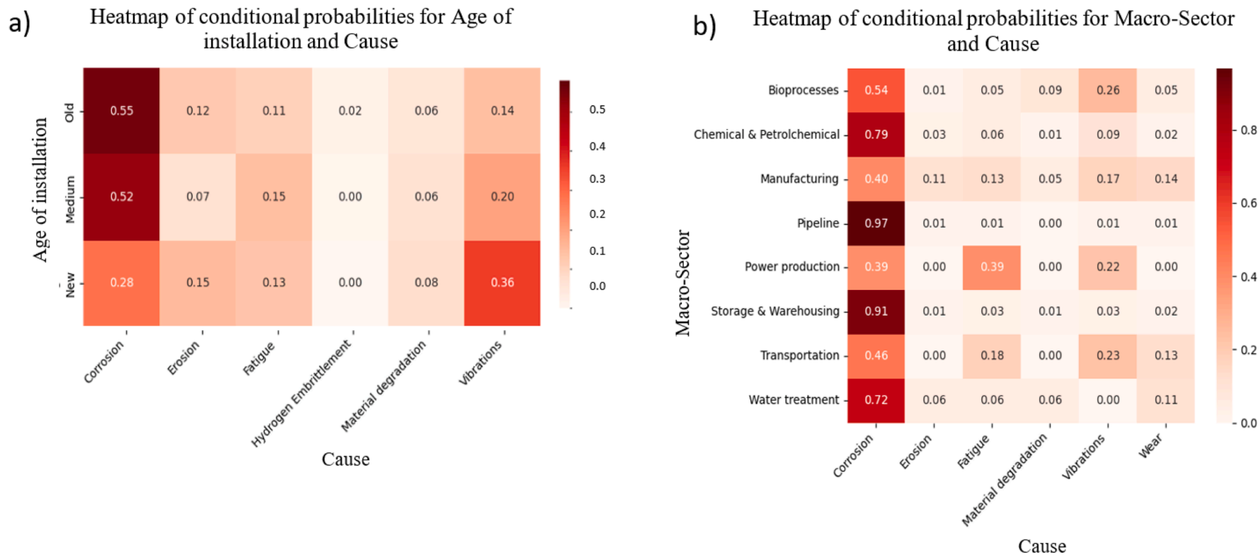


Fig. 19. Heatmap with conditional probabilities. A) Heatmap for age of installation and cause. B) Heatmap for macro-sector and cause.

the identification of the main degradation mechanisms of materials in the industrial process sector, highlighting the most critical vulnerabilities.

- The results show that the majority of the data comes from the NRC database, highlighting a predominance of events recorded in North America.
- In Europe, there has been an increase in events after 2000, with a peak in 2019.
- Corrosion is the most frequent failure mechanism, followed by vibration and fatigue.
- The most affected industrial sectors are the Chemical and Petrochemical and Pipeline.
- In America, the Pipeline sector is more frequently affected by material degradation than in Europe.
- Primary containment systems are the most vulnerable equipment.
- Over 90% of the events analysed resulted in a loss of containment (LOC).
- In America, LOC is a more recurrent scenario than in Europe.
- Corrosion is often associated with environmental contamination, while vibration is also linked to the dispersion of toxic gases.
- Most of the substances involved have multiple risks, increasing the complexity of risk management.
- Over 70% of the events involved installations older than 25 years.
- In 90% of the cases, inspection plans had to be revised after the event, indicating a lack of preventive controls.
- Environmental losses are the most frequently documented, followed by human and economic losses.
- Comparison of human losses data with NaTech events showed a higher availability of data in the present study.
- The ETA shows that, in case of corrosion-caused events environmental contamination is the most likely scenario.
- Two real case studies were conducted, validating the ETA model and positioning them in the risk matrix, both classified as medium risk, demonstrating how a rare but catastrophic event can have a comparable risk to a frequent event but with less severe consequences.
- The BNs showed conditional relationships between key variables, highlighting the influence of the industrial sector and the type of equipment on the final scenario. The application of BNs allowed the calculation of the conditional probabilities between the analysed variables, confirming that corrosion is more frequent in old plants and in the pipeline and storage sectors, while vibrations are more common in new plants. Furthermore, the analysis showed an increase in the probabilities associated with LOC, compared to a reduction in the probabilities of accidents and near misses.

Due to the high uncertainty of the data, caused by the presence of a significant number of missing data classified as "Unknown", mathematical algorithms were implemented to provide a meaningful alternative perspective on the unclassifiable data within the set. The event tree and Bayesian network analysis enable the estimation of the conditional probabilities of events, providing a systematic and scientific approach to exploring situations characterized by uncertainty.

The analysis has allowed for a more precise identification of areas of vulnerability and possible points of failure in the system, an important information in a context of resilience. While a comprehensive prototype decision-support tool is the object of future work, the developed BN-ETA framework ability to identify critical failure points and estimate conditional probabilities provides the crucial analytical foundation for the risk visualization and mitigation simulation capabilities such a tool would offer.

Furthermore, the constructed database allows for a deeper study of specific subcategories, with the extraction of subsets of data relating to specific situations, allowing targeted analyses in particular contexts, as highlighted in the study by Vitale et al. [59].

The study adopts the analytical approach proposed in the paper by Castro Rodriguez et al. [14] to ensure data homogeneity and to facilitate integration into an advanced analytical framework. The aim is to increase awareness, preparedness, and recovery, in order to increase system resilience.

The study provides insights for researchers working in industrial process safety and equipment integrity, with a large-scale analysis of material degradation mechanisms and possible consequences. The integration of Bayesian networks and event tree analysis demonstrates how probabilistic tools can be applied to incomplete historical data to support predictive modelling. Furthermore, the results are relevant for regulators and inspectors, providing a prioritization of material degradation issues in the process industry. Indeed, although the Seveso III Directive (Directive 2012/18/EU) highlights the importance of major accident prevention and mentions material degradation as a risk factor, it does not provide detailed operational guidance on how to assess it. The study aims to partially fill this gap, contributing to broadening the knowledge of material degradation in the process industry. Further research will be implemented to bridge the gap between operational vulnerabilities caused by material degradation and the conditions to which they are subjected, both due to the external environment and to stresses deriving from operational conditions. In particular, the correlation between degradation mechanisms and the age of the plants will be explored. Furthermore, the integration of databases from Asia and Africa will be planned, to extend the validity and representativeness of the model. Further developments will also concern the analysis of prevention and protection measures adopted in the documented cases, with the aim of evaluating the effectiveness of such strategies in relation to the events occurred.

Data availability

The data used in this study were extracted from a database, which is accessible and can be consulted at https://doi.org/10.17632/6hd3xky6kb.1 [58].

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Ethics statement

This research did not involve any applicable ethics statement, and all research procedures were carried out following the requirements for ethical principles.

CRediT authorship contribution statement

Morena Vitale: Writing – review & editing, Writing – original draft, Visualization, Investigation, Conceptualization. **Huxiao Shi:** Writing – review & editing, Writing – original draft, Visualization, Investigation, Conceptualization. **David J. Castro Rodriguez:** Writing – review & editing, Methodology, Conceptualization. **Antonello A. Barresi:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Data curation, Conceptualization, Funding acquisition. **Micaela Demichela:** Writing – review & editing, Supervision, Resources, Data curation, Conceptualization, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Barresi Antonello reports financial support and article publishing charges were provided by MUR. Vitale Morena reports financial support was provided by MUR. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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